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Review Paper

Art to use Electrospun Nanofibers/Nanofiber Based Membrane in Waste Water Treatment, Chiral Separation and Desalination

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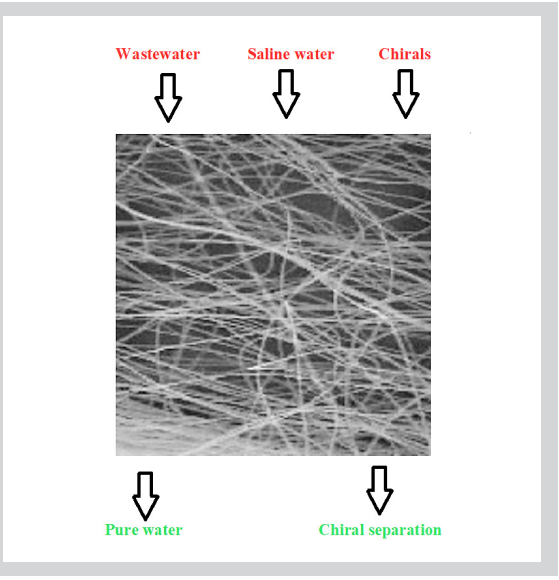
Highlights

- The art to prepare elecrospun nanofibers membranes/fibers for the waste water treatment.
- Recent use of electospun nanofibers/ membrane for chiral separation and toxic materials (heavy metals) removal from contaminated water
- Recent progress to use eltrospun nanofibers membrane in membrane distillation for desalination and separation of VOC from water etc.

Graphical abstract



Abstract

The technique to fabricate nanofibrous mat by electro-spinning has been known for a long time. However, the attempts to use the electospun nanofiber mats, also known as electro-spun nanofiber membranes (ENMs), for filtration purposes began only recently. Among many membrane filtration processes, air cleaning by the removal of dust particles has already been commercialized and the product has been in the market for some time. On the other hand, the application of ENMs for liquid separation has a much shorter history and its commercialization has not yet been achieved. Since a large number of researches report in the open literature every year, its commercialization looks only a matter of time. For example, many papers are now available on the pressure driven membrane separation processes such as RO, NF, UF, MF by ENMs, and as many papers have been published on the other membrane separation processes including pervaporation, membrane distillation, forward osmosis and membrane adsorption. It is needless to say that ENMs have gained popularity within a short period due to the facile fabrication, interconnectivity and large area/volume ratio. Despite these advantages, ENMs pore sizes are intrinsically very large (fractions of micrometer to few nanomter), which makes modification of surface chemistry and especially reduction of the ENM pore size indispensable for wider applications of ENMs for membrane separation processes.

Contents

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1. Introduction

"Energy and the environment are the most important factors that influence the shape of society in the 21st century. Nanosized fibers have great advantages due to their high surface area to volume ratio, electrospun nanofibers have potential applications in the field of clean energy (solar cells, fuel cells and batteries), electronics, health (biomedical scaffolds, artificial organs), and environment (filter membranes)" [1].

Water resources including lakes, rivers, oceans, aquifers, and groundwater are polluted by contaminants when discharged directly (effluent outfalls from factories, refineries, waste treatment plants, etc.) or indirectly (contaminants that enter the water supply from soils/groundwater systems and from the atmosphere via rainwater). Contaminants can be broadly classified into organic, inorganic, radioactive, and acid/base. Moreover, bacteria and virus represent another dangerous class [2]. Inexpensive and easy methods to clean freshwater and wastewater are therefore in high demand. Lovering [3] reported that Liquidity, Alameda, California-based start-up, has developed a low cost water filter made from electrospun nanofibers which will reduce water-borne diseases in poor countries. Kriklavova and Lederer [4] discussed several examples of nanofiber technology in combination with biological removal of toxic xenobiotics in the application of industrial wastewater treatment.

Nanofibers can be made from different polymers and inorganic materials, and, hence have different physical properties and application potentials. Electrospun inorganic nanofibers are generally made of nano-sized grains or crystals. Examples of natural polymers include collagen, cellulose, silk fibroin, keratin, gelatin and polysaccharides such as chitosan and alginate. There are many different methods to make nanofibers, including drawing, electrospinning, self-assembly, template synthesis, and thermally induced phase separation. Among those, electrospinning is the most commonly used method to generate nanofibers because of the straightforward setup, the ability to mass-produce continuous nanofibers from various polymers, and the capability to generate ultrathin fibers with controllable diameters, compositions and orientations [5]. Electrospun nanofibers can be tailored for many applications by changing diameter, composition, morphology, and shear alignment. The ability of reducing the diameter of polymer fiber materials from micrometers to nanometers shows several remarkable features, such as very large surface area to volume ratio, flexibility in surface functionalities, superior mechanical performance (e.g. stiffness and tensile strength), allowing the production of fiber with a wide variety of sizes and shapes [6].

In summary, the unique advantages of ENMs over traditional membranes are as follows;

i) High porosity
ii) Tailoring, by changing the parameters, etc., during electrospinning
iii) Interconnected pore structures
iv) Large surface-to-volume ratio
v) Capability for chemical/physical functionalization which can be done very easily
vi) Cost-effectiveness

Thus, ENMs have a potential to be used for water treatment or in biotechnology. Ramakrishna et al. predicted that. *"In the future, we may no longer be dependent on crude oil thanks to more efficient conversion of other energy sources to electricity. With the ability to mass-produce nanofibers, electrospinning may well be one of the most significant nanotechnologies of this century"* [7]. Some examples of ENMs (polymer or inorganic) applications in water treatment are removal of nano- or micro-particles from wastewater, e.g., pre-filters to minimize contaminations, removal of oil from water, and reducing the fouling of the membrane prior to UF or NF. Botes and Cloete [8] discussed the applications of nanofibers in water purification. According to them, the application of nanofibrous filters either alone or along with conventional filters for the removal of VOCs, nanoparticles and bacterial contaminates in the air is very promising. ENMs are also applicable for wastewater treatment, food processing, and treatment of pharmaceutical products by membrane distillation (MD) [9]. Nasreen et al. [10] published a review paper entitled '*Advancement in electrospun nanofibrous membranes modification and their application in water treatment*' and mainly discussed on the methodologies of the membrane modification and its applications in water treatment. Wang et al. [11] discussed the application of nanofibrous sorbents for oil spill cleanup, nanofibrous membranes for oil/water separation and nanofibrous aerogels (NFAs) for emulsified oil/water separation. Amin et al. [12] briefly overviewed the availability and practice of different nanomaterials (particles or fibers) for removal of viruses, inorganic solutes, heavy metals, metal ions, complex organic compounds, natural organic matters, nitrate, and other pollutants present in surface water, ground water, and/or industrial water.

The applications of nanofiber membranes in water and wastewater treatment have been explored by many researchers [8, 13-16]. Suja et al. [17] made a detailed description of recent research works in non-woven electrospun water purification membranes. Easy functionalization, high surface area to volume ratio and interconnected fibrous nonwoven membrane has 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. Shirazi et al. [18] discussed applications of elecrospun membranes for membrane processes (MF, UF, NF, FO and MD), in which coalescing filtration and adsorptive separations were reviewed. The physical and chemical properties of nanofibers can be manipulated for any applications. Electrospun nanofiber membranes are used in many applications such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and forward osmosis [19, 20]. RO membrane provides the highest purity of water. For the detection of selected industrial pollutant, electrospun nanofibers are highly sensitive due to its high surface area.

As FO only produces diluted draw and concentrated feed solution, the process cannot be used for water desalination on its own, but is becomes usable when paired with a secondary process for draw recovery and clean water extraction. Nanofibers fulfill all requirements needed for FO membranes and it is a very promising material to develop the new-generation FO membranes for water treatment [21]. Nanofiber membranes can remove micron-sized particles from aqueous phase at a high rejection rate but with significant fouling [7]. Besides, functional nanomaterials can be easily doped into the spinning solutions to fabricate nanoparticle impregnated nanofibers [5].

There are many established ways to improve the performances of nanofiber membranes such as sol-gel synthesis, in situ polymerization, surface modification, plasma induced grafting, graft polymerization, blending, polymer-inorganic composites formation techniques etc. Physical morphology and mechanical properties vary depending on the polymeric concentration and spinning condition employed during the process. In addition to the above mentioned surface modification techniques, other techniques such as oxidation process, plasma treatment, solvent vapor treatment and surface coating are also used [10].

The mechanical properties are one of the key parameters for the separation membranes. The drawback in nanofibers is that they are poor in mechanical strength and thus they cannot face harsh conditions. Huang et al. [22] demonstrated that the post-treatment on exposing ENMs to the solvent vapor improved the mechanical strength due to the solvent-induced fusion of inter-fiber junction point. Yalcinkaya [23] reported that the mechanical strength of the nanofibers can be enhanced by using special lamination technique on a supporting layer. Using this technique, Yalcinkaya developed a novel high-performance polyamide 6, polyacrylonitrile and polyvinylidene fluoride nanofibers of industrial scale as micro filters. From experimental tests it was revealed that the mechanical strength of the nanofibers was enhanced more than 5 times while high porosity and liquid permeability were retained. Inappropriate storage of electrospun nanofiber membranes could alter their performances including water filtration performances [24].

2. Separation of organic contaminants

Water quality is highly sensitive to the presence of organic contaminants, such as oil, protein, humic acid, etc. Such organics, even at their very low concentrations, e.g. no more than 1% of the pollutants in the river, make the water free of any life [7]. The performances of the new generation of nanocomposite/hybrid nanofibrous membranes can perform well in environmental remediation [25].

2.1. Oil water separation

Due to growing oil and gas exploration activities, oil spills caused a large number of environmental problems. Various techniques such as skimming, ultrasonic separation, air flotation, gravity processing and coagulation-flocculation are available to remove oil from water. However, most of these techniques are low-efficient, costly and produce secondary pollution. It was claimed that the most effective way to remove the emulsified oil is by using membranes. Membrane separation offers higher oil removal efficiency, lower energy consumption and cost, and more compact design compared to skimming, DAF (dissolved air flotation) and chemical treatment [26]. Padaki et al. [27] published a review paper entitled '*Membrane technology enhancement in oil–water separation*' in which they discussed the development of advanced membrane technology such as surface modification, addition of inorganic particles in polymer membrane and the fabrication of ceramic membranes, presenting future outlook for removal of oil from wastewater. Ma et al. [28] discussed the development of superoleophobic/superhydrophilic electrospun fibers for oil-water separation. Due to their unique properties such as stability in aggressive and adverse environments (e.g. vapor or solvents, and non-oxidizing acids or bases, high temperature and pressure operation) carbon based nano materials are considered as a good alternative for membrane material for treatment of oily wastewater [29]. Fabrication of nanofibrous materials as sorbents and membranes, has shown a rapid expansion of research due to its simple and effective oil/water separation.

Nanofibers have the capabilities in oil–water separation, particularly in sorption process when the material in use has the oleophilic and hydrophobic surfaces. Raza et al. [30] discussed the wetting phenomenon in the oil spill cleanup process by absorption and cross-flow filtration. The discussions were focused on the characteristics of nanofibrous oil sorbent materials, fluid flow through nanofibrous materials, and types of nanofibrous materials. Nanofiber sorbent/membrane/filter has recently gained interest for oil-water treatment due to the following reasons:

i) High surface area
ii) Good physical property
iii) High sorption capacity

Beside of the above, performances of the membrane can be modified easily by surface modification. There are various factors that can affect the efficiency of oil removal by nanofibers. These factors may be due to the characteristics of the nanofibers or of the surrounding liquid such as sorption selectivity between oil and water, the specific surface area, the surface roughness, buoyancy, sorbent contact angle, surface tension, and the spinning solution's viscosity [31]. Gupta et al. [32] discussed the progress of oil/water separation technologies based on filtration and absorption methods using various materials that possess surface super wetting properties.

2.1.1 Rejection by UF, MF, NF.

Ultrafiltration is a membrane-based process used in many industrial processes where higher separation efficiency than that of MF is required, including water purification, biological filtration, and beverage clarification. Nanofibers were used as a supporting scaffold in ultrafiltration (UF) for oil/water emulsion separation. Yoon et al. [33] reported a new type of high flux UF/NF medium based on an electrospun nanofibrous scaffold (e.g. polyacrylonitrile, PAN) coupled with a thin top layer of hydrophilic, water-resistant, but water-permeable coating (e.g. chitosan). The membrane showed higher flux (one order of magnitude) than commercial NF membrane in 24 h of operation, while maintaining the same rejection efficiency (>99.9%) for oily waste-water filtration. The same group [34] also fabricated a high flux thin film nanofibrous composite (TFNC) membrane system based on polyacrylonitrile electrospun scaffold coupled with a thin barrier layer of cross-linked polyvinyl alcohol. The membrane was very useful for UF applications. It exhibited a very high flux (i.e., 12 times higher than that of conventional PAN UF membranes) and excellent rejection rate (>99.5%) for separation of oil/water mixture (1500 ppm in water) for a long time period.

Ma et al. [35] used ultrafine polysaccharide (i.e., cellulose and chitin) nanofibers containing TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl 85)/NaBr (sodium bromide)/NaClO (sodium hypochlorite) as barrier layers of TFNC membranes for UF applications. The performances of the membranes were studied in the treatment of oil/water emulsions. The contact angle of cellulose based TFNC membrane was 10.9°. The membrane showed 10-fold higher permeation flux when compared with two commercial UF membranes (PAN10 and PAN400 with 99.5% rejection ratio for UF of oil/water emulsions). The oil concentration in the permeate was < 5.4 ppm. Pure water permeability of the ultrafine cellulose-based TFNC membrane was around 18 times higher than that of PAN10 and 1.7 times higher than that of PAN400.

Ma et al. [36] developed a dual pH- and ammonia-vapor-responsive polyimide (PI)-based nanofibrous membrane for oil-water separations. The developed membrane showed high flux and stability. The proposed membrane was prepared by dip-coating electrospun PI with decanoic acid (DA)-TiO_2 and silica nanoparticles (SNPs). The membrane SNP/DA-TiO_2/PI showed superhydrophobicity in air and superoleophilicity in neutral aqueous environments resulting in only water permeation during oil-water separations. The membrane had extremely high flux (6500±100 L m^{-2} h^{-1}) and separation efficiency (>99%) and was reusable.

Dobosz et al. [37] improved membrane performance by enhancing UF membranes with electrospun nanofibers. It was demonstrated by them that electrospun nanofibers can effectively improve the performance of UF membranes due to their better mechanical integrity. Cellulose and polysulfone were electrospun into a layer that was 50 μm thick and consisted of randomly accumulated 1-μm-diameter fibers. Fouling resistance was improved and selectivity was retained.

Cao et al. [38] demonstrated a novel type of UF or NF composite membranes consisting of a coated thin layer of hydrophilic jute cellulose nanowhiskers and an asymmetric electrospun PAN nanofibrous support. The membrane showed good mechanical properties with efficient filtrating capacity for nanoparticles and oil/water separation (with rejection of over 99%).

Obaid et al. [39] developed a novel and highly hydrophilic membrane based on PSf (polysulfone) nanofibers. The modification was made by incorporation of NaOH nanoparticles inside the PSf nanofibers, and formation of a thin layer from a polyamide polymer on the surface of the electrospun mat. The permeability of membrane was determined for the oil/water feed. By adding 1.7 wt.% NaOH nanoparticles to the spinning dope solution containing 20 wt.% PSf, the electrospun membrane' surface showed a decrease in the water contact angle from ~130° to 13°. It was revealed that the membrane having the lowest contact angle could separate oil–water mixture in three successive cycles with complete removal of the oil at a relatively high water flux; 5.5 m^3 m^{-2} day.

Obaid et al. [20] studied hexane-water (50:50 v) separation with three electrospun membranes (pristine PSF, PSF–SiO_2, and PSF–GO) and reported that the PSF-SiO_2 had the maximum flux of hexane. The flux increased 8 times compared to the pristine PSF membrane. On the other hand, addition of GO showed 40% increase in the flux. Digitally, the obtained daily flux was 23, 37 and 187 m^3 m^{-2} for pristine, GO-doped and SiO_2-doped PSF electrospun membrane, respectively. It was claimed by the authors that the nanosilica obtained from rice husk agriculture waste can be utilized to prepare effective PSF-based electrospun nanofiber membrane for petroleum oil fractions/water treatment with daily flux of 100, 115 and 187 m^3 m^{-2} for gasoline, kerosene and hexane, respectively.

Ganesh et al. [40] fabricated robust oil–water separation membranes by electrospinning of poly(vinylidene fluoride-co-hexafluoropropylene) and fluorinated polyhedral oligomeric silsesquioxane composite mixture. These hybrid membranes showed highly hydrophobic/superoleophilic behavior for water and oil (hexane) and efficiently separated low viscous oil from water in a single-step (separation efficiency of nearly 100%). It was suggested by the authors that the PVDF-HFP-FPOSS nanofiber membrane can be used for real-time industrial wastewater treatment applications.

Wang et al. [41] fabricated a smart (according to the authors) membrane by electrospinning TiO_2 doped polyvinylidene fluoride (PVDF) nanofibers. The smart membrane enables reversible separation of oil/water mixtures by allowing only water or oil to pass through. It was suggested that the as-formed beads-on-string structure and hierarchical roughness of the nanofibers contributed to its super wetting/resisting property to liquids, which is desirable in oil/water separation. The fabricated membrane possessed outstanding antifouling and self-cleaning capacity resulting from the photocatalytic property of TiO_2. The approximate fluxes of water and oil through the membrane were ~2.63×10^4 and ~3.12×10^4 L m^{-2} h^{-1}, respectively. The membrane needs a prior wetting with water before conducting the water passing/removing process after UV irradiation.

Ma et al. [42] fabricated by combination of electrospun core-sheath structured PI/CA nanofibers and a novel in-situ polymerized F-PB functional containing SNPs (silica nanoparticles). Membranes had superhydrophobic (water contact angle 162° and the oil contact angle approached 0^0) and

superoleophilic surface wettability property. It was reported that newly designed PI/CA/F-PB-1/SNP-4 membranes can effectively separate various oil (DMF)-water mixtures, solely driven by gravity, with a high flux (3106.2 ± 100 L m^{-2} h^{-1}) and a high separation efficiency (>99%), and thus possess great potential for oil–water separation.

Shirazi et al. [43] tested the performance of electrospun polystyrene membrane for treatment of biodiesel water-washing effluent. The effluent was a complex emulsion system of water, glycerol, biodiesel, un-reacted oil, soap and catalyst with the water, soap and pollutants forming agglomers which are larger than the pore size of the membrane. The membrane is able to remove the agglomers through size exclusion. After passing through thermally treated membrane, COD (chemical oxygen demand), BOD (biological oxygen demand), TS (total solid), TDS (total dissolved solid) and TSS (total suspended solids) reduction rates were around 75%, 55%, 92%, 96% and 30%, respectively. It was suggested that the AFM is a powerful and practical analysis method for characterization of electrospun microporous membranes.

Superhydrophobic and superoleophilic nanofibrous membranes robust for oil–water separation performance was prepared by Shang et al. [44], via a facile combination of electrospun cellulose acetate (CA) nanofibers with polymerized fluorinated polybenzoxazine (F-PBZ) functional layer that incorporated silica nanoparticles (SiO_2 NPs). The membranes FCA-1/SNP-2 (FCA-1 represents 1wt% BAF((4,4′-hexafluoroisopropylidene)disphenol)-tfa (m-(trifluoromethyl)aniline) monomer, SNP- 2 represents 2 wt.% silica) were superhydrophobic with water contact angle of 161° and a superoleophilicity with the oil contact angle of 3°. The resultant membranes exhibited fast and efficient separation of oil–water mixtures (dichloromethane and water (50% v/v)) with excellent stability towards a wide range of pH (2–14). No external force was employed during the fast separation process. On filtering oil/water mixture, oil quickly permeated through the membranes due to the superoleophilicity. Meanwhile, water was retained above the membranes because of the superhydrophobic and low water-adhesion properties of the membranes. It was suggested by the authors that these membranes are promising for practical oil-polluted water treatments and oil spill cleanup.

Si et al. [45] described the preparation of a method for creating super elastic and superhydrophobic aerogels with a hierarchical cellular structure that consists of bonded electrospun nanofibers, called “fibrous, isotropically-bonded elastic reconstructed” (FIBER) aerogels. They selected polyacrylonitrile and SiO_2 nanofibers as the major building blocks to construct the hybrid fibrous networks. The fiber aerogels can effectively separate surfactant-stabilized water-in-oil emulsions, solely using gravity, with high flux (maximum of 8140 ± 220 L m^{-2} h^{-1}) and high separation efficiency, which matches well with the requirements for treating the real emulsions.

Liao et al. [46] developed a novel membrane with switchable super-wettability for oil and water. The novel composite membrane was developed by electrospinning a hierarchically porous polyvinylidene fluoride-silica composite nano/micro-beaded top layer and a PVDF nanofibrous intermediate layer on a non-woven support. The membrane flux was up to 2000 Lm^{-2} h^{-1} with high separation efficiency (> 99.99% in terms of water and oil purities in the permeate) in the cross-flow filtration process. It also exhibited an excellent robustness under harsh conditions, including strong acidic or alkaline solutions, hot water and petroleum. In addition, it presented remarkable antifouling and easy-cleaning properties, which were demonstrated in a 50-h continuous operation.

Islam et al. [47] via electrospinning technique fabricated a high flux and antifouling polyvinyl acetate-coated nylon 6/Silica (N6/SiO_2) composite MF membrane. The fabricated MF membrane was robust. The membrane achieved a water permeability of 4814 LMH bar^{-1} during MF of O/W emulsions at 4 psi of applied pressure. The oil rejections of 98.80%, 99% and 99.20% were achieved from oil concentrations of 250 mg L^{-1}, 500 mg L^{-1} and 1000 mg L^{-1}, respectively. The fabricated membrane also showed antifouling properties with a water flux recovery of 85% with an O/W emulsion.

Makaremi et al. [48] prepared electrospun PAN nanofibrous membranes, reinforced by 1, 2, and 3% w/w of halloysite nanotubes (HNTs) in order to improve their mechanical properties, thermal stability and water filtration performance for the possible application as water filtration membranes. The oil/water separation performance of the membranes with 200 µm thickness was evaluated using a dead-end filtration module (Syringe Filter Holder 25 mm, Sartorius) at a constant flow rate of 0.4 mL min^{-1}. Rejection ratio of 99.5% was obtained while heavy metal ion adsorption of the membrane remarkably increased by 760 % when the membrane was reinforced with 3% w/w HNTs. It was suggested that these PAN modified membranes had high potential to be used in water filtration technology.

Li et al. [49] described the fabrication of a smart nanofiber membrane by depositing pH-responsive copolymer fibers on a stainless steel mesh through electrospinning. The precursor material poly(methyl methacrylate)-block-poly(4-vinylpyridine) (PMMA-b-P4VP) was synthesized using copper(0)-mediated reversible-deactivation radical polymerization. The as-prepared fiber membrane has accomplished on-demand oil/water separation using gravity alone by switching the pH of the medium. Initially, oil selectively passes through the membrane, whereas water remains. The separation process is reversed after wetting the membrane with acidic water (pH ~3). Both separations exhibit high efficiency and flux that is attributed to the porous fiber structure of the membrane.

Liu et al. [50] developed a method to fabricate electrospun carbon nanofibers having inside micropores by using sublimation technique. Terephthalic acid (PTA) was used as the sublimating agent. During carbonization of electrospun PTA polyacrylonitrile composite nanofibers, PTA sublimed and macropores were created within the carbon nano fiber. The resulting membrane (MCNFF) was inflexible and self-sustained carbon film. The MCNFF membrane showed superhydrophobic and superoleophilic properties including large porosity degree of 89 %. due to the porous electrospun nonwoven structure, and possessed high oil-absorption capability. The carbon nanofiber film showed excellent oil adsorption property with maximum capacities of 62.6, 73.8, 64.0, 94.0 and 138.4 g $g^{-1}$for ethanol, pump oil, mineral oil, corn oil and silicone oil.

Tai et al. [51] fabricated a free-standing and flexible SiO_2–carbon composite nanofibrous membrane via electrospinning technique followed by thermal treatment for oil-water separation. The SiO_2–carbon composite nanofibrous membrane showed excellent separation performance. The membrane allows ultrafast oil–water separation by solely gravity. The fluxes of various oils permeating through the membrane were measured. The average permeate flux for petroleum spirit, *iso*-octane, and hexane was found to be 3032.4 ± 234.6, 1719.1 ± 36.2, and 2648.8 ± 89.7 L m^{-2} h^{-1}, respectively, when a 213.3 ± 21.8 µm thick membrane (effective membrane area, 0.000962 m^2) was used. Tai et al.’s free-standing carbonaceous composite membranes with tunable flexibility could be very promising for the production of purified water from oil/water mixture. Tai et al. [52] fabricated a novel TiO_2 nanosheet anchored carbon nanofibers via solvothermal method. The hierarchical TiO_2 micro/nanostructure that grows on the surface of carbon nanofibers renders the membrane superhydrophilic and underwater superoleophobic. From the experimental results, it was suggested that the membrane had a stronger affinity for oil than water. During the filtration of oil-water mixture, as water contacted with the membrane, the surface was immediately wetted (instantaneous water spreading behavior) and a water barrier was formed. The oil did not wet the surface. The oil retained on the membrane surface could be easily washed away by rinsing the membrane with water and the membrane could be reused. It was revealed that the membrane possessed excellent oil-water separation efficiency and high chemical and thermal stability. The membrane was capable of separating oil from water by gravity (separation 99%). Further, oil break through pressure was up to 3.63 m which was the highest breakthrough pressure ever reported

Waisi [53] fabricated activated carbon embedded nanofiber nonwoven (ACNFN), which is a form of activated carbon from polymeric solution using the electrospinning method, followed by subsequent thermal steps. A dead-end normal flow system was used to investigate the operating conditions for the removal of emulsified oil from water using nonwoven media. It was observed that the oil droplets were removed by size exclusion and adsorption mechanisms (removal efficiency of up to 95%.).

Ao et al. [54] introduced a superhydrophilic graphene oxide (GO) embedded electrospun cellulose nanofiber (CNF) membrane which exhibited a high separation efficiency including antifouling properties and high flux for the gravity-driven oil/water separation (three kinds of oils and organic solvents including hexane, toluene and petroleum ether). The membrane exhibited superhydrophilicity with a CA (contact angle) of almost 0° for water in air. The separation efficiency of the membrane reached 99.4%, 99%, 99.8% for hexane, toluene and petroleum ether, respectively.

Chong et al. [26] used electrospun membranes of poly(trimethyl hexamethylene terephthalamide) (PA6(3)T) for microfiltration of oil (dodecane) emulsions in water. Rejection of the emulsified dodecane increased from (4.3 ± 0.9) % to (85 ± 5) % when the ratio of droplet diameter to fiber diameter (dp/df) increased from 0.57 ± 0.04 to 2.5 ± 0.4, respectively. It was observed that the flux was much higher than the flux obtained from commercial membranes, but the rejection was comparable. Rejection was initially higher (t < 100 s) for the higher operating pressure (4 psi) but the rejection at different pressures became similar (~50%) at long filtration time. The normalized flux of electrospun membranes was approximately three times higher than that of a commercial phase inversion membrane of comparable bubble point diameter. Several models were discussed to characterize the effect of fouling on performance for the electrospun membranes.

Yalcinkaya et al. [55] tested electrospun nanofibrous membranes of PAN/PVDF for oil water (water/vegan oil with the volume ration of 1/1) separation using dead-end filtration unit. It was revealed that the oil water

permeability of the PVDF/PAN mixture depends on the fraction of polymer in the blend, and, PVDF affected the surface character of the prepared material. The oil content of permeate remarkably decreased by raising the amount of PAN in the polymer blend. Higher oil rejection could be achieved by using neat PAN., but the neat PAN nanofibers were fragile and could be easily damaged. It was concluded that the neat PAN nanofibrous membranes were the best for water permeability while neat PVDF facilitated oil permeability.

Jiang et al. [56] constructed Janus membrane by electrospinning hydrophilic polyacrylonitrile electrospun nanofiber (PANEN), which was then coated, only on one side, with a hydrophobic carbon nanotube (CNTs) network. The CNTs@PANEN membrane exhibited asymmetric wettability on both side i.e. the hydrophilic PANEN side had underwater oleophobicity, and the hydrophobic CNTs side had underwater oleophilicity. Thus, the CNTs@PANEN membranes had a switchable oil/water separation performance in different operating mode: highly efficient oil-in-water emulsion separation with the PANEN side and water-in-oil emulsion separation with the CNTs side.

The Obaid group [57] also introduced super-hydrophilic membrane based on PSf nanofibers. The membrane was synthesized by electrospinning of polysulfone solution containing NaOH nanoparticles followed by activation of the dried electrospun membrane by deposition of polyamide layer on the surface using *m*-phenylenediamine and 1,3,5-benzenetricarbonyl chloride. The fabricated membrane was highly stable in oil media. To check its stability, the membrane was put into soybean oil for 50 days and it was found that there was no physical change. Figure 1 shows the performance in soybean oil-water mixture (1:1 volume ratio) separation process. It was revealed that the water flux was stable after the first cycle.

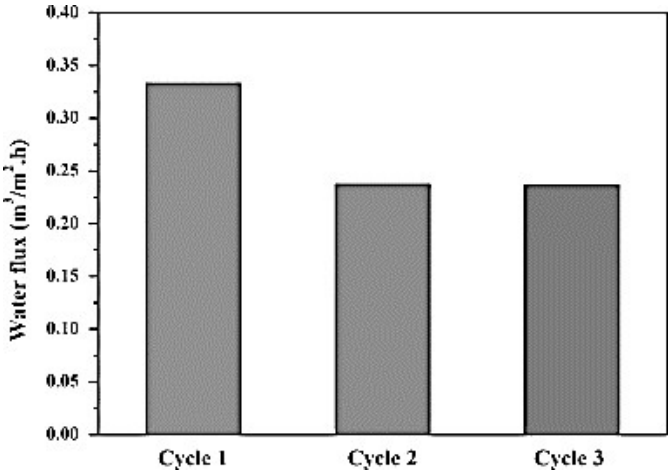

Fig. 1. Water flux for three successive cycles in water-oil mixture separation process [57].

In another work, Wu et al. [58] fabricated a reusable and recyclable hydrophilic polymer nanofiber membranes for oil-in-water emulsion separation. The cross-linked composite NF membranes were prepared using P(NIPAAm-*co*-NMA) {*N*,*N*-isopropylacrylamide-co- *N*-methylolacrylamide} as the polymer matrix, while using bio-based chitin nanowhiskers (ChNWs) as the reinforcement and cross-linking hub. The membrane had superhydrophilicity and high underwater oleophobicity including good structural stability and resistance to creep deformation during the swelling in water. The membrane was tested under acidic, alkaline, and salty conditions and showed steady separation performances as those in neutral circumstances with a very good separation performance for toluene emulsion, with a flux of 1100–1300 L m^{-2} h^{-1} and a separation efficiency of >99.5%.

Jian et al. [59] fabricated by electrospinning a superhydrophobic polystyrene-coated mesh (Al), which was then folded around a three-dimensional (3D) miniature box. It was used to remove oils (both heavy and light oils) from water with a separation efficiency of up to 99.92 %. The separation process was driven by gravity and the membrane showed excellent corrosion resistance.

Graphene and its derivatives have been widely studied and applied to prepare high-performance materials or functional materials. Zhang et al. [60] fabricated hierarchically structured membrane via controlled assembly of GO sheets on the surface of electrospun APAN (aminated polacrylonitrile) fibers and the gap between fibers. The membrane was superhydrophobic, exhibitibg low-oil adhesion. The membrane also exhibited ultra-high flux (around 10.000 LMH) with 98% rejection ratio when an oil (lubricating oil)-water (1:1000 w/w) emulsion was treated. The antifouling capacity of the membrane was high. Table 1 summarizes the recently developed nanofiber membranes to be applied for the oil/water separation.

2.1.2 Membrane adsorption

Selective adsorption of the oil from oil-water mixture generally depends on the oleophilicity and hydrophobicity of the membrane surface. Nanowire (nanofiber) membranes can selectively absorb the oil up to 20 times the material's weight in preference to water through a combination of superhydrophobicity and capillary action [61]. Adsorption is commonly employed as a polishing step to remove organic and inorganic contaminants in water and wastewater treatment. Nanofibers have the capabilities in oil–water separation, particularly in sorption process when the material in use has the oleophilic and hydrophobic surfaces. These characteristics enable the nanofiber to be used as a tool to combat either oily waste-water from domestic household and industrial activities, or oily seawater due to the oil run down to the ocean from oil transportation activities and oil tank cleaning on a vessel [31]. Wahi et al. [62] discussed the use of natural fibrous sorbent for removal of oil from wastewater, and its current development. Due to their excellent oil removal properties, environmental friendliness, easy availability, and feasibility, natural fibrous sorbents are an attractive alternative for oily wastewater treatment.

Sorption selectivity in an oil/water medium is an important parameter for the selection of the sorbent used in an oil spill cleanup. Electrospun nanofibers (porous) prepared directly by electrospinning of hydrophobic–oleophilic polymers (e.g., polystyrene) can be used effectively as oil sorbents from oil/water system. Xue et al. [63] discussed "oil-removing" type materials with superhydrophobicity and superoleophilicity (that selectively filter or absorb oil from oil/water mixtures), "water-removing" type materials with superhydrophilicity and superoleophobicity (that selectively separate water from oil/water mixtures), and smart controllable separation materials.

Lee et al. [64] fabricated superhydrophobic-super-oleophilic membranes by single-step deposition of polystyrene (PS) nanofibers onto a stainless steel mesh via electrospinning. The contact angles of diesel and water on the prepared PS nanofiber membrane were 0°and 155°± 3°, respectively. It was observed that the PS nanofiber membranes separated several liters of oil from water in a single step, within only a few minutes' duration time.

Lin et al. [65] fabricated a nonporous oleophilic-hydrophobic PS fibers via electrospinning process and used it as oil sorbents for oil spill cleanup. It was revealed that the porous PS fibers with smooth surfaces and small fiber diameters have the highest oil sorption capacities. The performance of PS nanofiber 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. Additionally, the sorbents also exhibit a relatively high sorption capacity for edible oils, such as bean oil (111.80 g g^{-1}) and sunflower seed oil (96.89 g g^{-1}).

Reshmi et al. [66] fabricated a novel superhydrophobic, superoleophilic electrospun nanofibrous membrane of beeswax (25 wt.% beeswax (PCL–25BW) and polycaprolactone) and reported that the prepared membrane could separate oil from contaminated water with high separation efficiency (98.1%) and good recyclability. Three types of oil water mixtures, such as petrol/water, diesel/water and kerosene/water were analyzed. The membrane exhibited high oil sorption capacity of 16.95–31.05 g g^{-1} in different oils. Moreover, it also showed high potential for gravity driven oil–water separation. PCL–25BW membrane exhibited reusability after 15 cycles of oil sorption and gravity driven oil–water separation.

Qiao et al. [67] fabricated a high-capacity oil sorbent by electrospinning a PS and PAN blend and investigated the influences of several processing parameters such as spinning solution concentration, environmental temperature, applied voltage, relative humidity etc. It was reported that the highest sorption capacity was obtained under the following conditions: the spinning solution concentration is 18%, the environmental temperature is 30℃, the applied voltage is 25 kV, the relative humidity is 40%, and the nozzle inner diameter of metal needle is 0.6 mm. The maximum sorption capacities of the polystyrene/polyacrylonitrile sorbent for pump oil, peanut oil, diesel, and gasoline were 194.85, 131.7, 66.75, and 43.38 g g^{-1}, respectively.

Table 1
Summary of the recently developed nanofiber membranes for the oil/water separations.

Nanofiber/Membrane	Separation of	Results	Ref.
PAN/Chitosan	Oil (vegetable, Dow Corning 193)/water	Pressure normalized flux ~1.1 $Lm^{-2}h^{-1}psi^{-1}$. Rejection > 99.9%	[33]
PVA/PAN- TFNC	Oil (soybean oil)/water emulsion (UF)	High flux (28.5 ± 3.4 $Lm^{-2}h^{-1}psi^{-1}$). Rejection > 99.5%.	[34]
Ultrafine polysaccharide TFNC	Oil (soybean oil and Dow Corning 193)/water emulsion. (UF)	WCA ~10.9 ± 0°. Flux ~ 490 $Lm^{-2}h^{-1}$. 10-fold higher than two commercial UF membranes (PAN10 and PAN400). Rejection 99.5%.	[35]
Jute cellulose nanowhiskers/PAN NFs	Oil (vegetable oil)/water (UF)	Filtrating capacity for nanoparticles and oil/water separation (rejection > 99%). Oil concentration of the filtrate was less than 5.5 ppm.	[38]
NaOH PATs/PSF/PA	Oil (Soybean oil) /water separation.	PA layer decreased the WCA ~130° to 13°. Water flux 5.5 $m^3m^{-2}day^{-1}$. Oil removal 100%. (PSF hydrophobic nanofiber mats modified to be a highly hydrophilic and permeable membrane. Can be used for oil–water separation process.)	[39]
VDF-HDP-FPOSS	Water/oil (hexane) (Filtration)	Low viscous oil from water in a single-step (separation efficiency of nearly 100%).	[40]
TiO_2 /PVDF (UV and heat treated)	Oil (n-hexane)/water (Filtration)	Reversible flow of water or oil by selectively allowing water or oil to pass through alone. Fluxes of water and oil ~2.63×10^4 and ~3.12×10^4 $Lm^{-2}h^{-1}$, respectively.	[41]
PI/CA/F-PB-1/SNP-4 (Core-sheath structured PI/CA)	Oil (DMF)-water mixtures. solely driven by gravity	WCA 162°, OCA approaches 0°. High oil flux (3106.2 ± 100 L m^{-2} h^{-1}), separation efficiency >99%.	[42]
PA6(3)T	Oil (dodecane)/water (Microfiltration)	Rejection was initially higher (t < 100 s) for the higher operating pressure (4 psi) but the rejection at different pressures became similar (~50%) at long filtration time. The normalized flux of EFMs was approximately three times higher than that of a commercial phase inversion membrane.	[26]
SNP/DA-TiO_2/PI	Oil (1,2-dichloroethane (DCE), hexadecane)/water	Extremely high flux (6500±100 $Lm^{-2}h^{-1}$) and separation efficiency (>99%).	[36]
Polystyrene	Oil/Water (biodiesel water-washing effluent) (Filtering)	COD, BOD, TS, TDS, and TSS reduction rates were around 75%, 55%, 92%, 96% and 30%, respectively.	[43]
FCA-1/SNP-2	Oil (dichloromethane /water (50% v/v) (Filtering)	Oil quickly permeated through the membranes due to the superoleophilicity. water remained over the membrane.	[44]
PAN and SiO_2 (hierarchical cellular structure that consists of bonded electrospun nanofibers) (aerogels)	Oil (petroleum ether)/water (Solely using gravity)	Superelastic and superhydrophobic membrane. High separation efficiency and high fluxes. Superior antifouling property. Fiber aerogels with 2 wt. % SiO_2 NPs contents: flux 350 ± 45 $Lm^{-2}h^{-1}$.	[45]
Hierarchically porous PVDF-silica composite nano/micro-beaded top layer and a PVDF nanofibrous intermediate layer on a non-woven support.	Oil (petroleum)/water (cross-flow filtration process).	Switchable super-wettability for oil and water. Flux 2000 Lm^{-2} h^{-1} , Separation efficiency > 99.99% in terms of water and oil purities in the permeate.	[46]
PVAc-coated nylon 6/Silica (N6/SiO_2)	Synthetic O/W emulsions. (microfiltration) (dead-end stirred cell filtration)	Water permeability 4814 LMH bar^{-1}. 99% oil rejection. Water contact angle 21°. Antifouling properties.	[47]
PAN/HNTs halloysite nanotubes	1350 ppm vegetable oil/water/125 ppm surfactant (using a dead-end filtration module)	Oil concentration of the filtrate < 7 ppm, indicating that performance of the membranes > 99.5%. Membrane containing 3% w/w HNTs, flux 92 L m^{-2} h^{-1}.	[48]
PMMA-b-P4VP	Oil (*n*-hexane) /water gravity alone	Oil selectively passes through the membrane, whereas water remains. Separation process reversed after wetting the membrane with acidic water (pH 3). Both separations exhibit high efficiency.	[49]
SiO_2–carbon composite nanofibrous membrane	Oil (petroleum spirit, *iso*-octane, and hexane)/water (Solely gravity)	Permeate flux for petroleum spirit, *iso*-octane, and hexane was found to be 3032.4 ± 234.6, 1719.1 ± 36.2, and 2648.8 ± 89.7 L m^{-2} h^{-1}, respectively.	[51]
TiO_2 nanosheet anchored carbon nanofibers on the surface	Oil (hexadecane, vegetable oil, olive oil and used pump oil) /Water (concurrent gravity driven)	Oil retained on the membrane surface. (separation 99%). Oil break through pressure was up to 3.63m.	[52]
GO@electrospun cellulose nanofiber	Gravity-driven oil/water separation	Superhydrophilic, separation efficiency: 99.4%, 99%, 99.8% for hexane, toluene and petroleum ether, respectively.	[54]
PVDF/PAN	Water/vegan oil (Filtration)	Both hydrophilic and oleophilic characteristics. Hydrophilicity and permeability enhanced by surface modifications (vacuum plasma treatment).	[55]
PS/Al mesh	Oil (kerosene, diesel, hexane, toluene, petroleum ether and chloroform)/water (Separation process was driven by gravity)	Superhydrophbic. Separation efficiency of up to 99.92. The membrane showed excellent corrosion resistance property.	[59]
Janus CNTs@PANEN	Water/petroleum ether (9:1V/V) (Filtration)	Switchable oil/water separation. Oil-in-water, PANEN side. Water-in-oil, CNTs side. Water-in-oil emulsion; Oil flux ~12,000 $Lm^{-2}h^{-1}bar^{-1}$. Rejection ~99.2%. Oil purity ~99.6%. Oil-in-water emulsion; Water flux ~80,000 $Lm^{-2}h^{-1}bar^{-1}$. Rejection ~99.7 (%). Oil content 8-10 mg L^{-1}.	[56]
GO sheets/electrospun APAN	Oil (lubricating oil)/water (continuous cross-flow separation system)	Superhydrophilic and low-oil-adhesion. Ultra-fast flux (~10,000 LMH) and rejection >98%. Antifouling performance.	[60]
P(NIPAAm-*co*-NMA)/ChNWs	Oil (toluene)/water emulsion	Hydrophilic in nature. Flux 1100–1300 $Lm^{-2}h^{-1}$. Separation efficiency of >99.5%.	[58]
PSf/NaOH/PA	Oil (soybean oil)/water	Superhydrophilic and stable. Flux was stable after the first cycle.	[57]

Wu et al. [68] fabricated a high-oil-adsorption film consisting of PS fibers by a facile electrospinning method. The oil adsorption capacity and oil/water selectivity depends on the porous structure and small diameter of fibers of the surface. Adsorption capacity of PS oil sorbent film for diesel oil, silicon oil, peanut oil and motor oil were approximate to 7.13, 81.40, 112.30, and 131.63 g g^{-1}, respectively which was higher than normal fibrous sorbent without any porous structure.

Uyar group [69] fabricated electrospun cellulose acetate nanofibers (CA-NF) modified with perfluoro alkoxysilanes (FS/CA-NF) and tailored their chemical and physical features aiming at oil–water separation purposes. Modified membrane was robust, superhydrophobic, stiff and easy to fabricate separation systems and yielded high amount of oil/water separation even in the repetitive applications. It was concluded that perfluoro groups consequently modified the hydrophilic CA nanofibers into superhydrophobic character and therefore FS/CA-NF could be used for future applications like water/oil separation with self-cleaning or water resistant nanofibrous structures. Table 2 shows summary of work (few and recent) reported for oil/water separation via sorption.

Table 2
Summary of work (few and recent) reported for oil/water separation via sorption.

Membrane/Fiber	Separation of	Results	Ref.
PS	Oil (gasoline, diesel, and mineral oil)/water	Contact angle of diesel 0°. CWA 155°± 3°. Adsorbs several liters of oil (gasoline, diesel, and mineral oil) from water in a few minute duration.	[64]
PCL–25BW	Oil water mixtures, (petrol/water, diesel/water and kerosene/water)	Oil sorption capacity of 16.95–31.05 g g^{-1} in different oils.	[66]
PS	Oil (Motor)/water	Oil sorption capacity of Motor oil 113.87 g g^{-1}. Bean oil 111.80 g g^{-1}. Sunflower seed oil 96.89 g g^{-1}.	[65]
PS fibers film	Oil (diesel oil, silicon oil, peanut oil and motor oil)/water	Adsorption capacity for diesel oil, silicon oil, peanut oil and motor oil- 7.13, 81.40, 112.30, and 131.63 g g^{-1}, respectively, which was higher than normal fibrous sorbent without any porous structure.	[68]
PS/PAN fiber	Oil (pump oil, peanut oil, diesel, and gasoline)/water	Maximum sorption capacities for pump oil, peanut oil, diesel, and gasoline 194.85, 131.7, 66.75, and 43.38 g g^{-1}, respectively.	[67]
FS/CA-NF	Oil/water	Superhydrophobic membrane.	[69]

2.1.3 Photocatalytic reaction

Photocatalysis is an advanced oxidation process that is employed in the field of water and wastewater treatment, in particular for oxidative elimination of micropollutants and microbial pathogens [70] and has shown a great potential as a low-cost, environmental friendly and sustainable water treatment technology. However, there are many challenges [71]. Chong et al. [72] discussed the recent R&D progress of engineered-photocatalysts, photoreactor systems, and the process optimizations and modelings of the photo oxidation process for water treatment.

Advantages of photocatalytic reaction for water treatment are:

- Large scale application.
- Catalyst optimization to improve quantum yield or to utilize visible light.
- Efficient photocatalytic reactor design and catalyst recovery/immobilization techniques.
- Better reaction selectivity.
- Low cost.

The essential application of the photocatalysts for environmental cleansing is the decontamination of microorganisms from wastewater. The photocatalytic cleaning of wastewater using ENFs membrane has attracted substantial research interest over the past few decades. Several types of photocatalysts have been tested for a variety of cleaning applications, for instance, bacterial pollutant and air contaminant removal with metal oxide containing nanofibers. In photocatalytic membranes, nanoscale inorganic photo-catalysts are embedded in a membrane matrix to enhance the properties of the resultant polymer. Photocatalyst can attack the bacterial cell wall by releasing metal ions when needed. For example, a zinc oxide nanofiber can produce zinc ions and a titanium dioxide nanofiber can release titanium ions.

Kang et al. [73] fabricated novel porous polytetrafluoroethylene (PTFE) nanofiber membranes containing Fe_2O_3 (Fe_2O_3/PTFE) via a three-step method by electrospinning, immersion and calcination. The membrane was used as a heterogeneous catalyst. The experiment showed that the porous Fe_2O_3/PTFE nanofibers exhibited high photocatalytic activity for the degradation of dye Acid Red under UV light irradiation. Under optimal conditions, the degradation efficiency of Acid Red was above 99% with UV irradiation and H_2O_2 within 80 min and the nanofiber membranes can be used over a wide range of pH values.

Li et al. [74] fabricated a novel photocatalyst supporting material, one-dimensional hollow PAN nanofiber mat (HPAN) via coaxial solution blowing method (CSB). The heterogeneous catalyst of Fe-AO-CSB-HPAN with average diameter of 735.93 nm was obtained by amidoximation and Fe coordination of CSB-HPAN. It was revealed that the membrane has excellent photocatalytic performance in the degradation of textile dyes in the presence of H_2O_2 under light irradiation.

Cozza et al. [75] demonstrated the photocatalytic activity of the nanofiber (poly(styrene-co-maleic anhydride) (PSMAn))/M-POSS system for degradation of the organic dye sulforhodamine B. Catalytic system was based on electrospun polymer nanofibers, which were modified with a metal-containing polyhedral oligomeric silsesquioxanes (M-POSS).

Cheng et al. [76] fabricated $BiVO_4$ nanofibers via electrospinning and controlled heat treatment. These $BiVO_4$ nanofibers showed an enhanced photocatalytic activity in the degradation of rhodamine-B under visible light irradiation. It was suggested that enhanced photocatalytic activity was due to the phase junction structure of the (s-t) and (s-m) phases in electrospun $BiVO_4$ nanofibers.

In another work, Taha [77] synthesized a mesostructured vanadium oxide embedded carbon nanofiber membrane decorated with Ag nanoparticles (Ag@V-CNF-1, ($AgNO_3$ = 0.05 gm) and Ag@V-CNF-2, ($AgNO_3$ = 0.1 gm) by combining the electrospinning technique with carbonization. It was revealed that membrane enhanced photocatalytic activity under visible light irradiation and the membrane exhibited excellent dye degradation (MB, MO, and RhB dyes) and bacteria (E. coli) disinfection.

Template-free porous carbon nanofibers embedded with WO_3 (WO_3–CNF) were prepared by Taha and Li [78] via combining electrospinning and carbonization process and exhibited excellent photocatalytic activity in the decomposition of different dyes (methyl orange (MO), malachite green (MG) and rhodamine B) under visible-light irradiation.

Polymer nanofibrous membranes functionalized with TiO_2 nanoparticles have already shown to be promising for photodegradation of dissolved organic matter, humic acids and bacteria [79, 80]. Geltmeyer et al. [81] used TiO_2 functionalized PA 6 (polyamide) nanofibrous membranes for methylene blue and isoproturon removal from water. The highest removal rate was obtained using the 35 wt.% inline functionalized PA (polyamide) 6 samples of the highest TiO_2 load. High photocatalytic activity was shown by methylene blue and isoproturon removal.

Prahsarn et al. [82] prepared webs of electrospun PAN/TiO_2 nanofiber from PAN/DMF and PAN/DMF/H_2O solutions containing different amounts of TiO_2 (0 to 3 wt.%). PAN webs containing 2 and 3 wt.% TiO_2 showed good photocatalytic activity in photodecomposition of MB (methylene blue) solution under UV irradiation.

Doh et al. [83] developed photocatalytic electrospun TiO_2 nanofibers for the treatment of organic pollutants (three kinds of dyes: basic blue 26, basic green 4 and basic violet 4). The surface of TiO_2 nanofiber was modified by coating TiO_2 particles by sol-gel method. On coating, photocatalytic activity and effective surface area of the membrane increased. The degradation rate ($k' = 85.4 \times 10^{-4}$ min^{-1}) of dye pollutants by the composite TiO_2 nanofiber was significantly higher than that (15.7×10^{-4} min^{-1}) of TiO_2 nanofibers and that (14.3×10^{-4} min^{-1}) of TiO_2 nanoparticles prepared by the sol–gel method. It was suggested that the composite nanofibers and nanoparticles TiO_2 be suitable for the degradation of organic pollutants.

Watthanaarun et al. [84] compared the photocatalytic activity of neat and silicon-doped titanium(IV) oxide nanofibers (both electrospun) with that of the reference anatase titania powder by following the photooxidative decomposition of methylene blue. Both the neat and the silicon-doped titania fibers exhibited much better activity than the reference titania powder.

Lin et al. [85] fabricated photo catalytically active Ag–ZnO composite nanofibers via electrospinning of Ag-ZnO containing PVP, followed by

removal of PVP and conversion of silver nitrate to silver nanoparticles. The hetero structure of the membrane promoted 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. From the investigation, it was revealed that the 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 was kept at 7.5 atom %. It was suggested that exploration of the catalytic activity of such composite structures may pave the way for designing useful nanoscale building blocks for photocatalytic and photovoltaic applications.

Ofori et al. [86] fabricated tungsten trioxide (WO_3) nanofibers by an electrospinning technique using polyvinyl pyrrolidone (PVP)/citric acid/tungstic acid as precursor solution. The photocatalytic properties of the as-synthesized nanofibers were also investigated by degrading methylene blue. Two-fold higher degradation efficiency was obtained than that of commercial WO_3 micro particles when the fiber diameter was small and the fibers were subjected to visible light illumination.

An et al. [87] fabricated three-dimensional nanofiber membranes decorated with photocatalytic titania nanoparticles. The membrane yielded 100% degradation of the methylene blue, which is often used as a model pollutant, within 90 min under a relatively weak UV irradiation (0.6 m W cm^{-2}).

On the other hand, Zhang et al. [88] studied two different systems of antimicrobial substrates based on polymer nanofibers such as:

i) electrospun nylon 6 nanofibers decorated with TiO_2 nanoparticles.
ii) solution-blown soy protein-based nanofibers coated with silver nanoparticles.

It was observed that TiO_2 decorated antimicrobial nanofibers inhibit growth of E. coli and kill them under UV light. On the other hand, soy protein nanofibers decorated with silver nanoparticles do not require any UV light activation because of the inherent antimicrobial activity of silver nanoparticles.

Xu et al. [89] demonstrated that Bi-doped TiO_2 nanofibers showed higher degradation activity of rhodamine B (RhB) and phenol in comparison with the degradation activities of TiO_2-sol under visible light irradiation ($\lambda >$ 420 nm). It was also revealed that 3% Bi:TiO_2 showed the highest photocatalytic activities.

Chen et al. [90] fabricated TiO_2/WO_3 composite nanofibers by coupling self-assembly of block copolymer containing the precursors of two metal oxides and the electrospinning technique and studied the photocatalytic decomposition of acetaldehyde by the resulting fabrics under visible light. It was revealed that the composite TiO_2/WO_3 fabrics showed improved photocatalytic activity compared with neat TiO_2 and neat WO_3.

A team of researchers in Singapore have claimed and developed a robust free standing TiO_2 nanofiber membrane which could be a cost and energy efficient way of cleaning wastewater [91]. The nontoxic TiO_2 nanofiber membrane acts as both filtration membrane and photocatalyst in water technologies. Singapore's team investigated the photocatalytic activity and anti-fouling ability of the TiO_2 nanofiber membrane using humic acid (HA) solution as the feed. It was reported that about 57% of HA was removed using the TiO_2 nanofiber membrane alone under the experimental conditions. On the other hand, under the same conditions, with UV irradiation on the membrane, the HA removal rate reached almost 100%. The team claimed that the TiO_2 nanofiber membrane has the potential to treat a large amount of water and wastewater.

Singh et al. [92] fabricated ZnO nanofiber by electrospinning of polyacrylonitrile and zinc acetate solution followed by sintering to generate pure ZnO nanofiber. The photocatalytic activity of ZnO nanofibers was studied by the degradation of naphthalene and anthracene dyes in the presence of light especially towards the ultraviolet range. It was observed that there was no drop in the photocatalyic activity of the membrane and in its physical structure after 6 cycles of testing and washing.

Sharma et al. [93] fabricated graphene-oxide-based hydrophobic PAN/GO nanofibers using electrospinning technique for photocatalytic degradation of Rhodamine 6G dye (carcinogenic dye) under natural sunlight illumination. Thus, graphene oxide nanofibers provide a scalable and novel route for photo-catalytic degradation of carcinogenic dyes from industrial water.

Liu et al. [94] investigated the photocatalytic activity of TiO_2/ZnO composite nanofibers, prepared by electrospinning, toward the decomposition of Rhodamine B and phenol. Almost 100% Rhodamine B and 85% phenol were decomposed in the presence of TiO_2/ZnO composite nanofibers under mild conditions. The results demonstrated that the blending of ZnO in the TiO_2/ZnO composite nanofibers increased the photocatalytic efficiency.

Liu et al. [95] fabricated coaxial nanofibers ZnO-TiO_2 via electrospinning and reported that ZnO-TiO_2 nanofibers possessed a photocatalytic activity higher than ZnO or TiO_2 nanofiber for the degradation of methylene blue under UV light irradiation. The separation improvement of Zn-TiO_2 may be due to ZnO-TiO_2 hetero junctions.

Table 3 shows summary of some recent works on photocatalysis for wastewater purification using electrospun nanofibers.

Table 3
Summary of some recent works on photocatalysis for wastewater purification using electrospun nanofibers.

Material/membrane	Removal /degradation of	Ref.
Fe_2O_3/PTFE	Dye Acid Red under UV light	[73]
Fe-AO-CSB-HPAN	Textile dyes in the presence of H_2O_2 under light irradiation	[74]
PSMA nanofibers/M-POSS	Dye sulforhodamine B	[75]
$BiVO_4$	Rhodamine-B under visible light irradiation	[76]
Carbon/Ag	Degradation (MB, MO, and RhB dyes) and bacteria	[77]
WO_3–carbon nanofiber	Methyl orange, malachite green and rhodamine B under visible-light irradiation	[78]
TiO_2	Organic pollutants	[83]
PAN/TiO_2	Methylene blue	[82]
TiO_2 functionalized PA 6	Isoproturon	[81]
WO_3	Methylene blue	[86]
PS-Titania mats	Methylene blue	[87]
Ag/ soy protein	Inhibit growth of E. coli and kill them under no UV light	[88]
TiO_2/nylon 6	Inhibit growth of E. coli and kill them under UV light	[88]
Si/titanium(IV) oxide	Methylene blue	[84]
TiO_2/WO_3	Acetadehyde	[90]
TiO_2 nanofibre membrane mat	Humic acid	[91]
ZnO	Naphthalene, anthracene dyes	[92]
PAN/GO	Rhodamine 6G dye	[93]
TiO_2/ZnO	Rhodamine B and phenol	[94]
ZnO-TiO_2 NF	Methylene blue	[95]

2.2 *Separation of macromolecular solutes (protein, NOMs etc.) from water*

ENFs form ineffective size-exclusion membrane for particulates removal from wastewater. Water decontamination is one of the most essential tasks for both environmental protection and wastewater reuse. The presence of contaminants, such as natural organic matter (NOMs) and trace organics accumulating in raw water create a major problem. NOMs have been shown to react with the major disinfectants (chlorine, ozone, chlorine dioxide, chloramines) to produce a host of disinfection by-products, such as trihalomethanes (THMs), haloacetic acids (HAAs), bromoform ($CHBr_3$), dibromoacetic acid (DBAA), and 2,4-dibromophenol (2,4DBP) etc. which are carcinogenic compounds. Micro/Ultra filtration (MF/UF) can produce high quality drinking water in small scale. But the main challenge for commercial membranes is their fouling caused by the deposition of contaminants such as NOMs as well as trace organics and microorganisms. High porosity of electrospun membrane per unit area makes it an appropriate candidate for filtration applications.

Lev et al. [96] studied a novel electrospun polyurethane nanofiber material for water-treatment by filtering artificial water spiked with *E*.coli. It was reported that membrane showed very high log10 removal efficiency, ranging from 5.8 to 6.8 CFU (colony-forming units) mL^{-1}, which was better results than those of the commercial membrane (3.8-4.6 $CFUmL^{-1}$).

Sato et al. [97] introduced a new class of nanofibrous composite membranes based on the infusion of surface-modified ultra-fine cellulose nanofibers (UFCNs) (5–10 nm in diameter) into an electrospun nanofibrous

scaffold. From filtration test, it was observed that these membranes have a high retention rate in removing bacteria (*E.* coli) and viruses (MS2 bacteriophage) in water, while maintaining high permeation flux. Greater than 99% of the beads as small as 500 nm were removed using gravity filtration.

Mataram et al. [98] used polyacrylonitrile, polyethersulfone and polyvinylidene fluoride nanofiber mats for the removal of pathogens by filtration from wastewater {wastewater from a general hospital (Palembang), water from a local pond (Inderalaya Pond) and water from local river (Inderalaya)}. The CWP (clean water permeability) is given in Table 4 for different nanofiber membranes. The values are high enough to treat large volumes of water in absence of particles that could obstruct the flow of water in the nanofiber membrane.

Table 4
Comparison of CWP-value

Membrane type	CWP ($Lm^{-2}h^{-1}bar^{-1}$)
Polyether sulfone	2134
Polyacrylonitrile	1982
Polyvinylidene fluoride	2001

In another article, Mataram et al. [99] reported the performances of PAN, PES and PVDF decorated with Ag nanoparticles for water treatment via micro filtration. The results showed a very good removal of TSS (total suspend solid) (94.83-97.34%), COD (89.32-95.27%) and NH_3-N (64.48-72.87%).

2.2.1 Ultrafiltration

Ultrafiltration is a membrane-based process used in many industrial processes where high separation efficiency is required, such as in water purification, biological filtration, and beverage clarification. Electrospun nanofibers can effectively improve the performance of ultrafiltration membranes. Dobosz et al. [37] demonstrated that polysulfone nanofiber-membranes had a 47% increase in permeance and a 35% increase in pure-water flux than the control ultrafiltration membranes at a TMP (transmembrane pressure) of 3.5 bar. The cellulose nanofiber-membranes and polysulfone nanofiber-membranes demonstrated a 90% improvement in fouling resistance over the control membranes, possibly because the presence of the nanofibers decreased the contact time between the protein and the membranes by 50%.

Yoon et al [100] reported that using DMF or mixed DMF/NMP as solvents, high quality electospun polyethersulfone membrane can be obtained and the membrane is very useful for water-purification. On oxidation treatment by using ammonium persulphate, electrospun PES membranes become more hydrophilic (contact angle around 28º). As for the performance of membranes, it was found that the polyethersulfone membrane electrospun from DMF showed slightly higher flux of 28261 $m^{-2}\,h^{-1}\,psi^{-1}$ than that (26261 $m^{-2}\,h^{-1}\,psi^{-1}$) for the mixed solvents (50/50). The 10% APS oxidation treatment of electrospun membrane showed the highest value of pure water flux (29131 $m^{-2}\,h^{-1}\,psi^{-1}$).

Hosseini et al. [101] separated the contaminants of a tomato industry wastewater using cellulose acetate butyrate (CAB) electrospun nanofiber membrane (ENM). The results demonstrated the potential of using CAB nanofiber membrane for wastewater treatment.

Ke et al. [102] demonstrated that the silane-grafted alumina fiber membrane can reject 100% bovine serum albumin, and 92% cellulose. The membrane can also retain 75% trypsin at the concentration of 400 ppm, while maintaining a permeation flux of 48 L $h^{-1}\,m^{-2}\,bar^{-1}$.

Goetz et al. [103] fabricated electrospun cellulose acetate membranes coated with chitin nanocrystals. Chitin nanocrystals (5%) increased the strength of CA random mat by 131% and also stiffness by 340% accompanied by decrease in strain. The pure water flux was as high as14217 L $m^{-2}\,h^{-1}$ at 0.5 bar. Due to high flux of the CA and CA-ChNC membranes, these membranes have the potential for microfiltration applications. It was suggested by Goetz et al. that these membranes have potential in future water purification of process wash water from food industry containing biological and organic contaminants.

Wang et al. [104] used surface modified electrospun RC (regenerated cellulose) nanofiber membrane with a fiber diameter of ~500 nm and membrane thickness of ~60 μm for UF. Surface of RC ENMs was modified with two types of polymer chains (i.e., poly(HEMA) (2-hydroxyethyl methacrylate) and poly(AAS) (sodium acrylate). Nanoparticles (with sizes of ~40 nm) and bovine serum albumin (BSA) molecules (with sizes of ~10 nm) were chosen for the evaluation of ultrafiltration performance of the modified membrane. It was reported that the HEMA-modified RC membranes could reject/remove more than 95% of the nanoparticles while they could not reject any BSA molecules; in comparison, the AAS-modified RC membranes had complete rejection of the nanoparticles and could even reject ~58% of the BSA molecules.

Hejazi and Mousavi [105] fabricated a double-layer chitosan (Ch)/polyvinyl alcohol (PVA)-polyacrylonitrile (PAN) and single-layer PAN nanofibrous membranes via electrospinning method and investigated its performance for wastewater treatment. It was observed that the maximum rejection values of chemical oxygen demand (COD), total dissolved solids (TDS), and turbidity using Ch/PVA-PAN nanofibrous composite membranes were 61.14, 34.6, and 99.8%, respectively.

Lee et al. [106] investigated the relationships between the structure and the water permeability and antifouling property of nafion/PVDF nanofibrous membranes which were fabricated through electrospinning process. The nanofibrous membranes revealed high porosities (>80%) and high densities of sulfonate groups on the membrane surface, leading to a high water permeability. These membranes showed superior water permeability values and antifouling performances against negatively charged oily foulants compared with a conventional CPVC microfiltration membrane due to the strong electrostatic repulsion between the negatively charged natural foulant and the negatively charged membrane surface. These membranes have also high permeability for water.

Ghani et al. [107] fabricated nanofibrous membranes based on a series of polyamide-6/chitosan composite onto a satin fabric and investigated the removal efficiency of two anionic (acidic and direct) dyes as a function of solution pH, initial dye concentration, electrospinning time, and chitosan ratio, by using central composite design (CCD). For both dyes the effect of increasing the chitosan ratio was positive. On the other hand, the effects of increasing the solution pH value and initial concentration were negative. As a result, the maximum removal efficiency was observed. It was reported that 93.2% Polar Yellow GN was removed from the solution under the following parameters: pH = 5, initial dye concentration = 100 mg L^{-1}, electrospinning time = 4 h, and chitosan ratio = 10 wt. %. For the 98.1 % removal of Solophenyl Red 3BL, the parameters were pH = 5, initial dye concentration = 50 mg L^{-1}, electrospinning time = 4 h, and chitosan ratio = 30.

Kim et al. [108] used polyvinylidene fluoride blended with polymethyl methacrylate (PMMA) electrospun nanofibrous membranes for the Seoul Zoo wastewater treatment plant. Suspended solids in the secondary effluent were completely removed, and a 48% removal of chemical oxygen demand was also achieved. It was revealed that the nanofibrous membranes have the potential to become a mainstream application in post-treatment of secondary effluent, which could lead to explore the use of nanofibrous membranes for diverse applications.

Zander et al. [109] explored the use of electrospun recycled bottle-grade PET (polyethlyene terephthalate) in the removal of particles (via liquid filtration) ranging from 30 to 2000 nm. The fibers were functionalized with biocidal materials to reduce biofouling and tested against the gram negative bacteria Escherichia coli (E. coli) and the gram positive bacteria Staphyloc. The flux was 230 ± 60 L $m^{-2}\,h^{-1}\,psi^{-1}$, which was on the high end of the range compared to other reported fluxes from nanofibrous membranes. It was reported that the rPET fibers without any surface treatment did not kill the bacteria. The functionalized rPET fibers with quaternary ammonium salt Lupasol only killed the gram negative bacteria, while the biguanide Vantocil proved effective against both gram positive and gram negative bacteria.

Asmatulu et al. [110] obtained highly purified water from various waste water sources by employing electrospun membrane PVC/PVP (polyvinylchloride (PVC) blended with polyvinylpyrrolidone (PVP)). Water was filtered through the fibrous membranes and collected in a beaker, and turbidity, pH, and TDS (total dissolved solids) were determined. Two chemical agents, Tanfloc (organic) and Alum (inorganic), were chosen for the flocculation/coagulation process. From test results it was revealed that when water suspensions were treated with the coagulants and filtered through the highly hydrophilic membranes, significantly better results were achieved. This can be a low-cost and low-pressure filtration option for the treatment of various waste waters.

Omniphobic membrane surfaces repel both water (hydrophobic) and oil (oleophobic). Lee et al. [111] synthesized an omniphobic membranes by constructing a hierarchical re-entrant structure. Negatively charged silica nanoparticles (SiNPs) were grafted on the positively charged electrospun nanofibers mats, prepared via electrospinning a blend polymer–surfactant solution of poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP)

and cationic surfactant (benzyltriethylammonium), via dip-coating to achieve multilevel re-entrant structures. Grafted SiNPs were then coated with fluoroalkylsilane to lower the surface energy of the membrane. The fabricated membrane showed excellent omniphobicity. The fabricated omniphobic membrane exhibited a stable desalination performance for 8 h of operation, successfully demonstrating clean water production from the low surface tension feed water. The developed fabrication process will impact water treatment which would benefit from highly wetting-resistant surfaces against water and organic liquids.

In another work, Messiry et al. [112] used nylon 6 electrospun nanofiber mats for wastewater treatment of Textile Company's dyeing and finishing unit. Filtration performance was tested for assessing the following properties.

i) COD (Chemical Oxygen Demand),
ii) TSS (Total Suspended Solids),
iii) TDS (Total Dissolved Solids),
iv) Turbidity NTU

The results of testing different designs indicated the improvement in the filtration efficiency.

Lee et al. [113] used electrospinning method to fabricate nanoscale polyacrylonitrile (PAN) fibers in which various amounts of exfoliated graphene oxide (GO) were systematically incorporated. Mechanical properties of the membranes were increased and water contact angle decreased with incorporation of GO. Protein (i.e. the BSA) rejection rate and water flux improved when compared with PAN only.

Faccini et al. [114] fabricated free-standing carbon nanofiber (CNF) mats by electrospinning of PAN precursor solution followed by thermal treatment. Tetraethoxyorthosilicate was also added to polymer solution to increase the specific surface area of the CNF. These membranes were capable of rejecting NPs of different sizes and natures (e.g., Au, Ag, and TiO_2) from aqueous solution.

Wang et al. [115] developed rGO/PAN nanofiltration membrane whose surface was overlaid with GO sheets after hot-pressing. This membrane had an initial water flux of 15.8 L m^{-2} h^{-1} and after 6 h of BSA filtration this value decreased to 6.8 L m^{-2} h^{-1} representing a 57.5% reduction in flux. Cleaning of this membrane with sonication regained 81% of the initial flux. Wang et al. claimed that rGO/PAN nanofiber membranes are promising nanofiltration media for water purification.

Nthumbi and Ngila [116] described a method to fabricate nanocatalyst-loaded polyvinylidene fluoride/polyacrylonitrile (PVDF/PAN) composite (Ag/PAN/PVDF-g-PAA-TiO_2/Fe–Pd) nanofiber by electrospinning and functionalization and reported that this composite membrane dechlorinated mixed pesticides (dieldrin chlorpyrifos, diuron, and fipronil) 90–99 % and mineralized to 35–45 %. Nthumbi and Ngila claimed that this composite has great potential for dechlorination and mineralization of pesticides in contaminated water.

Kiani et al. [117] used thermally treated polyphenylsulfone (PPSU) ENFs membranes and determined pure water flux. The membrane was used for filtration of canned beans production wastewater. The remarkable pure water flux of 7323 L m^{-2} h^{-1} was obtained with 100% turbidity rejection. The chemical oxygen demand and total dissolved solids rejections were 30 and 29% for the untreated membrane and 27 and 25% for the heat-treated one, respectively.

Gopakumar et al. [118] investigated and compared the performance of a polyvinylidene fluoride (PVDF) electrospun membrane, unmodified cellulose nanofiber (CNF) based PVDF membrane, and meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) modified CNF-based PVDF membrane against the Fe_2O_3 nanoparticle filtration and crystal violet (CV) dye adsorption. All membranes showed high filtration capacity against the Fe_2O_3 nanoparticles. It was also observed that meldrum's acid modified CNF-based PVDF membrane was the efficient media that could concurrently eliminate the Fe_2O_3 nanoparticles and CV dyes from the water. The authors suggested that their study opens a new path for the surface modifications of cellulose nanofibers via solvent-free techniques, which can enhance the economic feasibility of the water treatment.

Fu et al. [119] synthesised a novel protein adsorbent, functionalizing eletrospun ethylene-vinyl alcohol (EVOH) nanofibrous membranes (NFM) with critic acid (CCA), in situ. The obtained CCA-grafted EVOH NFM (EVOH–CCA NFM) membrane was presented as an excellent integrated adsorbent.

Celebioglu et al. [120] fabricated a highly efficient molecular filter membrane based on bio-renewable material, cyclic oligosaccaharides known as cyclodextrins (CD). Without any additional polymeric carrier, cross-linked insoluble poly-CD nanofibers were produced by using electrospinning technique. Electrospun cross-linked poly-cyclodextrin nanofiber exhibited significant affinity to a common class of organic pollutants (i.e. methylene blue (MB)). It was reported that the removal efficiency was above 90% with extremely high flux (3840 L m^{-2} h^{-1}) including rapid uptake of MB from liquid environment. It was suggested that the bio-based flexible electrospun poly-CD nanofibrous membrane represents a highly efficient molecular filter for wastewater treatment. Table 5 shows summary of the few recent works on ENFs membrane used for the purification of pollutants.

2.3 Separation of VOC from water

Treatment of water contaminated with volatile organic compounds (VOCs) is a major problem for chemical industry. At present, VOCs are removed from moderately contaminated wastewater streams by processes such as steam stripping and from dilute wastewaters by air stripping combined with a carbon adsorption off-gas treatment system. But now it seems membrane technology is promising to VOCs removal. Scholten et al. [121] reported that electrospun polyurethane fibers removed VOC from air with rapid VOC adsorption. The ability of a material to remove VOC is influenced by a few factors including surface area and chemistry of the material. ENMs are very promising for the VOC removal from wastewater.

2.3.1 Pervaporation (PV)

Pervaporation (PV) has been considered as one of the most active and promising areas of membrane technologies to separate water or organics from close boiling or azeotropic liquid mixtures. Over the last decade, efforts have been made to apply PV for VOC removal from water and its technical and economic feasibility. PV is believed to be a promising technology in treating dilute VOCs in either groundwater or aqueous effluents. In PV, the feed liquid contacts one side of a membrane, which selectively permeates one of the feed components. The permeate enriched in this component is removed as a vapor from the other side of the membrane. The driving force for the process is the low pressure generated by cooling and condensing the permeate vapor.

So far separation by PV has been tested for the following three categories,

(i) Dehydration of organics,
(ii) Removal of trace organics from aqueous solutions,
(iii) Organic-organic separation, etc.

However, very few works have been reported of PV by using electrospun nanofiber membranes for water treatment.

Yeh et al. [122] reported, for the first time, about the performance of the separation membrane consisting of a cross-linked PVA hydrophilic top layer, an electrospun cellulose nanofibrous buffer layer, an ENM layer with high porosity and fully interconnected pore structure, and a PET support layer (see Figure 2). The separation factor of the new membrane in ethanol dehydration was 80.8, and flux was 765 kg m^{-2} h^{-1}.

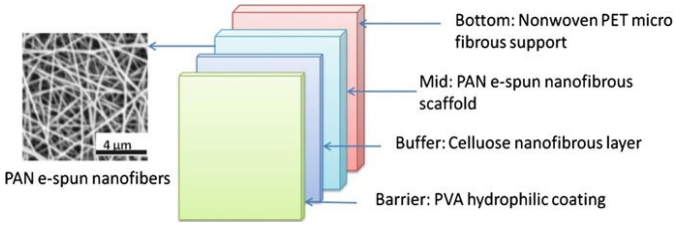

Fig. 2. Schematic representation of a high-flux pervaporation membrane with a four-layer structure [122].

Lu et al. [123] used the membrane prepared by the combination of perfluorosulfonic acid/SiO_2 nanofibers and a poly(vinyl alcohol) (PVA) pervaporation layer for the PV assisted esterification of acetic acid (HAc) and ethanol (EtOH). The esterification–pervaporation experiments were carried out in a continuous membrane contactor. It was found that the conversion of HAc at 60 °C after 10 h was 10–15% more than the equilibrium conversion and further improved to 45% over the equilibrium conversion after 55 h. The yield of ethyl acetate (EtAc) was higher than 90%, which demonstrates that the difunctional membrane could enhance the esterification process greatly through the in-situ removal of water. The results demonstrated that the membranes had good catalytic activities even at low temperature because of the nanofibrous structure of the catalysis layer.

Table 5
Summary of the few recent works on ENFs membrane used for the purification of pollutants.

Membrane/material	Used/results	Ref.
Polyurethane nanofiber	Very high log10 removal efficiency for Escherichia coli from water, ranging from 5.8 to 6.8 CFU (colony-forming units) mL^{-1}, which was better results than those of the commercial membrane (3.8-4.6 CFU mL^{-1}).	[96]
UFCNs	High retention rate in removing bacteria (Escherichia coli) and viruses (MS2 bacteriophage) in water.	[97]
PAN, PES and PVDF nanofibers mats	Removal of pathogens by filtration from wastewater.	[98]
PAN, PES and PVDF/Ag NPTs	Removal of TSS (94.83-97.34%), COD (89.32-95.27%) and NH_3-N (64.48-72.87%).	[99]
PS ENF membranes	47% increase in permeance and 35% increase in pure-water flux over the control ultrafiltration membranes at a TMP (transmembrane pressure) of 3.5 bar.	[37]
Cellulose/PS nanofiber-membranes	90% improvement in fouling resistance over the control membranes.	[37]
Functional PES ENF membrane	Water purification. Contact angle around 28°.	[100]
CAB ENF membranes	Tomato industry wastewater treatment.	[101]
Silane-grafted alumina fiber membrane	Reject 100% BSA protein and 92% cellulose.	[102]
Cellulose acetate/ chitin nanocrystals	Water filtration flux 14217 $Lm^{-2}h^{-1}$ at 0.5 bar. MF application.	[103]
RC ENFs/Poly(HEMA) or Poly(AAS) chains	HEMA-modified RC membranes reject/remove > 95% of the nanoparticles while they could not reject any BSA molecules. AAS-modified RC membranes showed complete rejection of the nanoparticles and could even reject ~58% of the BSA molecules.	[104]
CS/PVA/PAN	Wastewater treatment. Rejection values of COD, TDS and turbidity were 61.14, 34.6, and 99.8%, respectively.	[105]
Nafion/PVDF	Superior water permeability values and antifouling performances against negatively charged oily foulants.	[106]
PA-6/Chitosan	Removal of acidic and direct dyes.	[107]
PVDF/PMMA	Used in Seoul Zoo wastewater treatment plant. Suspended solids in the secondary effluent were completely removed.48% removal of chemical oxygen was also achieved.	[108]
Bottle-grade PET ENFs	Removal of particles (via liquid filtration) ranging from 30 to 2000 nm. Fibers functionalized with biocidal materials reduced biofouling and killed bacteria Escherichia coli (E. coli) and Staphyloc. Flux 230 ± 60 $Lm^{-2}h^{-1}$ psi^{-1}.	[109]
PVC/PVP	Filtration of micro and nanosize suspended articles from water.	[110]
(PVDF-HFP)-silica NPTs	Desalination.	[111]
Nylon 6 ENFs mat	Wastewater treatment of textile company's dyeing and finishing unit.	[112]
PAN-GO	Water purification. Removal of protein etc.	[113]
CNF mats	Capable of rejecting NPs of different sizes and natures from aqueous solution.	[114]
rGO/PAN	Can reject ~ 90% $MgSO_4$ with high water flux. Initial water flux of 15.8 $Lm^{-2}h^{-1}$. After 6 h of BSA filtration this value decreased into 6.8 $Lm^{-2}h^{-1}$ representing a 57.5% reduction in flux..	[115]
Ag/PAN/PVDF-g-PAA-TiO_2/Fe–Pd	Dechlorination and photodegradation of pesticides in contaminated water (90–99 %) and mineralization (35–45 %).	[116]
PPSU ENFs	Filtration of canned beans production wastewater. Water flux of 7323 $Lm^{-2}h^{-1}$. 100% turbidity rejection. COD and TDS rejections were 30 and 29% for the untreated membrane and 27 and 25% for the heat-treated membrane, respectively.	[117]
EVOH–CCA NFM	Protein (take lysozyme as the model protein) adsorption capacity of 284 mg g^{-1}.	[119].
Cellulose NF/PVDF	Remove Fe_2O_3 nanoparticles on filtration	[118]
poly-CD nanofibers	Water purification. Organic pollutant (i.e. methylene blue (MB)).	[120]

2.3.2 Membrane distillation (MD)

In membrane distillation, membranes on the basis of their selective properties are not involved in the mass transport phenomena, but are involved in heat transport from the hot side to the cold side. Membrane distillation (MD) is a thermally driven process in which a hydrophobic porous membrane only allows for passage of water vapor, but not liquid water. The hydrophobic membrane repels liquid water and prevents it from entering the pores. Vapor molecules, on the other hand, cross the membrane and are condensed at the permeate side or are removed by vacuum or a sweep gas in order to maintain the vapor pressure difference across the membrane. There are four different types of membrane distillation processes, including direct contact membrane distillation (DCMD), air-gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), and vacuum membrane distillation (VMD). Conventionally, microfiltration or ultrafiltration membranes have been used for this purpose and the membrane should be made of a hydrophobic polymer such as PVDF, polypropylene (PP), and Teflon to repel liquid water. Tijing et al. [124] wrote a review and discussed the progress in the application of nanofibrous membrane fabricated by electrospinning for MD application.

Feng et al. [125] described the removal of a volatile organic compound (chloroform) from water via membrane gas stripping (SGMD) using electro-spun poly(vinylidene fluoride) (PVDF) nanofiber membrane. Nitrogen was used as sweeping gas. The overall mass transfer coefficient of chloroform through the nanofiber membrane was found to be 2×10^{-5} m s^{-1} at room temperature which was more than the highest value obtained earlier for a hollow fiber air-stripping system.

Table 6 shows the summary of the recent works reported for the separation of VOC by using nanofiber/ nanofiber membrane.

Table 6
Summary of the recent works reported for the separation of VOC by using nanofiber/ nanofiber membrane.

Membrane/material	Removal of	Result	Ref
Pervaporation			
PVA/cellulose/PET	Ethanol dehydration	Separation factor 80.8. Flux 765 $kgm^{-2}h^{-1}$.	[122]
Perfluorosulfonic acid/SiO_2 NF/ PVA)	Esterification of HAc and EtOH. Removal of water	Conversion of HAc at 60 °C after 10 h was 10–15% more than the equilibrium conversion. It was about 45% more than the equilibrium conversion after 55 h. Yield of EtAc > 90%.	[123]
Membrane Distillation			
PVDF ENFs membrane	Chloroform removal from water	Mass transfer coefficient of $CHCl_3$ 2×10^{-5} ms^{-1} at room temperature.	[125]

2.4 Separation of chiral isomers

Optical isomers, also called *enantiomers,* of a chiral compound are distinguishable from their mirror images. This property of a compound is called chirality. In human body, the chirality of the chiral compounds plays an important role in controlling the biosynthesis and metabolism. Though optical isomers have exactly the same chemical structure, their biological properties are very different. To use chiral compounds properly for their purpose/effect, they have to be in single enantiomers. Living organisms are composed of chiral biomolecules such as amino acids, sugars, proteins and nucleic acids. In nature these biomolecules exist in only one of the two possible enantiomeric forms, e.g., amino acids in the L-form and sugars in the D-form. Current methods of enantiomeric analysis include such non-chromatographic techniques as polarimetry, nuclear magnetic resonance, isotopic dilution, calorimetry, and enzyme techniques. High performance liquid chromatography (HPLC) is one of the best methods for the direct separation and analysis of enantiomers [126]. The disadvantage of this method is that the separation cannot be easily scaled up. The amount of material produced will increase linearly with time. This process is also too costly. The crucial factor for the creation of a successful enantioselective separation by HPLC system is the proper choice of a chiral selector or chiral stationary phase.

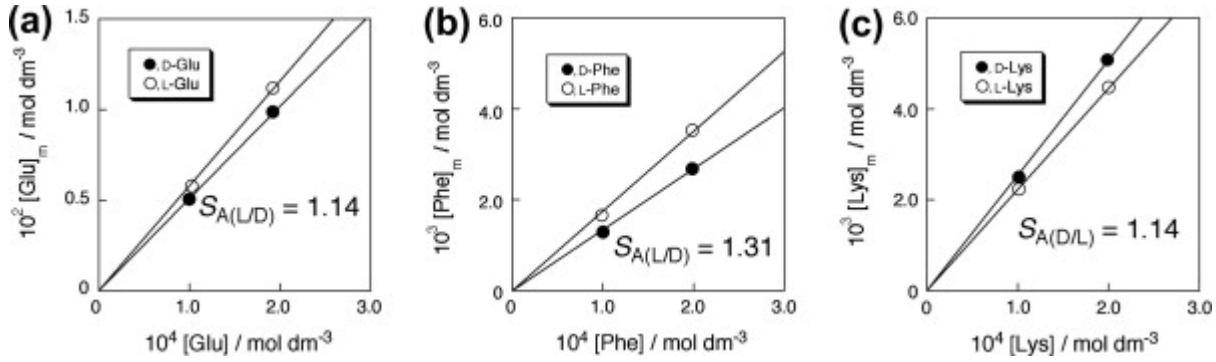

Fig. 3. Adsorption isotherms of d-isomer and l-isomer of Glu (a), Phe (b), and Lys (c) in the chitin nanofiber membrane at 40 °C [129].

Yoshikawa et al. [127] demonstrated that polymeric materials can be directly converted into molecular (chiral) recognition nanofiber membranes by simultaneously applying an electrospray deposition and an alternative molecular imprinting during the membrane preparation process.

Yoshimatsu et al. [128] encapsulated molecularly imprinted nanoparticles into poly(ethylene terephthalate) (PET) nanofibers through electrospinning. Upward 100% of propranolol-imprinted nanoparticles could be easily encapsulated into poly(ethylene terephthalate) nanofibers. These membranes were chiral-selective. The composite nanofibers were used as a sorbent material for batch solid phase extraction of propranolol.

Shiomi and Yoshikawa [129] fabricated chitin nanofiber membranes by electrospray deposition and revealed that chitin nanofiber membranes have chiral separation ability. The nanofiber membrane adsorbed l-isomer from racemic mixture of Glu and Phe in preference to the corresponding antipodes, while d-Lys was preferentially incorporated into the membrane. Figure 3 shows the adsorption isotherms of d-isomer and l-isomer of Glu (a), Phe (b), and Lys (c) in the chitin nanofiber membrane at 40 °C. As could be observed in Figure 3, all enantiomers were incorporated into the nanofiber membrane without any specific interaction, in other words, those were simply adsorbed.

Shiomi et al. [130] fabricated molecularly imprinted nanofiber membranes from chitin with imprinted phenylalanine derivative. From the experimental test it was noticed that the permselectivity was exponentially increased with the increase in the membrane thickness, implying that multi-stage cascade membrane separation was carried out within the nanofiber membrane. It was claimed by Shiomi et al. that a molecularly imprinted nanofiber membrane is one of suitable membrane forms for the separation membrane with relatively high flux and permselectivity.

Sueyoshi et al. [131] also studied chitin nanofiber membranes for chiral separation by adopting concentration gradient as a driving force for membrane transport. The chitin nanofiber membrane transported the D-isomer of glutamic acid (Glu), phenylalanine (Phe), and lysine (Lys) faster than the corresponding L-isomer. Yoshikawa et al. [127] demonstrated that non-chiral polymeric materials can be directly converted into molecular (chiral) recognition nanofiber membranes by simultaneously applying an electrospray deposition and an alternative molecular imprinting during the membrane preparation process. They studied molecularly imprinted nanofiber membranes from polysulfone with carboxylic acid as a functional moiety bearing oxygen atom. Aldehyde group is another functional moiety bearing oxygen atom.

In another work, Sueyoshi et al. [132] prepared two types of membrane i.e. molecularly imprinted membranes (MIPMs) and molecularly imprinted nanofiber membranes (MINFMs). These were prepared from polysulfone with aldehyde (PSf-CHO-05 or PSf-CHO-10) and N-α-benzyloxycarbonyl-d-glutamic acid (Z-d-Glu) or N-α-benzyloxycarbonyl-l-glutamic acid (Z-l-Glu) as a print molecule. Both membrane showed chiral separation ability by filtration. The fluxes though the molecularly imprinted membranes gave one to two orders of magnitude higher than those of usual molecularly imprinted membranes without depression of permselectivity.

Mizushima et al. [133] prepared chiral selector membranes from polysulfones bearing a derivative of alanyl residue that were synthesized by reacting benzylamine-modified polysulfones with *N*-α-acetyl-D-alanine (PSf-Ac-D-Ala) or *N*-α-acetyl-L-alanine (PSf-Ac-L-Ala). PSf-Ac-D-Ala membrane preferentially adsorbed the D-isomer of Glu from a racemic mixture of Glu and vice versa; that is, L-Glu was selectively incorporated into PSf-Ac-L-Ala. The permselectivity of PSf-Ac-D-Ala toward D-Glu ($\alpha_{D/L}$) was 1.40, and that of PSf-Ac-L-Ala toward L-isomer ($\alpha_{L/D}$) was 1.48. Mizushima et al. [134] electrospan PSf with three types of alanyl residue ((*N*-α-acetylalanine (Ac-Ala-OH), *N*-α-benzoylalanine (Bzo-Ala-OH), and *N*-α-benzyloxycarbonylalanine (Z-Ala-OH)) as chiral selectors (prepared by polymer reaction) and showed adsorption selectivities toward racemic Glu (adopted as model racemates). Flux values for those nanofiber membranes were two to three orders of magnitude enhanced comparing with the corresponding typical dense membranes, without reduction of permselectivity. PSf-Ac-d-Ala membrane transported l-Glu in preference to d-Glu and *vice versa*, while PSf-Bzo-Ala and PSf-Z-Ala membranes hardly gave any permselectivity.

Kawasaki and Yoshikawa [135] prepared cellulose triacetate (CTA) electrospun nanofiber membranes with and without molecular imprinting. CTA nanofiber membrane without imprinting incorporated L-Glu in preference to D-Glu. Z-L-Glu molecularly imprinted nanofiber membranes showed adsorption selectivity for Z- and L- isomer, respectively. The affinity constant between L-Glu and the control CTA nanofiber membrane was 3.8×10^3 mol^{-1} dm^3 while that for CTA-L was 7.9×10^3 mol^{-1} dm^3. The permselectivity for the CTA nanofiber membrane was determined to be 1.47. Those nanofiber membranes gave high flux values, and the molar mobility for those was over 1.0×10^{-8} mol cm cm^2 J^{-1}h^{-1}. Ifuku and Saimoto [136] fabricated chitin nanofibers from the exoskeletons of crabs and prawns and reported that chitin nanofibers showed chiral separation ability. It was reported that the chitin nanofiber membrane transports the D-isomer of glutamic acid, phenylalanine, and lysine from the racemic amino acid mixtures faster than the corresponding L-isomer.

Table 7 shows the summary of some recent works on chiral separation by nanofiber/nanofiber membrane.

2.5 Miscellaneous

Kayaci and Uyar [137] developed cyclodextrin (CD) functionalized electrospun PET (polyester) nanofibers by using three different types of native CD (a-CD, b-CD, and c-CD) having 25% (w/w) loading. From the characterization of membranes via XRD, it was observed that CD molecules were distributed in the nanofiber matrix without any crystalline CD aggregation. The performance of membranes was tested by studying entrapment of aniline from vapor phase to the PET/CD membranes. Higher amount of aniline was entrapped by PET/CD nanofibrous webs when compared to pristine PET web. The entrapment efficiency of aniline vapor was found to be better for PET/c-CD nanofibers compared to PET/a-CD and PET/b-CD nanofibers. It was suggested by the authors that the electrospun PET nanofibers functionalized with CD may be used as filtering material for removal of VOC (volatile organic compounds) in air filtration.

Taheran et al. [138] fabricated a series of polyacrylonitrile/activated biochar nanofibrous membranes (NFMs) with different loadings of biochar (0–2%, w/w) via electrospinning. It was reported that at 1.5% of biochar loading, the surface area reached the maximum value of 12.4 m^{2}g^{-1} and the membrane can efficiently remove micropollutants, such as CTC (chlortetracycline) from aqueous media. It was suggested that these types of systems can be used in the removal of contaminants from aqueous environmental streams. However, further research is needed to increase the adsorption capacity of fabricated membranes.

Liang et al. [139] reported that carbon Microfibers with Hierarchical porous structure from electrospun fiber exhibited good adsorption property toward organic vapor. Liang et al. [140] developed uniform carbonaceous nanofibers (CNFs) membranes. These membranes exhibited larger adsorption

capacities than commercial granular active carbon (GAC) and carbon nanotubes (CNTs) because of their large surface area, high uniformity, and numerous active sites on the surface of nanofibers. From membrane filtration experiments it was proved that the CNF membranes could remove methylene blue (MB) efficiently at a very high flux of 1580 L m^{-2} h^{-1}, which is 10–100 times higher than that of commercial nano- or ultrafiltration membranes with similar rejection properties. Thus, due to high adsorption and regenerability performance of the CNF membrane, it has potential applications in water purification.

Silver is a widely-used and recognized broad spectrum biocidal agent that is effective against bacteria, fungi and viruses but is non-toxic to human cell. In the past few years, silver-containing electrospun nanofibers have attracted interest as a novel form of antimicrobial material [104, 141, 142]. Wang et al. [143] used cellulose acetate nananofiber, decorated with Ag, for treatment of the dye wastewater (rhodamine B aqueous solution). The membrane showed effective adsorption performance including remarkable antibacterial property when compared to the CA nanofibrous membrane without silver NPs. The silver-loaded highly porous CA nanofibrous membrane could be considered as an ideal candidate for treatment of the dye wastewater.

Table 7
Summary of some recent works on chiral separation by nanofiber/nanofiber membrane.

Membrane	Removal	Result	Ref
Molecularly imprinted into PET nanofibers	Chiral isomers	These membranes were chiral-selective.	[128]
Molecularly imprinted nanofiber membranes from carboxylated polysulfone	Chiral isomers	Non-chiral polymeric materials can be directly converted into molecular (chiral) recognition nanofiber membranes by simultaneously applying an electrospray deposition and an alternative molecular imprinting during the membrane preparation process.	[127]
Chitin nanofiber membranes	Chiral isomers	Membrane can separate chiral isomers. Adsorbed L-*isomer* from racemic mixture of Glu and Phe in preference to the corresponding antipodes. Multi-stage cascade separation was demonstrated adopting racemic mixture of amino acid.	[129]
Molecularly imprinted chitin nanofiber	Chiral separation	Molecularly imprinted nanofiber membrane is one of suitable membrane forms for the separation membrane with relatively high flux and permselectivity	[130]
Chitin ENFs membranes	Chiral separation	Separation ability. Concentration gradient as a driving force for membrane transport.	[131]
Molecularly imprinted polysulfone-aldehyde (MINFMs)	Chiral separation	Abilityof chiral isomer separation. Molecularly imprinted ENFm gave high flux without depression of permselectivity.	[132]
Polysulfones bearing a derivative of alanyl residue (PSf-Ac-L-Ala.)	Chiral separation	Preferentially adsorbed the D-isomer of Glu from a racemic mixture of Glu and vice versa.	[133]
PSf with three types of alanyl residue	Chiral separation	Adsorption selectivities toward mixture of racemic Glu. Flux values two to three orders of magnitude enhanced comparing with the corresponding typical dense membranes, without reduction of permselectivity.	[134]
CTA molecular imprinting	Chiral separation	Ability to separate chiral isomers. Affinity constant between L-Glu and specific adsorption site in the control CTA nanofiber membrane 3.8×10^3 mol^{-1} dm^3.	[135]
Chitin nanofibers from the exoskeletons of crabs and prawns	Chiral separation	Chiral separation ability. Transports the D-isomer of glutamic acid, phenylalanine, and lysine from the racemic amino acid mixtures faster than the corresponding L-isomer.	[136]

Shalaby et al. [144] reported that Ag/polyacrylonitrile (Ag/PAN) hybrid nanofibers prepared by electrospinning have a high bactericidal effect. Antimicrobial PAN nanofibers containing silver nanoparticles (Ag-NPs) were prepared by simple electrospinning technique and used in water disinfection. It was reported that E. coli bacteria significantly reduced (>97%) when bacteria in water contacted with Ag/PAN hybrid nanofibers. It was claimed in this work that PAN nanofibers are excellent candidate for carrying silver nanoparticles and for being used in water treatment.

Foroozmehr et al. [145] used polyacrylonitrile ENFS functionalized with β–cyclodextrin (βCD) to treat a reactive dye wastewater stream by dynamic method. It was revealed that the dye removal efficiency was increased from 15.5% for PAN to 24% for PAN/βCD nanofiber mats.

Celebioglu et al. [120] suggested that the bio-based flexible electrospun poly-CD nanofibrous membrane represents a highly efficient molecular filter for wastewater treatment. Min et al. [146] fabricated a novel micro-nano structure poly(ether sulfone)/poly(ethyleneimine) (PES/PEI) nanofibrous membrane and studied its performance as an adsorbent for anionic dyes or from aqueous solutions. The adsorption equilibrium data were all fitted well to the Langmuir isotherm equation, with a maximum adsorption capacity values of 1000.00 mg^{-1}, 344.83 mg^{-1}, 454.44 mg^{-1} for Sunset Yellow FCF, Fast Green FCF, respectively.

Zhu et al. [147] fabricated a superhydrophilic/underwater superoleophobic graphene oxide (GO)-coated cotton for wastewater purification. GO was attached onto the surface of cotton fibers by means of hydrogen bonds between oxygen-containing groups of GO and cotton. The water contact angle was 0° and an underwater oil contact angle was 170° ± 1° on the GO-coated cotton. The GO/cotton membrane can effectively purify various oil-in-water emulsions, dye wastewaters and even mixtures of both. Most of oils could be filtered with the removal efficiency over 99% and dyes could be absorbed with removal efficiency of over 97%.

The word "*Piezoelectricity*" means electricity resulting from pressure and heat. A piezoelectric polymer is a material having piezoelectricity (it is the ability of materials, which is the property that the polarization of a material change by applying stress and/or strain) [148]. Electrospun nanofiber membrane which have piezoelectric property guarantee the high water productivity and maintenance. Bae et al. [149] fabricated a PVDF nanofiber membrane for a piezoelectric MF membrane application. The fabricated piezoelectric ENM showed high potential for water treatment in terms of water flux and antifouling effect. The optimized pENM exhibited three times higher water permeability (5573 LMH bar^{-1}) and rejection performance (99.87%) for particulates (0.1 g L^{-1} Kaolin solution at 0.25 bar pressure) than a commercial MF membrane. The advanced performance of the pENM shows that it has a strong potential for water-treatment applications.

Table 8 shows the summary of some recent works on chemical separation (miscellaneous) by using electrospun nanofiber/nanofiber membrane.

3. Separation of inorganics from water

3.1 Desalination

3.1.1 Desalination by PV, RO, NF, FO

Attempts have been made to desalinate salty water using ENMs. Some were by RO/NF and the others are by MD. Because of the large pore sizes of ENMs, most of the works were done by the membrane distillation (MD) process.

The hydrophilicity of ENM's surface can be enhanced in the presence of MWCNTs (multiwall carbon nanotubes) [150]. The produced fiber can be used to remove cations and anions from water using electrochemical capacitive deionization (CDI) reactor achieving high water recovery. Kaur et al. [151] investigated the influence of heat pressing on polyacrylonitrile electrospun nanofibrous membrane properties on the separation of salt by RO after interfacial polymerization of the surface of ENM. It was reported that composite nanofiber membranes showed very high flux in comparison with the flux obtained by commercial membranes (NF90 and NF270 FilmTec). However, rejection was approximately 8–12% less than the commercial membranes.

3.1.2 Desalination by MD

For MD process, commercially available microfiltration membranes are often used but they are not necessarily suitable due to their low permeation flux and pore wetting issues [152]. Many attempts have been made to replace commercial MF membranes by ENMs of enhanced hydrophobic property, high porosity, and adequate pore sizes.

Since the first application of ENM in 2008 [153], a number of researchers have improved its NF property by fabricating new composite, unique hybrid designs such as dual layer [154, 155] and triple layer [157] membranes. In most cases, hot pressing and surface modification were adopted to reduce the

pore size of ENMs down to those of RO and NF. Feng et al. [154] are the first to investigate desalination of salty water by MD. Electrospun PVDF nanofibrous membrane was used in air gap membrane distillation (AGMD) in their experiments. The results showed that drinking water can be obtained (<280 ppm NaCl) from up to 6 % salt solution with fluxes as high as or higher than commercial PVDF membranes.

Woo et al. [155] used dual-layer nanofiber nonwoven membranes for desalination by air gap membrane distillation (AGMD). The top layer of the membrane was hydrophobic polyvinylidene fluoride-co-hexafluoropropylene (PH) supported on different hydrophilic layer made of either polyvinyl alcohol (PVA), nylon-6 (N6), or polyacrylonitrile (PAN) nanofibers. The dual-layer ENMs showed a water permeate flux of about 10.9–15.5 L/m^2 h (LMH) using 3.5 wt.% NaCl solution as feed, which was much higher than that of a commercial PVDF membrane (~ 5 LMH). It was revealed that the wettability and characteristics of the support layer affects the AGMD performance. The PH/N6 dual-layer nanofiber membrane showed flux and salt rejection of 15.5 LMH and 99.2%, respectively.

Table 8
Summary of some recent works on chemical separation (miscellaneous) by using electrospun nanofiber/nanofiber membrane.

Membrane/material	Separation of	Result	Ref.
CD functionalized electrospun PET nanofibers. ((a-CD, b-CD, and c-CD))	Aniline in vapor phase.	Higher amount of aniline was entrapped. PET ENFs functionalized with CD may be used as filtering material for removal of VOC (in air filtration).	[137]
PAN ENFS functionalized with βCD	Reactive dye wastewater stream by dynamic method.	Removal efficiency increased from 15.5% for PAN to 24% for PAN/βCD nanofiber mats	[145]
PAN/activated biochar NFMs	CTC from aqueous media	Efficiently remove micropollutants.	[138]
Carbonaceous nanofibers (CNFs) membranes.	Methylene blue (MB)	Larger adsorption capacities than GAC CNTFs. Flux of 1580 L m^{-2} h^{-1}. Potential applications in water purification.	[140]
HEMA-modified RC	Nanoparticles	Remove >95%	[141]
AAS-modified RC membranes	Nanoparticles and BSA molecule	Rejection of the nanoparticles 100% and ~58% of the BSA molecules.	[142]
Ag/CA ENFs	Rhodamine B in aqueous solution	Ideal candidate for treatment of the dye wastewater.	[143]
Ag/PAN hybrid ENFs	E-coli bacteria	Reduced > 97%. Ag/PAN best for water treatment.	[144]
PVDF NF nanofiber (piezoelectric electrospun nanofiber membrane for MF)	Kaolin particles (0.1 g/L Kaolin solution at 0.25 bar pressure) (turbidity)	Water permeability 5573 LMH bar^{-1}.Kaolin rejection rate >99%.	[149]
Cellulose NF/PVDF	CV dyes from the water	Remove by membrane adsorption,	[118]
PES/PEI nanofibrous membrane	Dyes removal from water	Maximum adsorption capacity : 1000.00, 344.83 and 454.44 mg g^{-1}, for Sunset Yellow FCF, Fast Green FCF and Amaranth, respectively	[146]
Go coated cotton	Oil-water removal	Effectively purified various oil-in-water emulsions, dye wastewaters and even mixtures of both.	[147]

Jiříček, et al. [157] tested electrospun PVDF membranes under various conditions on a direct contact membrane distillation (DCMD) unit, and determined the optimum conditions for the maximum flux. Nanofibers were collected on a nonadhesive paper substrate and laminated on a Meyer (DE) flatbed laminator at 1.5 m min^{-1}, using a pressure of 10 N cm^{-2} at 135°C. The sodium chloride containing 0 to100 g kg^{-1} was demineralized in a distillate circuit. It was reported that thinner membranes have higher fluxes and lower distillate purity. In another article, Jiříček et al. [158] fabricated four self-sustained electrospun polyurethane (PUE) nanofiber membranes with varying thickness and tested to find the optimum structural parameters and operational conditions for the best MD performance in waste water treatment. The highest flux was achieved with the thinnest membranes and the best energy efficiency was achieved with the thickest membranes. All membranes had salt retention above 99%.

Li et al. [159] fabricated, electrospun superhydrophobic organic/inorganic composite nanofibrous membranes by a facile route combining the hydrophobization of silica nanoparticles (SiO_2 NPs) and colloid electrospinning of PVDF matrix. These membranes showed excellent DCMD performance. The silica nanoparticle sizes have a decisive influence on the nanofiber morphology, fiber diameter distribution, surface wettability, and membrane structural attributes. The DCMD test was conducted with 3.5 wt. % NaCl aqueous solution as feed, and the permeate tank was distilled water (a conductivity of around 2.45 μs cm^{-1}). The feed solution was heated to 60 °C by one heating system and circulated with a flow rate of 0.6 L min^{-1} by a diaphragm laboratory pump, while the permeate side was maintained at 20 °C by one chiller to condense the permeate vapors and circulated by another diaphragm laboratory pump at the same flow rate. It was reported that >99.99 % rejection was observed with PVDF-S-40 and PVDF-S-167 under experimental conditions. Thus desalination evaluation results indicated that the superhydrophobic PVDF-S-x ENMs (S-x represents size of SiO_2 in nanometers) showed superior DCMD performance in the NaCl solution system, which demonstrated the feasibility of designing and manufacturing of novel PVDF-S-x ENMs for MD applications.

Lee et al. [160] prepared ENMs incorporating fluorosilane-coated TiO_2 nanocomposite for DCMD. Functionalized with 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane, TiO_2 was added in doping solution of polyvinylidene fluoride-*co*-hexafluoropropylene (PH) before electrospinning. The ENMs containing 10% TiO_2 exhibited better flux and stable salt rejection than the commercial membrane (PVHP, HVHP Millipore) and ENMs without TiO_2. The membrane electrospun from the spinning dope containing 20% PH with 10% TiO_2 exhibited a flux of approximately 40 L m^{-2} h^{-1}.

Francis et al. [161] investigated the performance of Matrimid 5218 for desalination by using MDA (membrane distillation application) technique, and observed high water vapour flux of 56 kg m^{-2} h^{-1} and 99.99% salt rejection under experimental conditions.

Essalhi and Khayet [162] fabricated self-sustained ENMs of different thicknesses (144.4 to 1529.3 μm) from PVDF for desalination via DCMD. It was revealed that the maximum permeate flux of the PVDF membrane via DCMD was 15.2 x 10^{-3} kg m^{-2} s^{-1} when the feed temperature was 80 ºC and permeate temperature was 20 ºC and the NaCl rejection was higher than 99.34% and no wetting was observed for 24 h operating time.

Zhou et al. [163] used polytetrafluoroethylene (PTFE)/PVA nanofiber membranes, after sintering at 380 °C for 30 min, in VMD. The membrane had unique uniform fiber network with a water contact angle above 150°. Pure water permeability and salt rejection was tested. The pure water flux reaches as high as 15.8 kg m^{-2} h^{-1} when trans-membranous pressure was 30 kPa and feed temperature was 80 °C. Membrane displays a stable salt rejection above 98.5% for 10 h operation when the feed NaCl concentration is 3.5%. as shown in Figure 4.

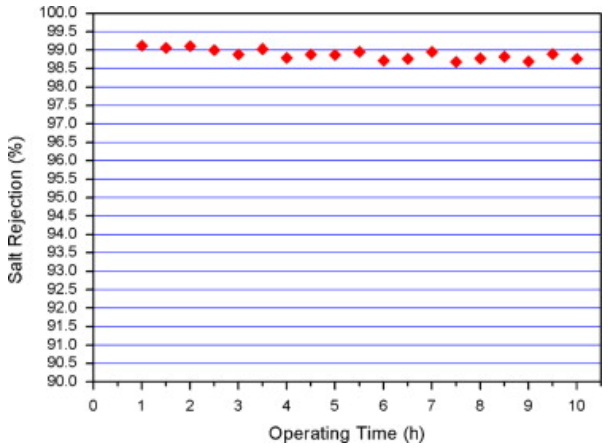

Fig. 4. Salt rejection of 10 h continuous VMD application [163].

Su et al. [164] studied the DCMD performance of two composite nanofibrous membranes of PVDF and poly(vinylidenefluoride-co-

hexafluoropropylene) (PVDF-co-HFP) prepared by the electrospinning process. The contact angle of the PVDF-HFP electrospun membrane (128°) was higher than the PVDF electrospun membrane (125°). The nanofibers with an average fiber diameter of 170 nm and a maximum pore diameter distribution of 0.3 µm were the best for DCMD system. From DCMD tests, it was observed that salt rejection was 99.9901% for the PVDF-co-HFP electrospun membrane, while for PVDF it was 99.9888 %. At the flow rate of 210 mL min^{-1}, the maximum permeation flux achieved was 10.9 kg m^{-2} h^{-1} for the PVDF-co-HFP electrospun membrane and 10.1 kg m^{-2} h^{-1} for the PVDF electrospun membrane.

Li et al. [165] fabricated a superhydrophobic and self-cleaning polysulfone-polydimethylsiloxane (PSU-PDMS) ENMs via *electrospinning* PSU followed by PDMS coating. The membrane was used for desalination by DCMD after cold-press post-treatment under different pressures. It was reported that the PDMS concentration dictates the surface morphology and hydrophobicity. Competitive permeate flux of about 21.5 kg m^{-2} h^{-1} was obtained from PSU-PDMS-1–4 (prepared with 1 g PDMS in 40 mL hexane and 4 MPa applied cold-press post-treatment pressure). It also exhibited stable low permeate concentration with an electrical conductivity of 4.224–4.523 µS cm^{-1} when using 30 g L^{-1} NaCl aqueous solution as feed and a temperature difference of 50 °C over a DCMD period of 12 h without detecting inter-fiber space wetting.

Oleophobic membranes resist the penetration of low surface tension contaminants such as cleaning agents, detergents, oils and chemicals. Omniphobic surface repels both water (i.e., hydrophobic) and low surface tension liquids such as oil (i.e., oleophobic). Woo et al. [166] investigated the AGMD performance of ENMs fabricated from omniphobic poly(vinylidene fluoride) (PVDF) and surface modified by CF_4 plasma. The AGMD performance of the membranes was evaluated using real reverse osmosis (RO) brine produced from coal steam gas (CSG) water. AGMD performance showed stable normalized flux (initial flux of 15.3 L m^{-2} h^{-1}) and rejection ratio (100%). Results obtained from CF_4 plasma-modified omniphobic ENM suggested that the omniphobic membrane has good potential for producing clean water from waters containing high salinity and organic contaminants.

Tijing et al. [154] tested membranes composed of a dual-layered structure of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) nanofibers and polyacrylonitrile (PAN) microfibers for desalination by DCMD. The membrane showed high water fluxes of 45 and 30 L m^{-2} h^{-1} for distilled water and 35 g L^{-1} NaCl solution, respectively, as feed. It was reported that the thinner, the more hydrophobic and the higher porosity layer would result in the better DCMD flux. More than 98.5% salt rejection was reported.

Prince et al. [156] developed a novel triple layer (PVDF nanofibers/PVDF casted/PET support) hydrophobic/hydrophilic membranes through wet casting and electrospinning process. PVDF nanofibers were electrospun on the PVDF side of the flat (PVDF casted/ PET support) membrane. Figure 5 shows SEM image of the various layers of the triple layer membrane.

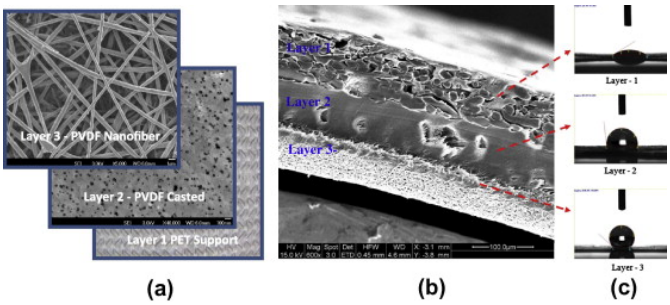

Fig. 5. SEM image of the various layers of the triple layer membrane. Layer 3 faces the hot feed water side and layer 1 faces the side with the air gap. (a) Top surface of the triple layer membrane in order of layer numbers from top to bottom. (b) Cross-section view of the triple layer membrane and (c) contact angle of the respective layers [156].

The membrane was tested for desalination by AGMD. In AGMD process, the top layer, consisting of PVDF ENFs faces the air gap. While the bottom layer, PET support faces the hot feed water side. The data obtained with triple layer was compared with double layer (without electrospun nanofiber) membrane. Figure 6 shows AGMD flux versus different feed temperature for the triple and dual layer membrane.

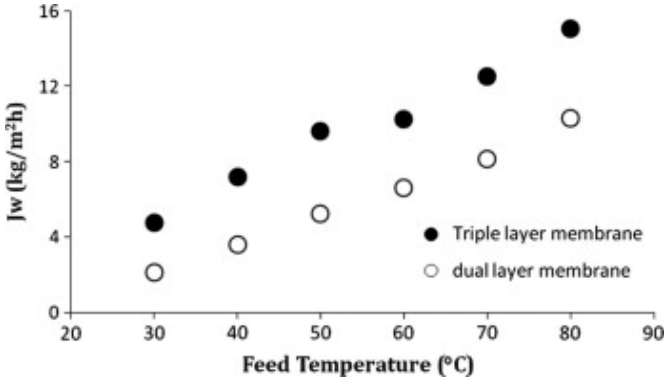

Fig. 6. AGMD flux versus feed temperature for the triple layer and dual layer membrane [156].

As could be observed in Figure 6, at each temperature the flux of the triple layer membrane is approximately 1.5 times higher than the dual layer membrane. The triple layer membrane could be operated continuously for more than 40 h without any significant change to permeate quality, whereas the dual layer membrane could only be operated for 10 h before pore wetting occurred.

Figure 7 shows the average salt rejection of the triple layer membrane and the dual layer membrane. It seems that the salt rejection of dual layer membrane was not as stable as the triple layer composite membrane. It also decreased as the feed temperature increased. Thus, adding a single layer of nanofiber on the top of dual layer membrane improved the performance of the membrane for MD applications.

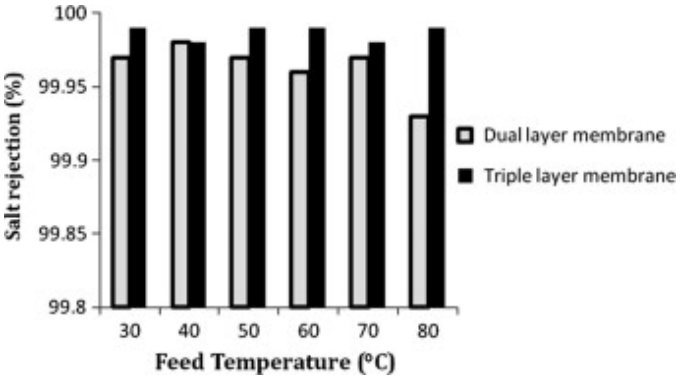

Fig. 7. Average salt rejection of the triple layer and dual layer membrane [156].

Furthermore, Prince et al. [167] enhanced the hydrophobicity of the PVDF membrane by incorporating Cloisite® clay in the electrospinning solution at concentrations of 2, 4, and 8 %. The contact angle measurements confirmed the direct correlation between hydrophobicity of the prepared ENMs and the clay concentration. The desalination experiments were conducted using a DCMD configuration with a 3.5 % NaCl solution. The feed temperature was varied between 50 and 80 °C and the permeate was maintained at 17 ± 2 °C. The results indicated that higher clay concentrations consistently resulted in higher fluxes. Also, incorporation of clay enhanced the salt rejection from 98.27 to 99.95 %.

Liao et al. [168] fabricated and optimized the PVDF nanofiber membranes for DCMD application, by controlling a series of factors including polymer dope compositions and spinning parameters. A permeation

flux of 21 kg m^{-2} h^{-1}, which was higher than those have already reported by Prince et al. [166] (DCMD) and Feng et al. [154] (AGMD) was achieved. However, the study did not report salt rejection. It was also revealed that heat-press post treatment could enhance the membrane performance in DCMD.

Dong et al. [169] fabricated a superhydrophobic nanofibrous membrane via electrospinning of PVDF. The PTFE nanofibrous scaffold coupled with a microporous PTFE substrate. On testing theses membranes by vacuum membrane distillation (VMD), a stable permeate flux of 18.5 kg m^{-2} h^{-1} and salt rejection higher than 99.9% was obtained throughout the entire testing period of 15 h. In another publication, Dong et al. [170] fabricated superhydrophobic ENMs by the electrospinning of poly(vinyl alcohol) (PVA), followed by chemical cross-linking with glutaraldehyde and surface modification via low surface energy fluoroalkylsilane (FAS). These FAS-PVA membranes showed a high and stable permeate flux of 25.2 kg m^{-2} h^{-1} in VMD process, 70% higher than those of the commercial PTFE membranes, with satisfying permeate conductivity (<5 μScm^{-1}) during a continuous test of 16 h (3.5 wt.%, 333 K and 9 kPa, respectively, for NaCl concentration in feed, feed temperature and permeate pressure). In another work, Dong et al. [171] used composite PVDF–SiO_2 nanofiber membranes endowed with superhydrophobicity by the fluorosilanization of the surface. It was reported that the optimal superhydrophobic nanofiber membrane maintained a stable flux of 31.5 kg m^{-2} h^{-1} with a permeate conductivity approximately 10 μScm^{-1} over the entire VMD test period. The results indicated that the superhydrophobic modification process rendered the nanofiber membrane anti-wetting properties without compromising its excellent permeability.

Liao et al. [172] fabricated two types of superhydrophobic PVDF ENMs, integrally-modified and surface-modified PVDF. Electrospinning was followed by surface modification, which included dopamine surface activation, silver nanoparticle deposition and hydrophobic treatment. The integrally-modified membrane achieved a high and stable MD water flux of 31.6 L m^{-2} h^{-1} using a 3.5 wt.% NaCl as the feed solution while the feed and permeate temperatures were fixed at 333 K and 293 K, respectively.

Woo et al. [173] demonstrated the application of graphene/PVDF-HFP (G/PH) ENMs in desalination by AGMD using 3.5 wt.% NaCl solution as feed. The nanofiber membrane with 5 wt.% graphene loading (G5PH) showed an adequate porosity (88.7%), pore size (0.86 μm), contact angle (162.7°) and high liquid entry pressure (LEP) (186.9 kPa). A high and stable AGMD flux of 22.9 L m^{-2} h^{-1} (LMH), compared with ~4.8 LMH for the commercial PVDF flat-sheet membrane, was obtained with 100 % salt rejection for 60 h of operation.

Obaid et al. [174] developed a process to produce PVDF-based thin-film composite forward osmosis (TFC-FO) electrospun membranes for enhanced desalination performance. The process is based on improving the surface properties of the PVDF electrospun nanofiber support layer using triethylamine (TEA). The modified TFC-FO membrane exhibited a high water flux, approximately 68 LMH and low reverse salt flux, about 2 g m^{-2} h^{-1} at 2 M NaCl draw solution, with >99.5% salt rejection.

Tian et al. [175] explored the use of electrospun PVDF nanofibers as substrates to make FO membranes. By using interfacial polymerization (IP), polyamide thin films were formed on two electrospun PVDF nanofiber substrates. The difference of the two membranes was their surface properties in terms of pore size and surface roughness. Water permeability of 1.21 L m^{-2} h^{-1} bar^{-1} and NaCl salt rejection of 93.6% at 5 bar pressure were observed by RO for the denser substrate which had smaller pore sizes. On the other hand, for the substrate with larger mean pore sizes of 0.41 ± 0.01 μm, water permeability of 3.15 L m^{-2} h^{-1} bar^{-1} and NaCl salt rejection of 84.4% were obtained under the same 5 bar pressure. Both membranes showed excellent performance in FO process because of their superior porous and interconnected open structure that resulted in reduced internal concentration polarization.

Wang et al. [115] fabricated GO sheet layers of various thicknesses surface-overlaid on the hot-pressed polyacrylonitrile (PAN) ENM via a vacuum-assisted filtration approach. From nanofiltration technique it was revealed that reduced GO (rGO) layer can reject ~90% $MgSO_4$ with high water flux (due to the size exclusion mechanism), making the prepared PAN-rGO membranes promising nanofiltration media for water purification.

Table 9 shows the summary of some of recent works on ENMs used for desalination.

Table 9
Summary of some of recent works on ENMs used for desalination.

Material/membrane	Result	Ref.
Two types superhydrophobic PVDF ENFs, integrally-modified and surface-modified PVDF ENMs, surface modified by Ag NPTs deposition and hydrophobic treatment	Integrally-modified membrane achieved a water flux of 31.6 L$m^{-2}h^{-1}$ with a feed solution of 3.5 wt. NaCl.	[172]
PVDF ENFs	Flux depended on the thickness of the membrane. Rejection 90%.	[157]
PUE ENFs membranes with various thicknesses	Higher flux was obtained with the thinner membranes. Salt retention above 99%.	[158]
SiO_2 NPs/PVDF ENFs	Permeate vapor flux 41.1 kg $m^{-2}h^{-1}$. Permeate conductivity ~2.45 μs cm^{-1}.	[159]
PVDF and PVDF-co-HFP	Salt rejection of PVDF-co-HFP (99.9901 %) and PVDF (99.9888 %) was almost the same as the PTFE commercial membrane (99.9951%). The permeate flux of the PVDF-HFP composite membrane was by 4.28 kg m^{-2} h^{-1} higher than the PTFE commercial membrane.	[164]
TiO_2/ PVDF-co-HFP (PH)	Flux of 40 L$m^{-2}h^{-1}$, permeate conductivities below 2.1 μS cm^{-1} for two days, and below 7.0 μS cm^{-1} for seven days.	[160]
PVDF ENFs	Permeation flux 21 kg m $^{-2}h^{-1}$.	[168]
Matrimid 5218	Water vapour flux of 56 kg $m^{-2}h^{-1}$ and 99.99% salt rejection.	[161]
PVDF ENFs with different thicknesses	Permeation flux 15.2 x 10^{-3} kg $m^{-2}s^{-1}$, NaCl rejection > 99.34%. No significant changes were observed for the diameter of the ENMs (1.0–1.3μm).	[162]
PSf-PDMS ENMs	Permeate flux 21.5 kg m^{-2} h^{-1}, permeate conductivity 4.224 – 4.523 μS cm^{-1}.	[165]
FAS/PVA ENMs	Flux of 25.2 kg $m^{-2}h^{-1}$, permeate conductivity <5 μm cm^{-1}.	[170]
Cloisite/PVDF	High flux, salt rejection 98.27 to 95%.	[167]
Dual layer PVDF-co-HFP/PAN	Flux 30 LMH, salt rejection >98.5%.	[154]
FAS- PVDF–SiO_2	Stable flux of 31.5 kg $m^{-2}h^{-1}$ with a permeate conductivity approximately 10 μs cm^{-1}.	[171]
PVDF	Salt rejection of 98.7–99.9%, flux around 11.8 kg $m^{-2}h^{-1}$ for 6 % feed salt solution.	[153]
Graphene/PVDF-HFP	Flux 22.9 L $m^{-2}h^{-1}$, salt rejection 100% for 60 h of operation.	[114]
PVDF modified with CF_4 plasma	Flux 15.3 L $m^{-2}h^{-1}$, rejection 100% for RO brine from CSG.	[166]
Triple layer PVDF nanofiber/PVDF casted/PET support	Flux 15.2 kg $m^{-2}h^{-1}$.	[156]
PA/ PVDF ENFs	Water permeability 1.21 L$m^{-2}h^{-1}bar^{-1}$, NaCl salt rejection of 93.6% for RO. Excellent FO performance.	[175]
TEA/PVDF ENFs	Water flux approximately 68 LMH, reverse salt flux, about 2 g $m^{-2}h^{-1}$ for 2 M NaCl draw solution. with >99.5% salt rejection.	[174]
PAN-rGO	Rejection ~90%	[113]

3.2 Removal of heavy metals from water

At present, the critical global issue is water pollution. The heavy metals such as Hg, Pb, Cu, and Cd, are one of the most important classes of inorganic pollutants and have great physiological significance. The source of these pollutants in the environment is mainly attributed to the release of metal-containing wastewaters from different industries [7]. Removal of heavy metals from waste water by adsorption is the most promising, easy and low cost technology. The performances of the novel generation of nanocomposite/hybrid nanofibrous membranes can contribute well to environmental remediation [25].

Toxic inorganic and organic chemicals of different forms are discharged into the environment as industrial wastes, causing serious water, air, and soil pollution. Thus, water pollution caused by toxic heavy metal ions has become a serious environmental problem. Heavy metals (such as Pt, Pd, Ag, Cu, Cd, Pb, Hg, Ni, Co, Zn, etc.) are also natural constituents of the earth crust and

present in the environment as a result of weathering and erosion of parent rocks. These toxic metal ions, even at low concentrations, have deteriorated water resources [176]. Adsorption is the capability of all solid substances to attract to their surfaces molecules of gases or liquids with which they are in close contact. Heavy metal ions can be removed from the water through adsorption to membrane followed by a regeneration process to recover the membrane for subsequent usage.

Huang et al. [176, 177] overviewed the researches done in the last decade concerning the development of electrospinning-based micro- and nano-porous membranes for efficient heavy metal removal. In addition to super-high surface-to-volume ratio of electrospun nanofibers, they possess a variety of surface groups which enable their further functionalization and functional nanoparticle incorporation. On comparing ENMs as adsorbents with typical adsorbents, it was found that ENMs are superior in many ways with higher permeation flux, lower pressure drop, flexible component adjustment, and even multi-target adsorption. Therefore, ENMs hold great potential on the treatment of heavy metal contaminants.

Compared with the traditional adsorbent (activated carbon, zeolites, silica gel), electrospun nanofibers are better for heavy metal ion adsorption for the following reasons:

i) Large surface area.
ii) Tailored pore structures.
iii) Good interconnecting pores.
iv) Potential to incorporate active chemistry or functionality of nanoscale.

Chitpong and Husson [178] reported that cadmium (Cd^{2+}) removal productivities of poly(acrylic acid) and poly(itaconic acid) modified cellulose ENMs were found to be 6–15 times higher than commercial ion-exchange resins, and the membranes could be reused at least five times without a decline in performance. In another article Chitpong and Husson [179] modified thermally treated surface CA ENMs by grafting with poly(acrylic acid) (PAA) for the removal of Cd^{+2} from water. They reported that polymer grafting can produce high capacity membranes and also discussed the mechanism.

Ma et al. [180] used functional ENMs to remove heavy metal ions through adsorption from contaminated water. These membranes showed higher permeation flux and lower pressure drop than conventional microfiltration membranes. These membranes also possessed a high surface-to-volume ratio and functionalizable surface that could remove toxic metal ions with a capability comparable to typical absorbents.

Yun et al. [181] fabricated nanofibrous membrane from zein protein which was derived from maize. The zein nanofibrous membrane (ZNM) was prepared by using an 80 % ethanol solution as a solvent. The membrane was used to separate Cr(VI) from water.

Lee et al. [182] developed rhodanine loaded nanofibrous membranes for the removal of heavy metal ions. They reported the performance of the membrane for the removal of Ag (I) and Pb (II) ions through dead-end filtration. The highest absorptivity value was found to be 65.1% and 60.4% of the initial silver ion and lead ion concentration respectively. Furthermore, the electrospun membrane could be reused after the recovery process.

Rad et al. [183] used electrospun PVA/zeolite nanofibers for the adsorption of Ni^{2+} and Cd^{2+} ions. The time of adsorption equilibrium was found to be 60 min with greater adsorption capacity for Cd^{2+}.

Karim [184] discussed the potential of PVA-Chitosan nanofiber membranes (NFMs) in wastewater treatment processes especially for toxic metal removals. The kinetic studies indicated that the adsorption of Pb and Cd onto NFMs best fit the pseudo-second order kinetic model. The equilibrium adsorption study revealed that the Langmuir model was the most appropriate to describe Pb and Cd adsorption behaviors on NFMs. The monolayer maximum adsorption capacities of Pb and Cd were found to be 199 and 68 mg g^{-1}, respectively. Therefore, the NFMs exhibited great potential for the removal of Pb and Cd from wastewater in engineering practices.

Li et al. [185] used electrospun chitosan nanofiber membrane module for removing Cr(VI) in contaminated water by adsorptive filtration. The maximum adsorption capacity obtained with 2 g m^{-2} nanofiber membranes in the module was 20.5 mg g^{-1} at 10% breakthrough. It was observed that the module could adsorb various metal ions separately but showed preferred adsorption of Cr^{6+} over Cu^{2+}, Cd^{2+} and Pb^{2+} when these metal ions were coexistent. Additionally, the fibrous chitosan membrane had much higher Cr^{6+} rejection and permeate flux, when compared with the performance of commercial NF membranes.

Yang et al. [186] prepared thiol modified natural polysaccharide chitin nanofibers and used as an absorbent material for arsenic (As(III)) removal. The arsenic adsorption performance of thiol-modified chitin nanofibers was evaluated under different pH conditions and at different metal ion concentrations, where the maximum adsorption capacity was found to be 149 mg g^{-1}.

Esmaeili and Beni [187] produced PVA/Chitosan (Chs) ENMs. The stability of PVA/Chs nano-fiber membrane was increased via thermal cross-linking. Adsorption experiments were carried out to investigate the effect of different adsorption parameters such as pH, adsorbent dose, biomass dose, contact time, and temperature. The maximum adsorption capacity of nickel and cobalt was observed at adsorbent doses of 0.48 g L^{-1} and 0.40 g L^{-1} respectively, with 79.28% and 77.12% removal efficiency.

Liu et al. [188] fabricated microfiltration ENMs having positive surface charges and capable of removing Cr(VI) from contaminated water. Polyacrylonitrile (PAN) was electrospun into a nanofibrous scaffold with an average fiber diameter of about 200 nm. Polyvinylamine (PVAm), a positively charged polymer was grafted onto the nanofibrous scaffold through cross-linking reaction by glutaraldehyde. It was found that at pH = 6, the PAN-g-PVAm membrane showed almost two times higher adsorption capacity than activated carbons, and about 20 times higher than some synthetic activated carbons. The PAN-g-PVAm membrane also exhibited excellent Cr(VI) adsorption capability in a dynamic filtration process.

Hota et al. [189] synthesized composite ENMs and investigated the removal of Cd^{2+} from aqueous solution. Two polymers, the hydrophobic/PCL and hydrophilic/Nylon-6 were chosen to serve as the support for the boehmite. It was reported that sorption capacity for Cd^{2+} was 0.20 mg g^{-1}. The membrane may be useful for commercial filtration application.

Bozorgpour et al. [190] studied the removal of nitrate and phosphate via chitosan/Al_2O_3/Fe_3O_4 composite nanofibrous adsorbent, prepared by electrospinning process, and the results were compared with chitosan/Al_2O_3/Fe_3O_4 composite bead adsorbent. The Box-Behnken design was used to investigate the interaction effects of adsorbent dosage, nitrate and phosphate initial concentrations on the nitrate and phosphate removal efficiency. The obtained results revealed the higher potential of chitosan/Al_2O_3/Fe_3O_4 composite nanofibers for nitrate and phosphate removal compared with chitosan/Al_2O_3/Fe_3O_4 composite beads.

Stephen et al. [191] used functionalized cellulose nanofibers as adsorbent, obtained through electrospinning and modification with oxolane-2,5-dione for the separation of Cd^{2+} and Pb^{2+} from model wastewater sample. The adsorption capacities of functionalized cellulose nanofibers are 1.0 and 2.91 mmol g^{-1} for Pb and Cd, respectively, compared to 0.002 mmol g^{-1} of raw cellulose.

Li et al. [192] fabricated chitosan ENMs with different fiber deposition densities on polyester scrim (PET scrim). These composite ENMs were used for the study of dynamic adsorption capacity for Cr(VI) ions. The maximum bed loading capacity for 1 mg L^{-1} Cr (VI) filtration at the breakthrough point was found to be 16.5 mg Cr g^{-1}-chitosan, higher than the static adsorption capacity of 11.0 mg Cr g^{-1}-chitosan using nanofiber mats, indicating the membrane's better potential for dynamic adsorption.

Shooto et al. [193] fabricated nanofibers via electrospinning from polyvinyl alcohol (PVA) and PVA incorporated with metal (Co) organic framework (PVA-CoMOF), and investigated the ability of these fibers to remove Pb(II) ions from water. It was reported that the sorption of Pb^{2+}ions on PVA-Co-MOF was twice as much as the PVA nanofiber.

Habiba et al. [194] prepared chitosan/PVA/zeolite composite ENMs. The adsorption capacity of chitosan/PVA/zeolite membrane for Cr^{6+}, Fe^{3+} and Ni^{2+} were 0.17, 0.11 and 0.03 m mol g^{-1} under experimental conditions, respectively. Alibadi [195] used chitosan/cobalt ferrite nanofibers for the removal of Pb^{2+} and Cr^{6+} from water. Haider and Park [196] studied the removal of Cu(II) and Pb(II) ions from aqueous solution, neutralized with potassium carbonate, by using chitosan ENMs via adsorption. It was reported by Haider and Park that chitosan nanofiber mats had good erosion stability in water and high adsorption affinity for metal ions. Chitosan ENMs can be applied to filter out (or neutralize) toxic metal ions and microbes without losing their original chitosan properties such as biocompatibility, hydrophilicity, bioactivity, non-antigenicity, and non-toxicity. The equilibrium adsorption capacities (from Langmuir isotherm data) for Cu(II) and Pb(II) were 485.44 mg g^{-1} (2.85 mmol g^{-1}) and 263.15 mg g^{-1} (0.79 mmol g^{-1}), respectively. The Cu(II) adsorption data were ~6 and ~11 times higher than the reported highest values of chitosan microsphere (80.71 mg g^{-1}) [197] and the plain chitosan (45.20 mg g^{-1}) [198].

Li et al. [199] synthesized novel zonal silica nanofibers by the sol–gel polymerization of (3-mercaptopropyl) trimethoxysilane on the electrospun PAN nanofibers and modified it by removal of PAN nanofibers using DMF to increase surface areas. The maximum adsorptive capacity of 57.49 m g^{-1} was attained within 60 min of contact time. On the other hand, pure silica nanofibers exhibited a very low adsorptive capacity of 1.36 mg g^{-1}.

Tian et al. [200] modified the surface of cellulose acetate (CA) nonwoven nanofiber membrane with poly(methacrylic acid) (PMAA) using Ce^{4+} initiated radical graft copolymerization and investigated the adsorption of

heavy metal ions (Cu^{2+}, Hg^{2+} and Cd^{2+}) on the membrane. The adsorption capacity increased with the increasing of initial pH value in the system. The membrane showed quite high adsorption selectivity for Hg^{2+} which was much higher than those of Cu^{2+} and Cd^{2+} at the same initial ion concentration. It could be due to the $–COO^-$ groups on the adsorbent which have strong tendency to form complexes with Hg^{2+}. The adsorbed metal ions can be easily de-adsorbed from the membrane surface by using saturated ethylenedinitrilo tetra acetic acid solution, and can be re-used for the metal ion adsorption.

Wong et al. [201] investigated the electrospun nanofibers of PAN for heavy metal adsorption. It was reported that modification of the PAN electrospun nanofibers, by grafting with polyethyleneimine (PEI) and polyvinyl amine (PVAm), enhanced heavy metal adsorption rates. The PVAm membrane adsorbed a greater amount of Chromium (VI) ions from the turbid water than the PEI membrane.

Min et al. [202] fabricated chitosan based ENMs for the effective adsorption of As(V) from aqueous solution. Maximum adsorption capacity of As(V) was found to be 30.8 mg g^{-1} which was higher than most of the chitosan related adsorbents reported in the literature.

Zhao et al. [203] used phosphorylated polyacrylonitrile-based nanofiber mat (P/PAN) for the removal of heavy metal ions (Pb^{2+}, Cu^{2+}, Ag^{+} and Cd^{2+} ions) from water. The adsorption equilibrium amount of Pb^{+2}, Cu^{+2}, Ag^{+1} and Cd^{+2} was 98.06, 78.03, 102.4 and 18.89 mg g^{-1}, respectively. Phosphorylated PAN fibers also showed high recyclable removal efficiency through the adsorption/desorption experiments.

Choi et al. [204] fabricated multifunctional hybrid composites of zeolite/palladium (Ze/Pd) on polymer nanofiber membranes and studied their performance for sustainable contaminant removal. It was reported that the multifunctional nanofibrous membranes (Ze/Pd on polymer nanofiber) were able to adsorb and remove NH_3-N. Palladium catalysts oxidized selectively NH_3-N to N_2 gas. The cycling of NH_3-N adsorption-oxidation, high flux, hydrophilicity, and flexibility of the membrane makes it a strong candidate for water treatment.

Taha et al. [205] fabricated amino ($–NH_2$) functionalized mesoporous polyvinyl pyrrolidone (PVP)/SiO_2 composite nanofiber membranes via electrospinning method using poly (vinyl alcohol), reidopropyltriethoxysilane and tetraethyl orthosilicate (TEOS) mixed with cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) as the structure directing agent. Ureidopropyltriethoxysilane was used for functionalization of the internal pore surfaces. The membrane was used for the separation of Cr^{+3} from water. Equilibrium adsorption was achieved after approximately 20 min and more than 97% of chromium ions in the solution were removed.

Huang et al. [206] synthesised chitosan/PNN nanofibrous mats via electrospinning and applied in the adsorption of metal ions. The fibrous structure of the soaked chitosan/PNN {poly(N-isopropylacrylamide-co-N-methylolacrylamide) (poly(NIPAAm-co-NMA)} mats was preserved by crosslinking using NMA (N-(methylol acrylamide)) and GA (glutaraldehyde) vapor. The adsorbed amount of Cu(II) on the chitosan/PNN (50/50) nanofibrous mats which was washed to pH 7 could reach 79 ± 2 mg g^{-1}-mats. The incorporation of poly(NIPAAm-co-NMA) significantly improved the desorption of Cu(II) from the nanofibrous mats.

Park et al. [207] fabricated electrospun poly(acrylic acid)/poly(vinyl alcohol) nanofibrous adsorbents for Cu(II) removal from industrial plating wastewater. It was demonstrated that nanofibrous adsorbents had Cu(II) removal capacity of 25.8–33.6 mg g^{-1} at the adsorbent dose of 0.4–2.0 g L^{-1} and Cu(II) concentration of 430.06 mg L^{-1}. The maximum Cu(II) removal capacity of nanofibrous adsorbent was 49.3 mg g^{-1} with a far higher selectivity for Cu(II) over Ni(II) in a binary system.

Martin et al. [208] functionalized the surface of poly(ethylene terephthalate) (PET) nanofibers chemically using aminolysis process. The functionalized membrane's (APET) adsorption capacity was up to 97% of Pb(II) in the mono-elemental synthetic solution. The APET nanofibers mat showed a high Pb(II) selectivity in the presence of interfering metal ions such as Cu(II) and Cd(II). The adsorbent presented a quick kinetic adsorption, reaching an extremely high maximum adsorption capacity of about 50 mmol Pb(II)/g adsorbent after just 30 min. Excellent performance was demonstrated by APET nanofibers in continuous-flow mode operation.

Mahapatra et al. [209] fabricated iron oxide–alumina nanocomposite by electrospinning method and reported that these nanocomposite fibers were efficient adsorbents for removal of heavy metal ions. The removal percentage was in the order of $Cu^{2+} < Pb^{2+} < Ni^{2+} < Hg^{2+}$.

Li et al. [210] fabricated Chitosan/PMMA composite ENMs with a single solvent system and observed that the composite nanofiber membrane enhanced Cr(VI) adsorption via filtration. Maximum adsorption capacity (67.0 mg g^{-1}) of Cr(VI) was reported with chitosan:PMMA ratio of 0.3:1.0 which was nearly three times higher than that of chitosan powder (22.9 mg g^{-1}). The adsorption capacity of Cr(VI) via filtration became even higher, where the maximum value was 92.5 mg g^{-1} at pH 3.0.

Islam et al. [211] reported that phosphine-functionalized poly(vinyl alcohol)/silica ENMs was highly effective for removal of aqueous manganese and nickel ions through adsorption via coordinate bond. The adsorption capacities of the pgf-PVA/SiO_2 nanofiber for Mn^{+2} and Ni^{+2} ions were 234.7 and 229.9 mg g^{-1}, respectively. The composite pgf-PVA/SiO_2 nanofibers (with 0.5 g L^{-1} fiber loading) removed almost completely (96–98%) both ions from aqueous solutions (initial concentration of 120 mg L^{-1}, pH 6) within 15 min of contact time.

Zhou et al. [212] used ureido-functionalized mesoporous polyvinyl alcohol/silica composite ENMs for the removal of Pb^{2+} and Cu^{2+} from wastewater. Pb^{2+} and Cu^{2+} adsorption behavior on the membranes followed a pseudo-second-order nonlinear kinetic model and maximum adsorption capacity of 26.96 mg g^{-1} was reported for Pb^{+2}. But Cu^{2+} adsorption was poor in comparison with Pb^{+2}.

Attia et al. [213] fabricated superhydrophobic electrospun nanofibrous PVDF membranes incorporated with superhydrophic Al_2O_3 nanoparticles and studied its performance in the purification of waste water with high concentration of lead via AGMD. It was reported by the authors that a high rejection percentage and flux rate were obtained by using 11 wt.% of PVDF concentration with 20 wt.% of superhydrophobic Al_2O_3. Figure 8 shows the flux performance and percent of rejection of an aqueous solution with 1000 mg L^{-1} lead concentration over a period of 5 h by implementing one commercial membrane and four fabricated membranes.

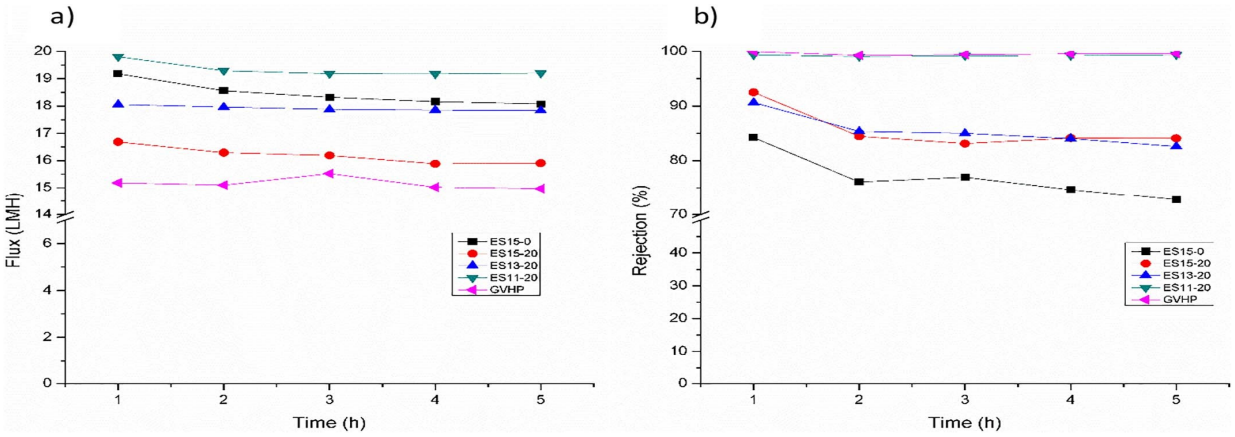

Fig. 8. a) Flux data and b) rejection percentage as a function of time for the commercial and the synthesized membranes. (The commercial PVDF membrane under the trade name GVHP 29325 and four PVDF ENMs with the indicated PVDF: Al_2O_3 ratios in the spinning dope {ES15-0 (PVDF:Al_2O_3 =15:0), ES15-20 (PVDF:Al_2O_3 =15:20), ES13-20 (PVDF:Al_2O_3 =13:20) and ES11-20 (PVDF:Al_2O_3 =11:20) [213].

As could be observed in Figure 8 (a), the commercial PVDF membrane exhibited the lowest flux of around 15 LMH (L m^{-2} h^{-1}). On the other hand, high fluxes between 16.5 and 20 LMH have been shown by the composite PVDF membranes with Al_2O_3 NPs. Figure 8 (b) shows the rejection percentage of Pb as a function of time. It is clear that the neat PVDF (ES15-0) has the lowest rejection % with decreasing rejection from 84.2 to 72.7% within the five-hour operation despite having a high flux rate. On the other hand, the modified membrane with 20 wt.% alumina (ES15-20) showed an improved rejection rate of 92.5% to 84% within 5 h. The highest rejection and a stable performance was achieved by membrane ES11-20 which showed over 99% metal rejection within 5 h. It is clear that the highly hydrophobic properties of the membrane are due to the presence of the super hydrophobic NPs.

Moradi et al. [214] evaluated the performances of electrospun poly (vinylidenefluoride) - titanium tetraisopropoxide (PVDF-TTIP) hybrid membrane in heavy metal removal from water via VMD. The effects of operating parameters such as flow rate, temperature and membrane properties (i.e. porosity) on contaminant removal and ultra-pure water production were studied. The feed solution contained different trace concentrations of various heavy metals [Co(II), Zn(II), Cu(II), Ni(II), Cd(II) and Pb(II) all in the specific concentration (10-100 ppm)]. After VMD experiment, the total concentration of the feed solution was changed from 250 ppm to 750 ppm, which caused increasing the conductivity from 120 µS cm^{-1} to 600 µS cm^{-1}. On the other hand, the conductivity of the distillate stream was almost constant during the same time period. From VMD study, it was concluded that asymmetric post-treated PVDF-TiO_2 hybrid membranes could be successfully employed in vacuum enhanced membrane distillation for the removal of trace heavy metal contaminants and ultra-pure water production in one step.

Min et al. [147] fabricated a novel micro-nano structure poly(ether sulfones)/poly(ethyleneimine) (PES/PEI) nanofibrous membrane and studied its performance as an adsorbent for the removal of heavy metals from aqueous solutions. The adsorption equilibrium data were all fitted well to the Langmuir isotherm equation, with maximum adsorption capacity values for Pb(II), Cu(II) and Cd(II) 94.34, 161.29 and 357.14 mg g^{-1}, respectively.

Modified with diethylenetriamine (DETA), aminated polyacrylonitrile (APAN) ENFs mats were used by Kampalanonwat and Supaphol [215] for the removal of Ag(I), Cu(II), Pb(II) and Fe(II) from aqueous solution. In another article Kampalanonwat and Supaphol [216] reported that, when modified surfaces via heterogeneous reaction with diethylenetriamine (DETA), polyacrylonitrile (PAN) nanofiber mats have the adsorption capacities for Cu(II), Ag(I), Fe(II) and Pb(II) ions of 150.6, 155.5, 116.5, and 60.6 mg g^{-1}, respectively.

Cai et al. [217] studied the adsorption performance of polyindole fibers, prepared via electrospinning method for Cu^{+2} ions. It was reported that the Cu(II) adsorption was highly pH dependent. The maximum adsorption capacities for electrospun polyindole nanofibers and polyindole powders were 121.95 and 18.93 mg g^{-1}, attained in 15 and 60 min at pH 6, respectively. It was suggested that electrospun polyindole nanofibers would have promising application for removal of Cu(II) from wastewater treatment.

Feng et al. [218] demonstrated the removal/adsorption of heavy metal ions from wastewater by amidoxime ployarcylonitrile/regenerate cellulose (AOPAN/RC) composite nanofibrous membranes that were prepared by combined hydrolysis and amidoximation of polyacrylonitrile/cellulose acetate (PAN/CA) composite ENMs. The membrane's adsorption amount of Fe(III), Cu(II) and Cd(II) ions reached 7.47, 4.26 and 1.13 mmol g^{-1}, respectively.

Teng et al. [219] synthesized polyvinylpyrrolidone (PVP)/SiO_2 composite nanofiber membrane for selective separation of Hg^{+2} ions and reported that adsorption maximum capacity of the membrane was 4.26 m mol g^{-1}.

Xu et al. [220] reported that the maximum adsorption capacity of malachite green on vinyl-modified mesoporous poly(acrylic acid) (PAA)/SiO_2 was 220.49 mg g^{-1} which was best fit with Redlich–Peterson isotherm. The removal of malachite green from the aqueous phase reached 98.8% in 240 min. Chen et al. [221] prepared an adsorbent which was synthesized by intercalating ethylenediaminetetra acetic acid (EDTA) into layered double hydroxides (LDH) and subsequently encapsulating into PAN polymer matrix using electrospinning. The synthesized ENM (MgAl-EDTA-LDH@PAN) was evaluated using Cu(II) as target metals by varying experimental conditions such as pH, contact time, initial adsorbent dosage, and temperature. The maximum adsorption capacity of MgAl-EDTA-LDH@PAN was 120.77mg g^{-1} with the initial Cu(II) concentrations ranging from 0.6 to 40mg/L.

Zahabi et al. [222] prepared functionalized nanofibrous ENMs prepared from Nylon 6 solution of 19% (w/w) in a formic acid/chloroform mixture (75:25 v/v). The ENMs were functionalized by (3-mercaptopropyl)trimethoxysilane (TMPTMS) and the performance was studied for the removal of cadmium and nickel ions from water. The maximum removal efficiency of 93.0 and 97.6%, respectively, were reported.

Table 10 shows the summary of some recent reports on electrospun materials for adsorption of heavy metals from water.

4. Summary

The electrospun nanofiber membranes (ENMs) have been employed in different applications including oil/water separation, waste water treatment, heavy metals removal from water and chiral separation. Among many polymers, cellulose acetate, PVA, PAN, chitosan and poly(lactic acid) are most often used. Due to superior separation performances, these membranes hold promising future in wastewater treatment, especially because the trade-off effect between the flux and selectivity can often be overcome by ENMs.

The surface modification by grafting, interfacial polymerization, nanoparticles coating, and thermal treatment (pressing) were found to be effective to alter the surface properties, improving the filtration performance and antifouling properties of ENMs. Beside this, triple layer and double layer membranes, with many promising results, may also be considered as different versions of surface modification. Moreover, piezoelectric polymer membranes could open a new avenue for the water treatment.

ENMs could separate oil/water emulsions and oil microparticles from water via filtration or adsorption or both. Indeed, a large number of works have been carried out on the separation of oil/water media by ENMs, but mostly on low viscous oil-water emulsions. The separation of high-viscous oil/water mixtures is more complex and not much attention has been paid. Although there are many advantages to use ENMs for oil/water separations, there are two main challenges:

i) Poor resistance against acid and alkali corrosion.
ii) Poor mechanical properties for industrial applications.

Therefore, some works have been done to improve the mechanical properties of ENMs.

In heavy metal ions removal, the adsorption capacities of ENMs were proven to be comparable or better than conventional membranes/commercial agents.

The application of nanofibers in membrane distillation (MD) and in desalination via FO-RO has potential as future technologies, if the pore size of the ENMs can be reduced to those of FO and RO membranes.

In conclusion ENMs will be widely used in the future in place of present conventional membranes.

Table 10
Summary of some recent reports on electrospun materials for adsorption of heavy metals from water.

Material	Targeted chemicals	Adsorption capacity	Ref.
PVA/chitosan	Ni^{2+}	Doses of 0.48 g L^{-1}, removal efficiency 79.28 %.	[187]
	Co^{2+}	Doses of 0.40 g L^{-1}, removal efficiency 77.12 %.	
CA/ PAA (modified with poly(glycidyl methacrylate))	Cd^{2+}	160 mg g^{-1}.	[179]
Chitosan/Al_2O_3/Fe_3O_4	Phosphate	135.10 mg g^{-1}.	[190]
	Nitrate	160.7 mg g^{-1}.	
Bohemite hydrophobic/PCL and bohemite hydrophilic/Nylon-6	Cd^{2+}	0.20 mg g^{-1}.	[189]
Chitosan ENFs mats	Cu^{2+}	485.44 mg g^{-1} (2.85 mmo lg^{-1}).	[195]
	Pb^{2+}	263.15 mg g^{-1} (0.79 mmol g^{-1}).	
PVA ENFs	Pb^{2+}	22.72 mg g^{-1}.	[193]
PVA/Co-MOF	Pb^{2+}	55.23 mg g^{-1}.	
PVA-Chitosan ENMs	Pb^{2+}	199 mg g^{-1}.	[184]
	Cd^{2+}	68 mgg^{-1}.	
Spiral wound chitosan ENM	Cr^{6+}	20.5 m g $^{-1}$.	[185]
Thiol modified chitin ENFs	As^{3+}	149 mg g^{-1}.	[186]

PVA/zeolite ENMs	Ni^{2+}	342.8 mg g^{-1}.	[183]
	Pb^{2+}	263.15 mg g^{-1}.	
Chitosan/PVA/zeolite	Cr^{6+}	0.17mmo lg^{-1}.	[194]
	Fe^{3+}	0.11 mmol g^{-1}.	
	Ni^{2+}	0.03 mmol g^{-1}.	
PVA/zeolite ENMs	Cd^{2+}	838.7 mg g^{-1}	[183]
Rhodanine/PMMA	Ag^{+}	125.7 mg m^{-2} .	[182]
	Pb^{2+}	140.2 mg m^{-2}.	
Mesoporous polyvinyl pyrrolidone (PVP)/SiO_2	Cr^{3+}	97 mg g^{-1}.	[205]
Vinyl-modified mesoporous poly(acrylic acid)/SiO_2	malachite green	220.49 mg g^{-1}.	[220]
Zc/Pd	NH_3-N	NH3-N oxidized to N_2 gas.	[204]
Oxolane-2,5-dione/cellulose	Cd^{2+}	2.91 mmol g^{-1}.	[191]
	Pb^{2+}	1.0 mmol g^{-1}.	
PAA/PVA ENFs	Cu(II)	49.3 mg g^{-1}.	[207]
Polyindole ENFs	Cu(II)	121.95 mg g^{-1}.	[217]
Chitosan/(polyvinylalcohol)/zeolite	Cr^{6+}	0.17 mmol g^{-1}.	[194]
	Fe^{3+}	0.11 mmol g^{-1}.	
	Ni^{2+}	0.03 mmol g^{-1}.	
Chitosan	As^{5+}	30.8 mg g^{-1}.	[202]
P/PAN	Pb^{2+}	98.06 mg g^{-1}.	[203]
	Cu^{2+}	78.03 mg g^{-1}.	
	Ag^{+}	102.4 mg g^{-1}..	
	Cd^{2+}	18.89 mg g^{-1}.	
Chitosan/PNN Mats	Cu^{2+}	79 ± 2 mg g^{-1}-mats.	[206] [205]
Modified APAN ENFs mats	Ag^{+}	4.53 ± 0.2 mg g^{-1}, 92.8% removal.	[215]
	Cu^{2+}	3.64 ± 0.3 mg g^{-1}, 74.6% removal.	
	Pb^{2+}	2.04 ± 0.3 mg g^{-1}, 41.8% removal.	
	Fe^{2+}	0.95 ± 0.2 mg g^{-1}, 19.5% removal.	
MgAl-EDTA-LDH@PAN	Cu^{2+}	120.77mg g^{-1}.	[221]
AOPAN/RC composite nanofibrous membrane	Fe^{3+}	7.47 mmol g^{-1}.	[218]
	Cu^{2+}	4.26 mmol g^{-1}.	
	Cd^{2+}	1.13 mmol g^{-1}.	
Modified PAN ENFs (amidino diethylenediamine chelating groups)	Cu^{2+}	150.6 mg g^{-1}.	[216]
	Ag^{+}	155.5 mg g^{-1}.	
	Fe^{2+}	116.5 mg g^{-1}.	
	Pb^{2+}	60.6 mg g^{-1}.	
Modified PET nanofibers mat	Pb^{2+}	50 mmol g^{-1}.	[208]
Fe_2O_3–Al_2O_3 ENFs (sintered at 1000 °C)	Cu^{2+}	4.98 mg g^{-1}.	[209]
	Ni^{2+}	32.36 mg g^{-1}.	
	Pb^{2+}	23.75 mg g^{-1}.	
	Hg^{2+}	63.69 mg g^{-1}.	
PES/PEI	Pb^{2+}	94.34 mgg^{-1}.	[147]
	Cu^{2+}	161.29 mgg^{-1}.	
	Cd^{2+}	357.14 mgg^{-1}.	
Chitosan/	Cr^{6+}	Max. value 92.5 mgg^{-1} at pH 3.0.	[192]
pgf-PVA/SiO_2	Mn^{2+}	234.7 mgg^{-1}.	[211]
	Ni^{2+}	229.9 mgg^{-1}.	
Ureido-functionalized PVA/silica	Pb^{2+}	26.96 mg g^{-1}.	[212]
polyindole ENFs	Pb^{2+}	121.95 mg g^{-1}.	[217]
Functionalized Nylon 66	Cd^{2+}	Removal efficiency 93.0 %.	[222]
	Ni^{2+}	Removal efficiency 97.6%.	

Abbreviations

ACNFN	activated carbon nanofiber nonwoven
AGMD	air gap membrane distillation
AOPAN	amidoxime ployarcylonitrile
APAN	aminated polyacrylonitrile
APS	ammonium persulphate
ATRP	atom transfer radical polymerization
BOD	biological oxygen demand
BSA	bovine serum albumin
CA	cellulose acetate
CAB	cellulose acetate butyrate
CCD	central composite design
CD	cyclodextrin
Ch	chitosin
CNF	cellulose nanofiber
CNTs	carbon nanotubes
COD	chemical oxygen demand
CSB	coaxial solution blowing
CSG	coal steam gas
CTAB	cetyltrimethyl ammonium bromide
CTC	chlortetracycline
DA	decanoic acid
DCMD	direct contact membrane distillation
DETA	diethylenetriamine
EDTA	ethylenediaminetetraacetic acid
ENM	electro-spun nanofiber membrane
ENF	electrospun nanofiber
F-PBZ	polymerized fluorinated polybenzoxazine
GA	glutaraldehyde
GAC	granular active carbon
Go	graphene oxide
HAC	acetic acid
HEMA	2-hydroxyethyl methacrylate
HFP	hexafluoropropylene
HNTs	halloysite nanotubes
IP	interfacial polymerization
LDH	layered double hydroxides
M	metal
MA	maleic acid
Man	maleic anhydride

MB	methylene blue solution
MCNFF	macroporous carbon nanofiber film
MINFMs	molecularly imprinted nanofiber membranes
NMA	*N*-methylol acrylamide
NFAs	nanofibrous aerogels
NFMs	nanofibrous membranes
NOMs	natural organic matter
NPs	nanoparticles
NPT	nanoparticle
PA	polyamide
PAA	poly(acrylic acid)
PAN	polyacrylonitrile,
PCL	polycaprolactone
PDMS	polydimethylsiloxane
PEGDA	polyethylene glycol diacrylate
PES	polyethersulfone
PET	polyethlyene terephthalate
PET	polyester
PMMA	poly(methyl methacrylate)
PI	polyimide
POSS	polyhedral oligomeric silsesquioxanes
PP	polypropylene
PPSU	polyphenylsulfone
PS	polystyrene
PSf	polysulfone,
PTA	purified terephthalic acid
PTFE	polytetrafluoroethylene
PUE	Polyurethane
PVA	polyvinyl alcohol
PVAc	polyvinyl acetate
PVC	polyvinyl chloride
PVDF	poly(vinylidene fluoride)
RC	regenerated cellulose
Rhd	rhodanine
SGMD	membrane gas stripping
SNPs	silica nanoparticles
SPPESK	sulfonated poly(phthalazinone ether sulfone ketone)
TEA	trimethylamine
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl) oxyl
TEOS	tetraethyl orthosilicate
TFNC	thin film nanofibrous composite
TMPTMS	3-mercaptopropyl trimethoxysilane
TS	total solid
TSS	total suspended Solids
UF	ultrafiltration
UOCA	underwater oil contact angle
VOC	volatile organic compounds
WCA	water contact angle
ZCCH	Zn-aminotriazolato-oxalate
ZNM	zein nanofbrous membrane

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