

# Electrospun filtration membranes for environmental remediation

Monika R. Snowdon<sup>1</sup> and Robert L. Liang<sup>1,2</sup>

*Author affiliations:*

1. Waterloo Institute of Nanotechnology, University of Waterloo, Waterloo, ON, Canada, N2L 3G1

2. Centre of Advanced Materials Joining, Department of Mechanical and Mechatronics Engineering, Waterloo, Ontario, Canada, N2L 3G1

Keywords: Electrospinning, nanofibrils, polymers, filtration, nanotechnology, fabrication, application, modification

## Abstract

A necessity for water filtration technology, due to global pollution and population growth, has led to an increase in attention to advanced nanomaterials that can aid in the purification of air and water. This size-dependent filtration is possible via nanofibrous membranes as they contain high porosity and this pore size is tunable through the fabrication process. Because of this tunability in the nanofibril membrane composition and structure, they possess promising straining abilities, such as high permeability and selectivity, as well as low fouling. There are a variety of polymer blends or organic/inorganic nanofillers that can be used depending on the need for environmental remediation, which involves the removal of contaminants in both ground and fresh water as well as soil and sediment. The production of nanofibers consists of various avenues such as synthetic templates, separation by different phases, nanoparticle self-assembly, and most widespread, electrospinning. Electrospinning is prevalent owing to its ease of use and low cost compared to template and self-assembly processes. This chapter describes the multifaceted progression governing electrospinning and its working factors as well as the environmental settings that form nanofibers and their resultant membranes. Additionally, the various designs of electrospinning apparatuses' and review of the methods used to prepare multifunctional composite electrospun nanofibrous membranes will be discussed. Past achievements and current challenges will be provided. Conclusions and perspectives are specified fitting to studied progress so far as well as future needs with regards to environmental remediation in water and air, with a focus on water purification applications.

## Introduction

Contaminants present in our precious drinking water and land can cause various health problems. Aboriginal and native reserves in Canada do not have pure drinking or clean bathing water, and limited contact to fertile land.<sup>1</sup> Access to fresh water is a problem not only present in developing nations but also areas of North America. Treatments for removing contaminants in the environment can be placed under three categories: physical, chemical and biological [1]. Biological methodologies incorporate anaerobic and aerobic bacterial ingestions, [2-4] whereas chemical purification involves disinfection and re-dox treatment [5-7]. Physical processes are most

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<sup>1</sup> <https://www.theguardian.com/global/2018/oct/04/ontario-six-nations-nestle-running-water>

commonly known under sedimentation and filtration [8-10]. Additionally, membrane technologies have become a hot topic of interest because of their potential in purifying air and liquid in very high-quality purity with lower energy input [11, 12]. This is particularly useful in concerning industry perspectives for increasing cost efficiency [13]. There is a broad scope of membrane technologies, which can be categorized according to their separation principles and the respective properties of the selected membrane. Reverse osmosis, ultrafiltration, nanofiltration and gas separation are all different forms of membrane filtration systems [14-18]. It is possible to optimize the properties of the membranes for filtration depending on the desired filtrate, making the process adaptable, in addition to having lower energy usage and straightforward settings for operation.

The membranes are a crucial component in membrane separation procedures. The synthesis of the membranes leads to their intrinsic properties. Polymeric membranes can be fabricated in many ways such as sintering and track-etching. The pros and cons of the many polymeric membrane fabrication methods can be found in a wide variety of resources. Here, we focus selectively on electrospinning. Although it is important to denote that most of the industry and commercially available polymer membranes are made via phase inversion. This method means the polymers are altered in a precise method to form a solid from the liquid material phase. However, in the past few years, electrospinning has become a practical methodology for making specifically nanofibrous polymer membranes. Additionally, membranes originating from electrospinning are made of up overlapped nanofibers with nanometer diameters. The creation of these electrospun nanofibrous membranes (ENMs) is founded on single direction elongation and strain of a viscoelastic jet resulting from a liquid of polymer(s) under a high electric field [19]. The nanomembranes can depict exceptional characteristics for water treatment such as high porosity and definite surface area, and augmented orientation of nanofibers. ENMs, therefore, are documented to be contenders for numerous applications in healthcare, bionanotechnology as well as energy and environmental applications [19, 20]. It is also possible to incorporate functional nanomaterials into the ENMs to provide novel modified membrane systems.

The chapter encompasses a review of progress in making and modifying ENMs for the specific application of water treatment. It will first delve into what ENMs are and their various kinds and applications in water treatment. The basics and principles of electrospinning will then be described followed by past success for ENMs in water treatment and where the prospects lie.

### **11.1.1 Membranes**

There are three main types of membrane systems, namely, inorganic ceramic and metal membranes, and organic polymer membranes which are the focus of this work. As shown in Figure 1, polymers exhibit a delicate balance between flexibility and stiffness, as well as density, as in they are neither too heavy nor too light for membrane functionalities.

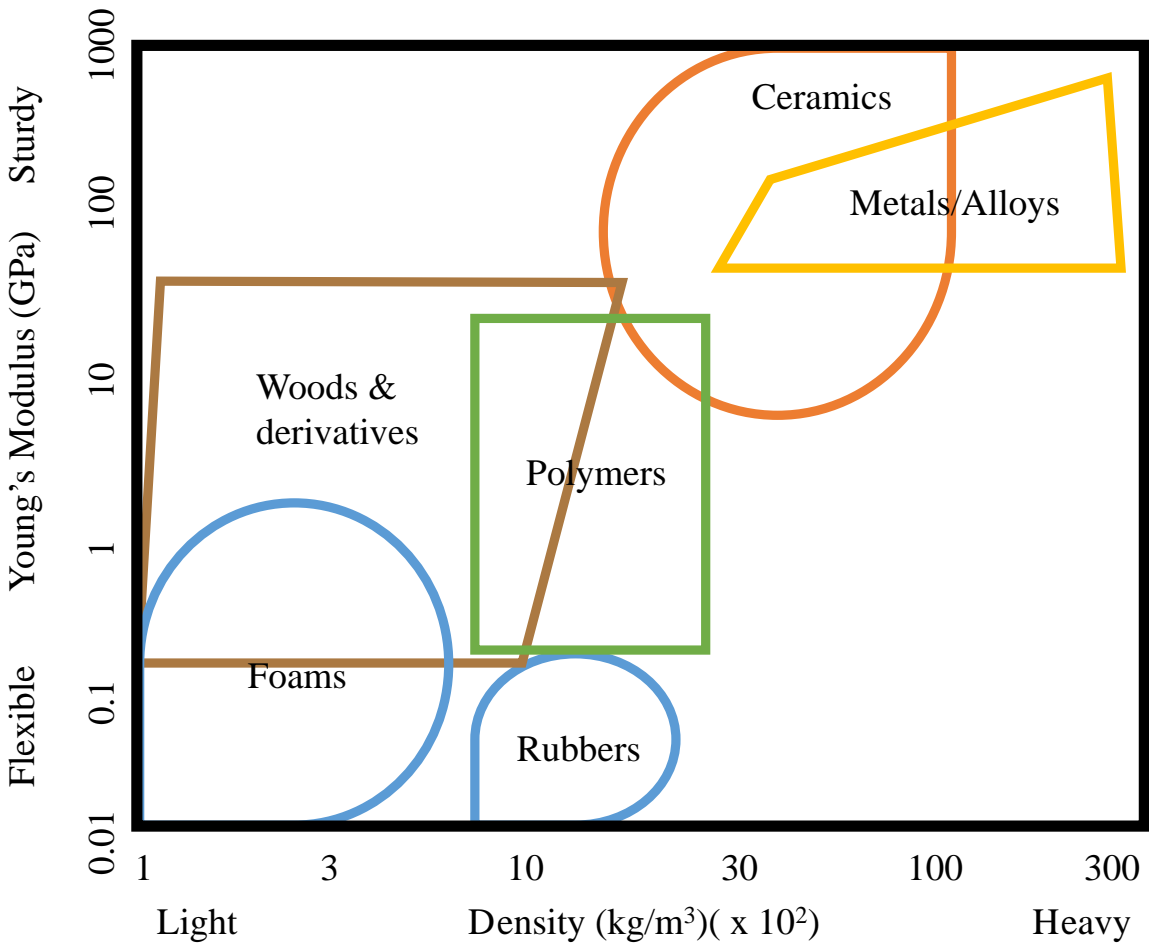


Figure 1 Diagram representing different kinds of materials that can become membranes with respect to young's modulus plotted against density. Based on [http://www-materials.eng.cam.ac.uk/mpsite/interactive\\_charts/stiffness-density/NS6Chart.htm](http://www-materials.eng.cam.ac.uk/mpsite/interactive_charts/stiffness-density/NS6Chart.htm)

### 11.1.2 Polymeric Nanofibrous Membranes

Fibrous materials at the nanoscale are desirable for creating selectively permeable membrane systems. These constituents have inherently high porosity due to small fiber diameters. For fiber to be qualified under the nanoscale, their diameters must remain sub 200 nm, and the bulk of these materials have a porosity 70% to > 95%, also defined as *void space* [21]. When the materials possess a high porosity, they will have low resistance to transport [21, 22]. Parameters for investigation and characterization involve porosity (%), pure water flux and the diameters of the fibers [23]. Raman or infrared spectroscopy is used when investigating hybrid ENM systems. Typically, scanning electron microscopy is used as an imaging technique for visualizing the nanofibers, though atomic force microscopy and tunneling electron microscopy can also be used.

For ENMs, the pores are connected between two material surfaces, known as through pores. Primarily, when the sample is exposed to water vapour, it will diffuse over the nanofibrous layer via the open space between the fibers. The path of the vapours will remain relatively straight through the layer, and few interactions will occur in between the fibers themselves. Hence, the

path that the diffusing water vapour will follow is within the range of how thick the ENM layer is. Due to this route, lower resistance for the transport of the diffusing molecules occurs, as the substances have a directed pathway through the nanofibrous layer as well as increased permeance, [22] leading to a low-pressure drop per filtration efficacy for ENMs [24]. These characteristics have led to the recent further development of nanofibrous composites for filtration [25]. Electrospun nanofibrous sorbents and aerogels also exist as filtration methods, but the focus here is on membranes specifically, as they are the most popular electrospun material and there are many more results to report on them on different water and air filtration processes[26].

## 11.2 Polymer types for nanofiber membranes

Nanofiber membrane materials can be composed of either all natural or all synthetic, or a composite mixture of both types of polymers. Other kinds of electrospun nanofibers also exist made up of ceramic. Based on the final usage of the nanofiber membrane, the intrinsic properties of the fibers that compose the membrane are chosen accordingly to the potential application. There are eight common polymer types for ENMs, depicted in Figure 2. The polymer is chosen based on the need of removing dyes, ions or metals from solution. Adsorption membranes are for the removal of organics such as dyes or metal ions. Filtration membranes are used for the split-up of biological agents as in bacteria and other infectious agents like viruses as well as oil/water emulsions. Air filtration membranes are primarily based on glass or charcoal nanofibers [12].

### *Polyacrylonitrile*

The acrylonitrile polymer is a hydrophobic entity with dynamic mechanical properties. Though hydrophobic, polyacrylonitrile (PAN) is a polymer for ENMs in the water filtration application because of its easily mouldable surface structure through pre-spinning and post-spinning procedures for polymer modification. The nitrile group can undergo various chemical reactions, such as nucleophilic substitutions or conversion into a primary amine [27, 28]. The membranes made from PAN have high mechanical stability and permeability, and can also be used for thin film nanocomposite membranes [29]. In agreement with the functionalization mechanism of the PAN ENMs, their potential in water purification is separated into either adsorption membranes or filtration membranes.

The ENMs that originate from PAN can have many active reagents incorporated into them for filtration and are mainly studied for separating organic dyes in water. Examples include the addition of polyamidoamine as dopant incorporated during spinning. These modified more prominent diameter fibers can remove anionic dye like Direct Red 80 and 23 with high adsorption retention in the range of 1600-2000 mg/g [30]. Grafting of PAN ENMs is also possible on the cyano group with compounds such as diethylenetriamine (DETA), for the removal of organic pollutants, like cationic dyes in water. Dyes that can be found in aqueous solutions like Rhodamine B, Methylene blue and Safranin T have been presented to adsorb onto ENMs via hydrogen bonding.

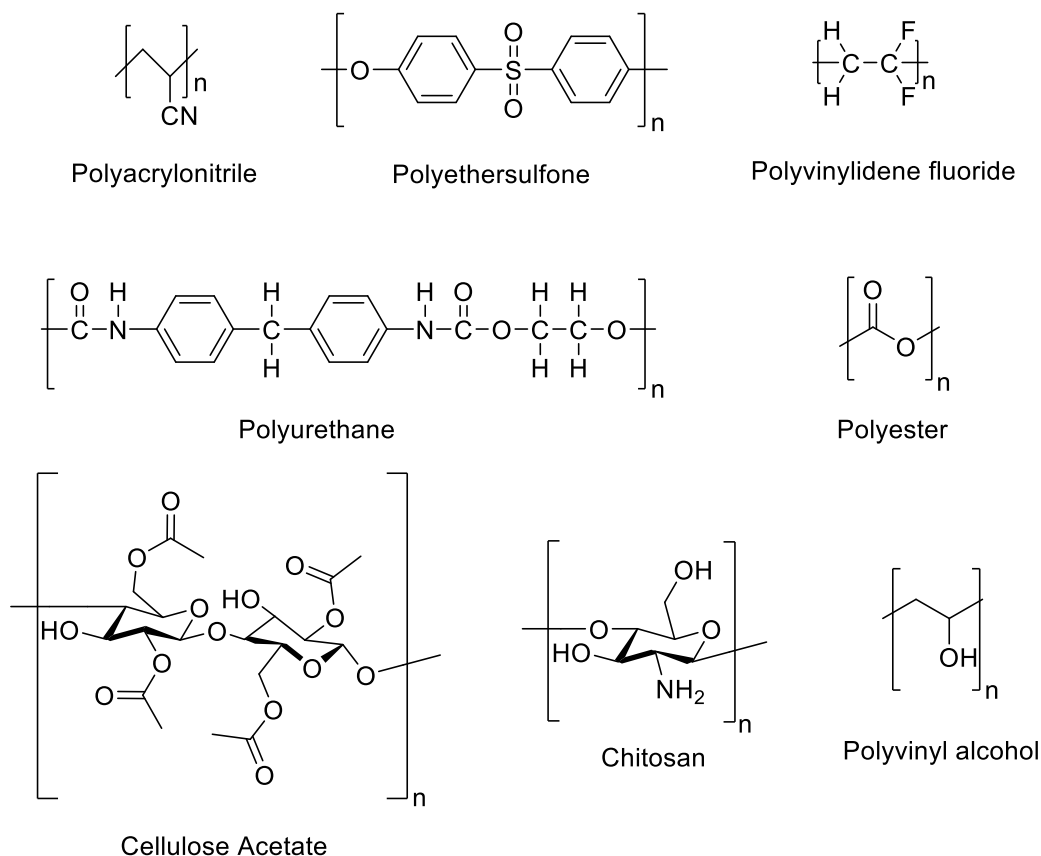


Figure 2. Molecular structure of 8 main polymer structures for electrospun nanofiber membranes in filtration.

PAN ENMs have moreover extensively been studied for the elimination of toxic metals [31]. For example, SH-modified/PAN cellulose nanofibers composite membranes have been created for purifying water from chromium and lead contaminants [32]. In this example, the adsorption efficiency was perceived to be three times higher than non-modified ENMs. Many chelating groups can also be introduced into the PAN ENMs system to adsorb metals like copper, lead, silver and cadmium [31, 33]. Utilizing phosphorylation after a crosslinking reaction and amination, phosphonyl and amino moieties can be present on the surface. It has also been studied that desorption of metal ions can occur by exposing the PAN derived sample to diluted nitric acid. The PAN nanofibers can therefore effectively remove toxic metals and dyes with adjustment of the functional groups [34].

Biofouling is an inherent issue with filtration membranes due to bacterial film formation on the surface of the membrane. There is a drive for creating ENMs with high stable anti-fouling properties. With PAN, a few studies have occurred in this domain for the antibacterial, fouling and cleaning properties of surface changed PAN ENMs. The modification can be done with ethers such as diglycidyl (GDGE) and polyethyleneglycol diglycidyl (PEGDGE) by reacting with the amino group on the membrane surface. Thin film nanocomposites with these fibers are also possible for membranes applications, [35] alongside combinations with graphene oxide [36, 37].

In terms of air filtration as another aspect of environmental remediation, PAN NPs combined with silica were able to filter gaseous media [38]. Work by Ding et al. inspected these composite NPs had a rough structural surface such that this enhanced filtration efficacy for air flow, particularly for multilayer membranes versus monolayer membranes of the same composite.

### *Polyethersulfone*

Another fundamental kind of polymer for ENMs are polyethersulfones (PES) that are used for ultra and nanofiltration due to having very good thermal properties and chemical stability. The chemical stability of this polymer is very high since it possesses no active functional groups for reactivity. Therefore, modifications to the ENMs system are minimal. But it is possible to create different polymer or composite blends with the system in order to change the pore sizing or selectivity of filtration species, or thermal and mechanical properties. Also, ENMs made with PES polymer is prone to biofouling, modifications to the system, such as photochemical procedures, can be used to prevent this [39]. Studies involving the stability of PES ENMs include heat and pressure stability for the filtration of TiO<sub>2</sub> nanoparticles [40, 41]. PES/zirconia particles are also a different approach to variety within the PES system. It has been observed that nanofibrous membranes that contain a 5 wt. % of zirconia NPs are resistant towards compacting, wetting and water permeability [41]. Some work has been done in using a PES blend with other polyimide aromatics for the separation of H<sub>2</sub> and CH<sub>4</sub>. The purification of air was shown to be increased when the membranes were exposed to UV radiation [42].

### *Poly (vinylidene fluoride)*

Halogen-containing electrospun polymer systems have a high mechanical strength associated with them, in particular those containing fluorine monomer units. They also possess high thermal stability and demonstrate low chemical reactivity. Polyvinylidene fluorides (PVDFs) are the most commonly used fluoropolymer used for water filtration. It is normally hydrophobic, so chemical modification has to occur to make it a suitable material for H<sub>2</sub>O filtration. The modifications also make the PVDF ENMs resistant to prevent fouling. This can be done by the incorporation of graphene oxide (GO) when PVDF is in a solution. It has been observed that when GO was incorporated into the polymer matrix, there was a development in mechanical traits in the material because of hydrogen bonding being present between the polymer and GO. The mixture of GO/PVDF is electrospun into a membrane and shows antifouling properties with a rejection value of +99% [43-45]. A superhydrophilic membrane from a similar PVDF composite has also been shown to exhibit oil/water filtration at high efficacy [46].

In combination with chitosan that has good antifouling characteristics, a composite with PVDF that has good mechanical properties is quite useful for making thin film membranes, specifically for ultrafiltration [47]. However, the chitosan containing composite has also been shown to be less effective for water filtration, as the chitosan layer is soluble in aqueous solution, and can thus be destroyed. But, if made with less than 1% chitosan, the composite is capable of higher flux for obtaining purified water. Recent development of PVDF air filtration-based membranes consist of diluted PVDF transformed into hollow nanofibers to form a membrane structure. Silica particles are incorporated in the spinning process and then removed with the use of base – in this case KOH. These fibers demonstrated ultra-high permeance when subjected to diethyl-hexyl-sebacat (DEHS) and sodium chloride. [48]

### *Polyurethanes*

Stable membranes for water treatment with thermal and mechanical as well as hydrolytic characteristics are shown by ENMs made up of polyurethanes (PU). There have been many examples exhibiting these characteristics of electrospun PU for filtration applications [49-51].

Namely, the synthesis of a multifunctional H<sub>2</sub>O filtering membrane with high solution ratio. It has been demonstrated that silver doped PU ENMs can be good for filtering off contaminants from sewage and waste liquids/water [52]. This work showed that by generating 5 nm silver nanoparticles in situ, a web structure is formed with decreased membrane porosity, which in turn improves membrane selectivity. This showed efficient filtration of organic dyes and carcinogenic ions such as arsenic and even TiO<sub>2</sub> nanoparticles from the water. A nontoxic alumina/titanium oxide composite with PU electrospun fibers formed via electrospaying silanes have also been shown to be able to remove fluoride ions from water with high adsorption capacity [53]. Additionally, studies were conducted with this kind of composite, and it was observed that it is also effective in removing nitrates from aqueous media.

Ordered structures of nanofibrous filters in a honey-comb like pattern have been created using PU in combination with polysulfones with needleless electrospinning [54]. Having the elaborated architecture increased filtration efficacy to 99% and a 105 N/g improvement in mechanical strength compared with the plan structures tested by Huang et al. Both organic kind and inorganic types of aerosols were tested and both gas types could be filtered to produce clean air. The system is aided by the incorporation of polysulfone that has a high charge/retention factor. This work paves the way for efficient air filtration methods that can be mass produced for environmental remediation in the atmosphere, particularly in areas of high aerial pollution [55].

### *Polyesters*

Polyesters have wide versatility and have proven to be very useful in adsorption filtration [56]. Thermal plastic esters have been developed that possess elastomeric properties when combined with iron alkoxides in ENMs, and are capable of removing chromium ions from solutions. The chromium is adsorbed and ultimately removed by binding to iron oxide that has been embedded onto the polyester nanofiber surface. This process is capable of removing Cr<sup>4+</sup> and reducing it to Cr<sup>3+</sup>, where it then can precipitate from the membrane [57]. Polyester ENMs can also remove organic particles from sewage. It has been observed that PET containing a multilayer web of cyclodextrin through polymerization with citric acid. This creates an uncommon roughness on the polyester surface, which then actually results in decreased surface area and pore diameter. A polluted phenanthrene dissolved in water was able to be filtered and the phenanthrene impurity was removed with high efficacy, but the membrane is not currently recyclable [57]. If possible, development should continue in the removal of polycyclic aromatic systems from water, as these are ever so present in everyday items that end up in fresh water originating from most commonly cosmetics and cleaning products.

Work by Air Liquid Advanced Technologies Inc. has demonstrated the use of polyesters and other polymers in their membranes to be used for the removal of CO<sub>2</sub> from the atmosphere [58], building off of previous work showing the efficacy of polyester-ether block chains for applicable gas separating membrane systems [59]. Work by Jung *et al.* has additionally shown that a polyester membrane coated with aluminum can also efficiently perform air filtration, but the composite was not made from electrospinning [60].

### *Cellulose acetate*

Cellulose acetate is a biobased material. In terms of water purification applications, nanofibers of functionalized cellulose have been shown to remove uranium and chromium from

aqueous solution [61, 62]. Removal of radioactive uranium was shown to be very efficient with camphor soot cellulose ENMs and within a one-hour time frame and has been illustrated by various adsorption isothermal models. In addition, composite cellulose ENMs can be formed via electrospinning sol-gel [63], through addition of amines onto cellulose acetate silica particles [64], creating a diameter of pores about 100-500 nm in range for the abstraction of  $\text{Cr}^{4+}$  in  $\text{H}_2\text{O}$  [32]. Surface functionalization with different chemical groups allows for variability and adaptability in the active sites of the CA surface. For example, as cyclodextrin modified polyesters can have increased selectivity of removing phenanthrene from water, the addition of cyclodextrin to CA can also be used for the ejection of aromatics in liquid water [65]. As has been reported, grafting of CA ENMs (Figure 3) occurs via click chemistry of azide- $\beta$ -cyclodextrin under  $\text{CuSO}_4$  with CA-propargyl nanofibers [65]. Efficacy of removal of phenanthrene was shown to improve from 50 % (un-doped) to ~65% for the cyclodextrin grafted CA ENMs due to inclusion complexation of the cyclodextrin by hydrophobic interactions and increasing surface area in the polymer fibers of cellulose acetate. These fibers are also beneficial in ultrafiltration applications [66].

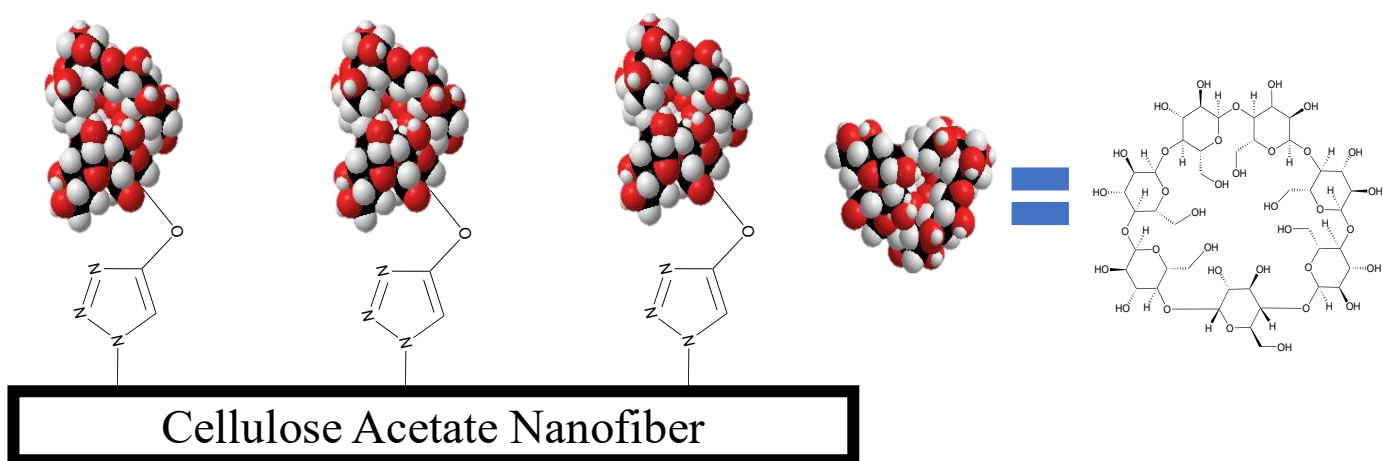


Figure 3 . Schematic representation of grafted cellulose acetate nanofibers with  $\beta$ -cyclodextrin with triazole ring binding. Adapted from work by Celebioglu et al.

In terms of other environmental remediation forms, it is possible to realize efficient aerosol filtration through the use of cellulose acetate/nylon blends [67]. The thin layer of ENMs can air filter 80% of particles at a threshold of 400 nm or greater and can withstand up to 200 °C. It has also been developed that CA ENMs can be infused with activated carbon for the removal of volatile organic compounds such as liquid fuels and degreasers at high temperatures – which indicate higher vapor pressures [68].

The best parts of using CA ENMs are that they are for the most part recyclable and reusable and that they can purify water contaminated with chromium and other metal ions that are toxic as well as organic hydrocarbons.

## *Chitosan*

Chitosan is also a biologically derived polymer useful for ENMs filtration and is the deacetylated derivative of chitin – a microfibril. The chemical structure of chitosan is derived from de-acetylated chitin with chelated –OH and –NH<sub>2</sub> groups. The benefits of using chitosan are that it is non-toxic and hydrophilic biopolymer that is also biodegradable, also exhibiting antibacterial and antifungal properties [69, 70]. However, it does have lower than average mechanical and thermal strength and stability when compared to the other polymers in this chapter, so its applications towards current water filtration are somewhat currently limited. Nonetheless, because of its cost and environmentally friendly factors, composites of ENMs containing chitosan have been researched extensively to try and find a happy medium of chitosan containing blend for filtration applications [71, 72]. By crosslinking chitosan with aldehydes, its water stability can be significantly improved.

Disruptive to ecosystems and health, toxic metals as in Cu, Pb, Cr, Ni, and Co can be filtered away using chitosan ENMs. Chitosan nanofibers that have been neutralized with potassium carbonate are highly efficient for the elimination of copper and lead [73]. As the surface becomes rough and microporous, chelation and diffusion through the porous membrane allow for metal ion removal. In this work, the ENMs made from the neutralized chitosan showed 2 times the removal of copper over lead, due to better diffusion of smaller copper ions through the pores of the membrane for water purification. Unfortunately, re-usability of the chitosan ENMs was not established, and the overall stability of the neutralized chitosan was not very durable. An alternative to this is by creating a graphene oxide composite ENMs with chitosan basis, and this has shown to be reusable, efficient as well as mechanically durable for removing lead and copper, as well as chromium from water [74]. There are many other examples following this kind of protocol. Namely, studying the pH and various thermodynamic properties of graphene oxide/chitosan composites. Nickel has also been shown to be actively removed.

Additionally, combining chitosan with PEO is also a plausible way of creating ENMs for water filtration (PEO being previously discussed) [75]. These nanofibers (120-140 nm fiber diameter) can remove a variety of toxic ions from aqueous mixtures. However, the absorbance of the metal ions is impacted by the pH of the media, being that max amounts of filtration can be achieved at a pH around 4 (acidic), and the rate of adsorption of the compounds has been described as inversely proportional to ionic strength in the solution.

ENMs of chitosan blended with polyamide 6 (PA6) have been produced and then used as a coating onto a high efficiency particulate air (HEPA) filter.[76] The results demonstrated that the ENM coating provided additional anti-bacterial properties against *Staphylococcus aureus*, though the overall filtration of air using a NaCl aerosol test showed only a 0.0083%. Nanofiber diameters in the range of 50 nm where shown to be optimal.

The evolution of using bio-based materials for water purification shows limitations in degradability and mechanical strength being overcome by creating composite mixtures at the price of bio-degradability, but also increasing the long-term use of the membranes. A balance between chitosan functionalization and its core properties must still be addressed for efficient use of ENMs derived from chitosan in water filtration processes.

## *Polyvinyl alcohol*

Polyvinyl alcohol (PVA) is identified as a biocompatible, water-soluble polymer that is non-toxic and widely used. The main limitation of PVA ENMs for water filtration is its solubility, same as with chitosan, though with PVA there is a wide range of strategies available to control its water solubility [77, 78]. The advantageous characteristics of PVA can be utilized by blending with zeolite or zinc oxide nanoparticle fillers before electrospinning. This leads to improvement in ENMs from PVA by increasing the water stability and overall mechanical stability and strength of the polymer nanofibers. This has proved useful not only for metal removal but also organic dye filtration as well as radioactive elements such as Cu, U, and Th. The removal of uranium with copper and nickel was shown using 20% ZnO nanofibers blended with PVA. The isothermic adsorption processes were also tabulated by work from Hallaji [79]. A combination of PVA with zeolite has also been shown to remove the cancerogenic cadmium and nickel from wastewater.

Removal of cobalt can occur via a blend of hydroxyapatite with PVA [80]. The hydroxyapatite being a pre-cursor solution prior to electrospinning, creating a mesoporous structure with high surface area. The cobalt was shown to be effectively removed, but unrecoverable from the membrane surface, so no re-usage was possible. Different isomers of arsenic, another toxic element found in water, has been shown that it can be filtered away from an ENMs made up of PVA/Fe. The membrane pores are between 600-800 nm, and treatment with ammonia demonstrated a higher rate of adsorption for the arsenic.

Regarding dye and organic compound removal with PVA, when blended with polyacrylic acid as an ENM, a water stable membrane is produced that is capable of removing methyl blue dyes from water [81]. This system also showed re-usability with a brine wash. The filtration of the dyes was shown to be most efficient in low acidic pHs, and the majority of the adsorption occurs with half an hour. PVA can also be modified using cyclodextrin to create a water-insoluble ENMs composite [82]. This system was shown to work using thermal crosslinking with citric acid. The methylene blue was also shown to be removed with this method.

Essentially, the most important thing to take away from PVA usage as an ENM for water filtration is that its hydrophobic characteristics and the fact that it can be used in various composite blends due to its structure that can be vastly functionalized. There is more information on PVA adsorption than PVA filtration membranes, so PVA ENMs currently have limited usage for water filtration. Green electrospinning technique in combination with thermal crosslinking has been used to create PVA nanofibers crosslinks with polyacrylic acid and silica-silver NPs[83]. The membranes showed a greater than 98% air filtration efficacy, comparable to HEPA filters with antimicrobial properties against E.Coli thanks to the silver particles. As well, no hazardous and toxic solvents were used in the preparation of the mats, which were also shown to be very durable. A combination of chitosan and PVA has also shown a 95.96% filtration efficiency in combination with drop in pressure. The two polymers can be combined as they interact favorably via hydrogen bonding. The blend was also shown to have antimicrobial properties over 90%, although these were produced with an alternative means to electrospinning[84].

As there are many kinds of polymeric blends to be listed here, some types of polymer ENMs and their blends for water filtration purposes are summarized in Table 1 with some of their most common affiliated properties.

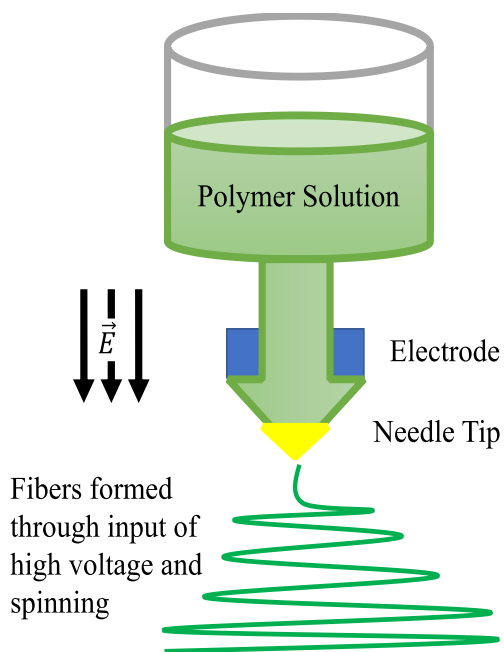
Table 1. Various kinds of polymer ENMs and their blends found in literature with properties for water treatment such as fiber diameter, flux and porosity as well as the common solvent they are electrospun in.

Polymer Composite	Water-likeness	Type	Common solvent	Fiber diameter (nm)	Pure Water Flux (L/m <sup>2</sup> /h/psi)	Porosity (%)	Ref.
PAN/Cellulose Nanofibers	Hybrid	Cr(VI) and Pb(II) Adsorption	DMF	195 ± 30	3000	78 ± 2	Yang, Aubrecht et al. 2014
PAN	Hydrophobic	Adsorption and filtration	DMF	180 ± 20	1000	83 ± 1	Yang, Aubrecht et al. 2014
PAN/GO	Hybrid	oil-water filtration	DMF	250-490	N/A	140 ± 12	Go, Lott et al. 2016, Zhang, Xue et al. 2017
PES	Hydrophobic	Micro-Filtration	DMF	1250	50	50	Homaeigohar and Elbahri 2012
PES/PET	Hybrid	Micro-Filtration	DMF	260 ± 110	60000	N/A	Homaeigohar, Koll et al. 2012
PVDF	Hydrophobic	Filtration	DMF	250	400	87	Wang, Zhang et al. 2016; Obaid, Mohamed et al. 2017
PVDF/ZnO	Superhydrophobic	Filtration	DMF	85	828	N/A	Liu, Wang et al. 2016
PU	Hydrophobic	Filtration	DMF, DMSO, THF	50-700	1000	N/A	Zhuo, Hu et al. 2008; Jiříček, Komárek et al. 2017
PE	Hydrophobic	Adsorption	DMF	200-2000	N/A	95	Feng, Zhang et al. 2014
Cellulose Acetate	Hydrophilic	Adsorption	DCM, formic acid, acetic acid, THF	500-900	37000	87	Zhou, He et al. 2011; Dobosz, Kuo-Leblanc et al. 2017
50% wt Chitosan-polycaprolactone (PCL)	Hybrid	Adsorption and filtration	TFA/TFE	200-400	2629.46 ± 97.3	N/A	Cooper, Oldinski et al. 2013
PS	Hydrophilic	Forward osmosis	DMAC/NMP	396	45000	75.7 ± 1.2	Zhang, Huang et al. 2017
(22 wt%) PES/PET	Hybrid	Forward osmosis	DMF	477	10000	N/A	Huang, Meng et al. 2018
PVDF-TEA	Hybrid	oil-water filtration	DMF	288 ± 13	20,664 ± 2861	63	Obaid, Mohamed et al. 2017
CNFs/TiO <sub>2</sub> -PAN	Hybrid	Pb(II), Cu(II), Cd(II) Adsorption	DMF	240	853	20	Kumar, Venkatesh et al. 2018
PAN-Chitosan	Hybrid	Bacteria filtration and ion adsorption	DMSO	500-1000	293	63	Makaremi, Lim et al. 2016
PCL	Hydrophobic	Filtration and adsorption	TFE	200	2756.8 ± 68.9	80	Cooper, Oldinski et al. 2013
Carbon nanofibers/PAN/TEOS	Hybrid	Ag, Au, TiO <sub>2</sub> nanofiltration	DMF	126 to 554	47620	99	Faccini, Borja et al. 2015

### 11.3 Fundamentals of Electrospinning: Concepts and Theory

Electrospinning is widely used for the formation of fibers that have a diameter in the nano-range. There are a wide variety of resources explaining electrospinning, [43, 85-88] so it will be briefly detailed here. The ENMs are desirable because of the nano-sized diameter, as this creates an increase in surface area (SA) to volume ratio within the formed strings and the nano-sized pores in the matrix as well as an increase in mechanical properties within the final membrane system. These characteristics are what makes the ENMs so sought out for the purification of waste water either by filtration or adsorption mechanisms.

Electrospinning requires a high voltage power supply, a syringe pump linked to a syringe with a needle and a metal collector, as in the schematic diagram in Figure 4. During the procedure,



a voltage is applied over time to the polymer liquid in the syringe. The metal collector contains the opposite charge found in the polymer solution. The charges in the polymer are attracted slowly to the metal end, creating a Taylor cone on the tip as the polymer solution ions overcome the force of surface tension. Fluid is ejected from the Taylor cone as the voltage is augmented. The outcome of the fibers is dictated by the environmental conditions and system parameters such as molecular weight of polymer, its dielectric constant and the overall conductivity during the process [89-92]. These can all affect the quality and diameter of the nanofibers. The fibers of the polymer solution are uniaxially stretched through a viscoelastic jet output very thin polymer strings. The system relies on evaporation of the solvents to create the fibers.

Figure 4. Schematic diagram demonstrating basic electrospinning for obtaining nanofibers.

Solution electrospinning is dubbed as easiest to configure compared with other electrospinning sub-methods, allowing for the formation of fibers at long lengths with uniform diameter control, and it is easier to alter the composition of the solution to created different fibrous composites. However, it is not a “green” method: solvent is not recoverable and can be toxic. We list some alternatives to conventional solution spinning.

#### 11.3.1 Melt electrospinning

Sometimes the polymer solution is formed by a mixture of heavy or halogenated solvents in the standard described electrospinning method above. An alternative is melt electrospinning, though it typically produces larger almost 1  $\mu\text{m}$  diameter fibers, it is a solvent-free method, but has decreased bending instabilities and whipping of the fibers that result [93]. Therefore there is less thinning of the fibers and they are bigger [94]. Although recently, adaptations of the method have shown that ultrafine fibers with various surface roughness and sensing characteristics are possible for applications in biotechnology as solvent toxicity is avoided. This method can also be

adapted for 3D printing [95]. The spinner has a shorter tip to ensure no loss of temperature, such that the polymer melt is consistent throughout the inside of the system until ejection. Typically, the polymer melts have a higher degree of viscosity. When the polymer is ejected through the needle tip it cools off and the fibers are created [96]. Usually, the polymers that can be used in this technique are those that have an established glass transition temperature/melting point, like the previously detailed PE and PU, and also polylactic acids and polymethyl-methacrylate (PMMA) [97]. The costs associated with melt electrospinning is also lower, but there is also a lower output of fibers with limited polymers that can be used and the needle can be clogged on the complex device [98].

### **11.3.2 Needleless electrospinning**

The electrospinning needles are expensive components that can wear and tear with large scale usage. An alternative for upscaled synthesis of nanofibers is to omit the needle component. This can be achieved by altering spinneret structures such as using a stationary wire and rolling cylinders [99]. Needleless electrospinning is beneficial in that it can have a high fiber throughput and there is no needle that can be clogged and changed. A more uniform electrical field can also be obtained. There are examples using this method for high throughput production, indicating this method is on the rise for use in making nanofibers. For the most part, there is either a rotating or stationary spinneret during the spinning process. Stationary spinnerets can come in many different forms, such as upward, downward or sideward. However, it can be tricky to maintain the concentration and viscosity of the solution. Yu et al. have provided a detailed review of the many different aspects of needleless electrospinning [99]. This methodology has the potential for creating ENMs for water filtration applications. For example, polypropylene nanofibers made from needleless electrospinning, having a guided orientation from the applied electric field [100]. Appropriate measures were taken to uncover the electrical field strength effects on the fiber diameter ratio. The pore size of the needleless EFMs was smaller than regular electrospun fibers [100].

### **11.3.3 Multi-spinner electrospinning**

To increase the output of fibers and production, multiple jets can be added into the system. This is also known as the multi-spinner or the multi-nozzle adaptation. The allocation of the jets has to be prudently dictated in order to evade issues with neighboring electric fields that could disrupt each other. This is a common industrial adaptation for increasing membrane throughput, however, it can become problematic to control and assess the homogeneity of the formed polymer mats as the fibers can repel each other as well. As well, frequent cleaning of the needles would also be employed, and therefore increased labor. Without a compromise in production rate, additional supplementary electrodes to relieve nozzle repulsions [101].

## **11.4 Electrospinning nanofibrous membranes**

Because electrospinning is so versatile of a technique and scientific methodology, even if a hydrophobic polymer is used to create the membrane for filtration, its shortcomings can be overcome by using different blending strategies and mixes with other hydrophilic polymers,

inorganic NPs and surface changes via hydrophilic reagents [102]. It is because of this and the fact that high surface area, porosity control, and tunability makes electrospinning so useful for ENMs.

### 11.4.1 Classes of filtrations

High porosity is desirable as this overcomes the low flux rate of standard phase membrane inversion. Care should be taken to prevent fouling on the membrane surface, as bacteria and protein can accumulate on the membrane surfaces of hydrophobic polymers, reducing filtration efficacy [102, 103]. Water purification is mostly defined by filtration through size exclusion or adsorption. As the pore sizing of the nanofiber mats can be controlled and therefore variable depending on the polymer chosen and electrospinning parameters, different kinds of impurities can be separated from water [102, 103]. There are four main kinds of filtrations as stated above and they are illustrated in Figure 5, microfiltration having larger pore sizes in the 100 -  $1 \times 10^3$  nm (thousands of nanometers) range that can filter off different bacteria. Ultrafiltration has smaller pores, in the size variety of 100-10 nm, capable of removing viruses, oils, colloids and larger molecules (proteins) [25].

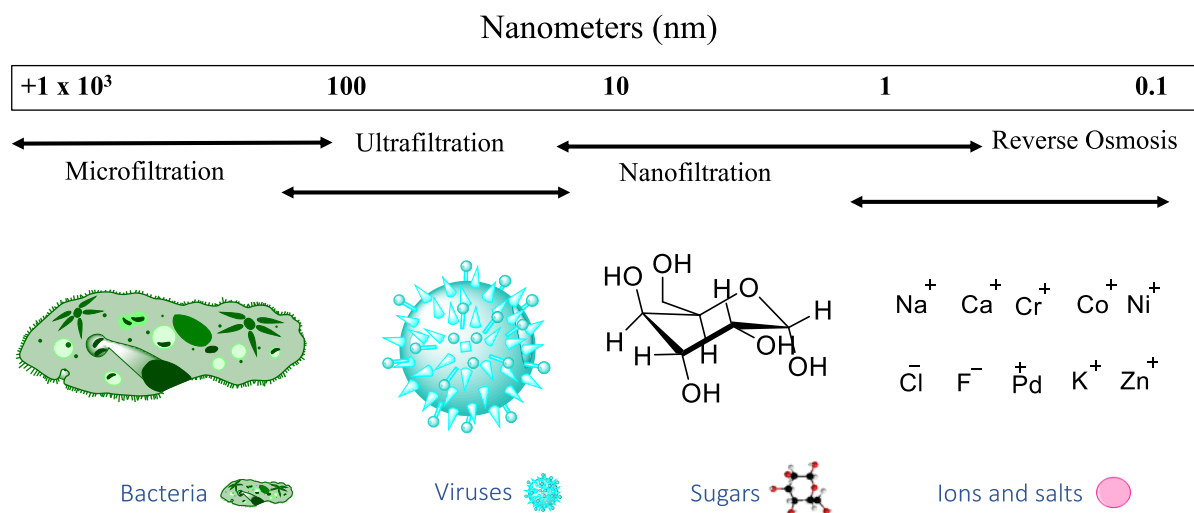


Figure 5. Schematic diagram of approximate values for the 4 main kinds of filtration with illustrations and examples of the smallest they can each respectively filter at the nanoscale.

### 11.4.2 Membrane water treatment specifications

The ability to create uniform and interconnective nanopores in the membranes are ideal for proper filtration of liquids, be it micro or nanofiltration (MF or NF), ultrafiltration (UF) or reverse osmosis (RO). Table 2 is included for additional information on the filtration systems regarding the concept behind the separation process as provided by R. Liang [104]. Forward osmosis (FO)

functions the opposite of RO but without the need for hydraulic pressure, though pressure can be used to increase speed of filtration [105]. Typically, thin film composite matrices are used that contain a polymer support at the base layer and an active top layer; so it is a two-part system requiring optimization [106].

Nanofiltration, as the term implies, has pores in the nanoscale range of 10-1 nm in size, and reverse osmosis is capable of filtering in the ~1-0.1 nm, as well. Hence why the attention is mainly towards nanoscale filtration, as the smaller size range for purification can equate to adsorption and separation of viruses in the water - see Figure 6 for the schematic diagram - preventing the spread of water-borne illness like diarrhea, and even removing hormones such as estrogen that can negatively impact human health globally. Particle filtration consists of filtration of large particles like sand or coal, hair, and pollen above 1 micron, though microfiltration can be just as effective and filter out bacteria and other organelles [86, 102].

Darcy's law rules the flow of the incoming water for MF and UF, and NF, RO and LO are governed by Fick's law. It is important to denote that NF can be categorized as loose RO kinds of membranes that have similar performance between UF and RO membranes [104]. Two main equations that govern water flow are Darcy's law and Fick's law:

$$Q = -KA \, dh/dl \text{ (Darcy's law)}$$

where:

Q = rate of water flow (volume per time)

K = hydraulic conductivity

A = column cross sectional area

dh/dl = hydraulic gradient

$$J = -D \, dc/dx \text{ (Fick's law)}$$

where:

J=flux

D= diffusion coefficient(diffusivity)

dc/dx= concentration gradient

The negative value is indicative of moving down the hydraulic or concentration gradient.

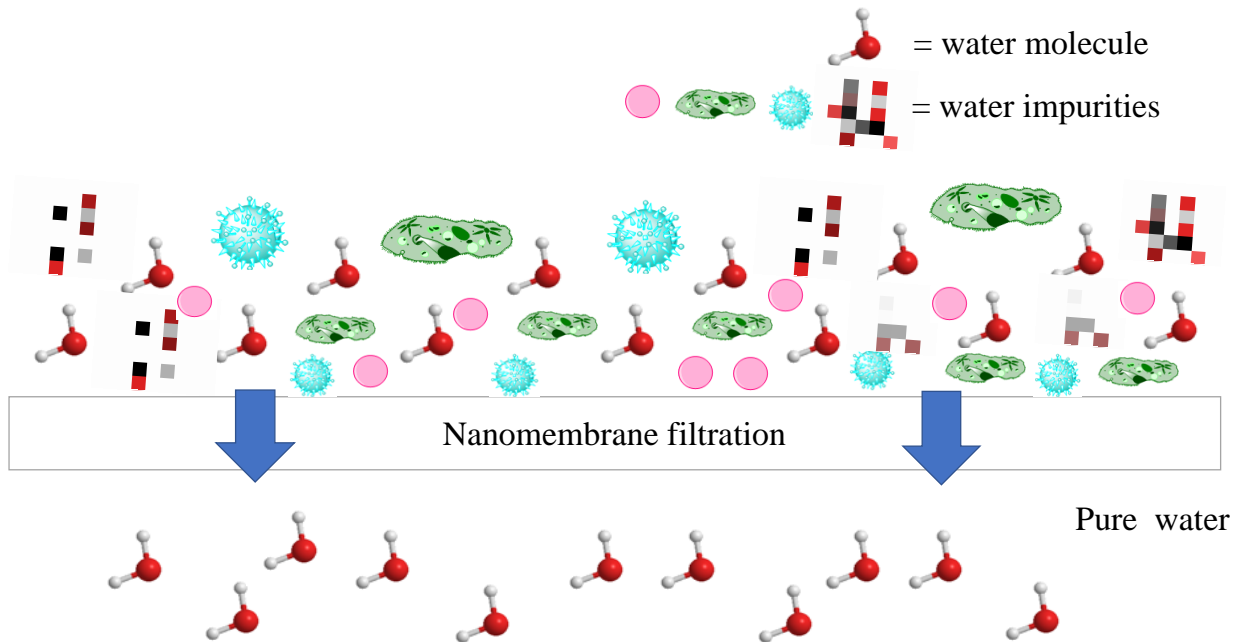


Figure 6. Schematic of nanofiltration process for removing water impurities

Table 2. Filtration processes for water treatment that electrospun nanofiber membranes are applicable towards. (Adapted from Liang, Hu et al. 2014)

Process	Pressure (atm)	Materials Passed	Equation
Microfiltration	1-5	Water & dissolved species	$Q = -KA dh/dl$
Ultrafiltration	2-10	Water & salts	$Q = -KA dh/dl$
Nanofiltration	5-50	Water & monovalent ions	$J = -D dc/dx$
Reverse Osmosis	10-100	Water	$J = -D dc/dx$
Forward Osmosis	~0	Water	$J = -D dc/dx$

### 11.5 Multicomponent electrospun polymer nanofiber membranes

Here, we further the discussion on hybrid and multicomponent systems of nanofibrous polymer systems formed through electrospinning, for the specific purpose of water purification. Many of the polymer ENMs discussed can be put onto different supports and mixed with different kinds of nanoparticles or inorganic/organic materials for H<sub>2</sub>O filtration and/or adsorption. Many nanomaterials can be included into electrospun nanofiber membranes, among some are ZnO and

TiO<sub>2</sub> to improve physical and chemical properties. TiO<sub>2</sub> is widely used as it is non-toxic with excellent thermal and chemical stability, and therefore useful for water purification applications.

As has been denoted, PAN ENMs are widely used and cost-effective, alongside with PAN being cheap and simple to handle, and control of the fibers is highly manageable through tweaking electrospinning parameters, but they have low mechanical strength, so they need to be mixed with fillers. These can be from other polymers to carbon fillers. Graphene oxide (GO) and carbon nanotubes (CNTs) have been recently examined as fillers for polymeric ENMs. In particular, GO can be inexpensive and does not disrupt the fiber diameters and pore size while still positively affecting the hydrophilicity as well as chemical stability. By systematically surrounding GO within the PAN ENMs, subsequently followed by high heat and pressure treatment to form composite sheets. Organic material removal was tested using BSA proteins, and it was observed that the best filtration was from 0.2-0.3 wt% GO, even though there was larger pore size. Though the authors argue this was due to the fact that the BSA functional groups interact with those present somewhere in the GO matrix. The BSA studies are also beneficial to assess the anti-fouling assets of the materials. The findings were associated with cellulose acetate and PAN conventional ENMs to prove efficacy in aqueous filtration [107]. GO-PAA hydrogel nanocomposites have also been formed utilizing cross-linking chemistry. With 3 wt% GO, increases in strength and water adsorption capacity were observed though not for specific wastewater filtration applications [108].

An even more complex system has been fabricated with electrospinning carbon nanofibers with the hybrid TiO<sub>2</sub>-PAN matrix. An analysis was conducted at different weight percentages as is usually the case for such membrane systems. The carbon nanofibers are easily formed from carbonizing electrospun PAN nanofibers through heat treatment and are a desirable addition as they possess excellent thermal and chemical resistance with high surface area. Diameters of the 3 component electrospun fibers were in the 200-260 nm range. The membranes were exposed to a range of acidic to neutral pH solutions for the elimination of toxic metallic ions such as lead, copper and cadmium as well as methylene blue (cationic dye). Results were studied for two days of wastewater filtration. Rejection efficacy percentage was in the range of 66-86%, essentially demonstrating that this is a possible hybrid ENMs that can be used for creating pure drinking water [109]. Using TiO<sub>2</sub>-PAN ENMs, adsorption of toxic metal ions with close to 100% adsorption capacity has also been observed for lead and cadmium in different solution pHs. Though possible agglomeration may occur at amounts of 5 wt% TiO<sub>2</sub> [110]. It was shown that ion removal is more effective at more alkaline solutions with hybrid membranes and only a slight decrease in overall tensile strength was observed.

Nanofiltration via ENMs coated with a hydrogel for dye removal has also been discovered. By electrospinning poly-hydroxybutyrate (PHB) to create a supporting layer, a thin film of a hydrogel containing calcium alginate as the top coat was fabricated for water NF experiments. It was observed that the bottom layer did not have good physical and tensile strength, so carbon nanotubes were blended within the electrospun PHB matrix, alongside calcium cross-linking to enhance even further the supporting layer for increased durability [111]. Pure water flux, oil/water separation and BSA fouling studies were conducted. It was observed that the nanofiber diameters were approximately 530 nm, and the hydrogel coating creates a smooth and very uniform ENMs. The hydrophilicity of the system increased dramatically based on contact angle analysis with the Ca<sup>2+</sup>-alginate coating along with increasing pure water flux. The organic dyes had a 90% rejection rate such as Hydrazine and Stilbene Yellows as well as Direct Orange S plus Procion Red mx-5b. Resistance to fouling during oil/protein separation was also shown to improve compared with only PHB ENMs, deeming this system worthy of further optimization and testing for wastewater

filtration from dyes, although fabrication and cost efficiency would also have to be improved upon [111]. Similarly, sodium alginate with polyethylene oxide ENMs with high adsorption for methylene blue has also been created [112].

Multiwalled carbon nanotubes (MWNTs) have also been shown to be applied to polymeric ENMs. For instance, polyacrylic acid (PAA) blended with PVA in a one-to-one ratio have been combined with MWNTs to form electrospun mats. These mats were then exposed and embedded with zero-valent iron nanoparticles in order to advance the elimination of organic coloring agents. These zero-valent kinds of iron particles have been shown to be efficient for pollutant removal, though not without some concerns for toxicity [113]. The PAA-MWNTs hybrid mats were then observed to be effective in separating chlorinated organics from water-based dispersions [114]. The MWNTs increase toughness in the material even with a 1% addition over single-walled carbon nanotubes [115].

The aforementioned systems are from synthetic polymer derivatives. Incorporating bio-based polymers has also been studied to promote green science and engineering. ENMs from PVDF with 0.5-1% chitin nanowhiskers have been applied towards oil/water filtrations. Tensile strength and water flux were shown to be improved compared with commercial PVDF nanofiber mats [116]. A biopolymer blend of polylactic acid (PLA) with polypropylene carbonate and PHB was also shown to have efficient waste water filtration, efficiently adsorbing pollutants [117]. To add, ENMs from cellulose acetate can be modified with perfluoro alkoxy silanes for improved oil-water separations as superhydrophobic membranes. It was shown that these kinds of hybrid mats can have selective and controllable fabrication, and are also considered to be self-cleaning membranes [118]. PVDF with tri-ethylamine basic dopant has also been shown to have interesting properties once equated to pure PVDF ENMs [119]. CA nanofibers textured with cellulose nanocrystals (CNCs) have also demonstrated 99% adsorption capacity of organic dyes [120].

In addition to cellulose acetate and chitosan/chitin, alginate, collagen, gelatin and aloe vera are also biopolymers that can be used for ENM applications in water purification. Alginate has potential in terms of metal ion chelation, being a support for anti-biofouling and heavy metal detection. Collagen also has potential as a metal chelating component for ENMs. Gelatin can be used for ENMs coatings and as a disinfecting additive. Aloe vera is applicable to restricting the movement of bacteria, enzymes and other biological unwanted agents in aqueous solution [121, 122]. A comprehensive chart of optimized biopolymer electrospinning conditions can be found in a review by Mokhena *et al.* 2015.

Disinfection of microbes in water using biological-based nanomaterials is desirable in that they will not form chemical disinfectant by-products. Hence, promoting the usage of photocatalytic species that can damage the cellular components of viruses and dangerous bacteria like TiO<sub>2</sub>, ZnO, and fullerol. Chitosan, CNTs, silver nanoparticles and carboxyfullerenes can also disrupt the cell membranes themselves. These listed materials have applications in water treatment for the control of microbes as well as for disinfection [123]. Although that is outside the scope of this chapter, it is important to denote the diverse applications of ENMs when incorporated with various components to tailor applications.

Commercial forward osmosis (FO) systems have a relatively lower water flux compared with the reverse osmosis counterpart. By means of electrospinning, polysulfone (PS) nanofibers with 0.25 wt% TiO<sub>2</sub> were fabricated to increase hydrophilicity, porosity and pore size for maximizing higher water flux in FO. Thin film nanocomposites polyamide membrane with a supporting layer of the electrospun PS nanofibers, having the titanium oxide blended into the casting solution to demonstrate the improvements on FO for water filtration [124]. This can further

be developed for proper desalination procedures. Additionally, polyamide layers can be made through cyclic interfacial polymerization (IP) on PES ENMs supported on PET mats to also increase flux for FO desalinations [105]. These composite ENMs by Huang et al. demonstrated multilayer activity of membranes due to various different polymers for the purification of wastewater over the long term.

Nanoparticles themselves can also be potentially found in water supply and subject living species to bio-accumulations of potentially toxic materials. Filtration of nanoparticles can be done by incorporating free-standing carbon nanofibers with electrospun PAN. It was observed by Faccini et al. that this system had a diameter range from approximately 150-550 nm and can be enforced with tetra-ethoxyorthosilicates for increased surface area and flexibility in the carbon nanofibers. The hybrid ENMs were found to filter off gold, silver and titanium oxide nanoparticles from 10-100 nm in diameter with high flux and efficacy [125]. Also, research has shown that the addition of copper nanoparticles with PAN to make ENMs have shown to filter out pathogens from water to make it potable [126].

Membrane distillation (MD) exists also as a method for aqueous waste treatment as well as a form of recovering resources from aqueous media, as in for example, dyes in water, oil/water separations and acids, juices and sugars from concentrated solutions. MD is useful as it can function at low operating temperatures and pressures, and necessitates less requirements in terms of the membrane mechanical properties. It functions well for ions and macromolecules as well as non-volatile molecules. There are fouling and wetting problems that inhibit this kind of filtration process as being marketable. The synthesis of a proper ENMs with strong resistance to membrane wettability and fouling would prove beneficial for MD as a form of wastewater treatment. In terms of progressing this field of research, An *et al.* investigated a superhydrophobic PVDF ENMs with the addition of hexafluoropropene (HFP) incorporating polydimethylsiloxane (PDMS) microspheres. Overall hydrophobicity and membranes roughness were shown to increase compared without PDMS, which also provided a high negatively charged membrane surface, deemed unusual. This created also an anti-fouling layer on the membranes surface when applied with differently charged dyes with increased flux. Remarkably, pure water was produced over continuous operation with complete removal of tested colored dyes [127]. This research forms a basis for future hybrid ENMs to be used for MD filtration for removing wastewater dyes.

There is a myriad of different combinations for polymeric ENMs for water filtration needs to help combat the water scarcity problem around the world. Mass production of these systems and cost of resources along with ecological and toxic effects are fundamental to be optimized first before effective implementation any of these systems.

## **11.6 Past industrial achievements of electrospun polymeric membranes in water treatment**

Many water filtration water bottles contain nanofiber membranes to effectively perform water purification. One such example is Liquidity's Naked Filter technology developed at MIT, made from electrospun PAN nanofibers for bacterial filtration at a 0.2  $\mu\text{m}$  range [128]. It is also capable of removing protozoan cysts containing diseases, very beneficial for removal in developing countries. WaterPure Technologies Inc. also provides nanofiber filtration products, including a stock of nanofiber filtration systems co-developed by NASA. Though the association with a space agency may be deemed as a marketing tool, it demonstrated the applications of water filtration ENMs technology is out of this world. These are examples of current market technologies using ENMs systems. Argonide water filtration systems in the United-States also possess rights to

NASA based electrospun water filtration technology, supplying aqueous purification for the worldwide market.

Nanopareil, previously known as nanofiber separations, produces random mats of electrospun nanofiber membranes marketing for the size and adsorptive properties of these materials, supplying them for water purification and desalination industries. Japan-based company Toyobo also has their own patented HOLLOSEP nanofiber filtration membrane that functions through reverse osmosis principles. The electrospun fibers consist mostly of cellulose triacetate, being able to tolerate high concentrations of chlorine in water to prevent biofouling and has been used successfully at large scale in Japan as well as for the global desalination market. The American market has a variety of different companies as previously briefly mentioned, and additionally Hitco Carbon composites, Foster Miltec, and KX industries. Other worldwide providers having large scale electrospun nanofibers for water filtration needs are Ahlstrom, Nicast Ltd and NanoNC [129].

Another example is start-up technology development company GABAE Industries, is also in the midst of pursuing nanofiber technology for filtration purposes through electrospinning, in order to stay in the top current technology market for their clientele and the ever-important filtration industry - not just regarding water, but also for air filtration. Harvesting water from the air using nanofibers is also a possibility, as it has been shown that a device made from ENMs can condense the moisture in the air into potable drinking water [130].

Desalination is also an important aspect where ENMs have had success, [131] and this is particularly useful given the vast amount of salt water that is present on the earth but is undrinkable. One largest desalination plant resides in Carlsbad, California – which cost about 1 billion USD, to help with the water scarcity in the Western hemisphere, and these sorts of systems are also in place in China and Australia. Mainly, research has shown reverse osmosis using ENMs can be highly applicable here [132, 133].

There are also many academic institutes applying their resources towards water filtering ENMs, and globally, many industries have made attempts for large-scale production for specific needs. Electrospinning technology for creating nanofibers is indeed a flexible and adaptable procedure, allowing for the creating of many emerging methods for aqueous purifications.

## **11.7 Current Challenges**

There are major issues that can plague the realm of ENMs and their applications towards wastewater or saltwater filtration and purification. These problems can arise from membrane pore size and selectivity, fouling and energy consumption all in conjunction with cost efficacy for production, maintenance, and industrial and economic widespread scalability.

To address first, the nanofibers that are formed spontaneously are not guaranteed to be of uniform diameter or distribution; no matter how much the parameters are controlled and regulated there will always be some percentage of outliers. Even 1% of non-uniform fibers waste can accumulate over time, especially over large tonne scaling as the pore sizing of the membranes is affected and results to be non-homogeneous and therefore ineffective for water filtration needs. However, the unevenly distributed waste fibers can find a use for air filtration instead, where nanofiber to particle adsorption dominates and less uniformity is required to filter out the impurities than with aqueous media [129].

Another challenge, even though there have been recently many small companies, the ability to modify and control electrospinning for such large scales is a problem. Some methods to adapt

electrospinning from laboratory use to industry is by multi-spinneret systems versus using a single-needle, and the multiple spinners can have different shapes depending on the type of polymer and function. This also allows for making nanofibers from different polymers all at the same time, creating and facilitating the development of various functional ENM systems [87]. However, multiple-spinner maintenance can be quite problematic in requiring frequent cleaning, and the spacing between the jets has to be calculated to ensure that the electric fields do not misalign each other.

Alas, the addition of multiple spinners have their limits, as too many jets placed close together can cause changes in the electric field and therefore alter the nanofiber shape and overall morphology of the membrane. Needleless electrospinning can be an alternative to avoid needle clogging at high solutions of polymer, but this also creates many variations in the resulting nanomembranes.

Looking towards different kinds of electrospinning methods, for solution electrospinning with multiple jet operations, vast volumes of solvents have to ensure proper chemical disposal or recycling, in particular, if the solvents are dichloromethane (DCM), chloroform, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) or, though most pre-dominant, dimethylformamide (DMF). It is possible to establish a solvent trapping arrangement for the electrospinning setup in order to recycle the organic solvent from a mixture, in order to prevent less waste and take on a greener initiative. If solvent recycling is not economically effective, an alternative is that the solvent/air exhaust can be incinerated prior to charging out into the air. This also creates issues for atmospheric and air pollution, which ultimately, can contaminate the water cycle [134]. Of course, another alternative as previously discussed is moving towards solvent free electrospinning, that also possesses its own unique advantages and disadvantages [135]. The effects and potential environmental dangers have still not been expansively studied for the outcomes of large-scale industrialization.

Hydrophobic polymer membranes are also significantly more prone to bacterial fouling, which can result in affecting the filtration of the water quite negatively, as this would yield overall lower flux. Plasma treatment of ENMs can be used to incorporate hydrophilic groups, [136] but this can produce alterations in the properties of the resulting polymer, which can be undesirable, as well as adding additional steps to the procedure, ultimately affecting time and effectiveness of the method.

## 11.8 Future Directions

Nanofiltration membranes are undoubtedly proven to be useful in water filtration techniques, as the membranes can be modified and structured by changing the type of electrospinning technique used and the polymer source to obtain results. The current market on a world-wide scale for nanofibers is projected to reach 2 billion USD by 2020 and has been noted to have a compound annual growth rate of almost 40% between 2015-2020 as stated by the market research report for the global markets and technologies on nanofibers<sup>2</sup>, indicating that most nanofibers are being made from electrospinning technique. Changes and adaptations to the electrospinning technique will be seen in the coming years to make way for the large-scale industrial market, whether it be targeting a nation's water filtration plants or the households looking for improved filtering of any metals or hormones that may go through the initial filtration plants. Multifunctional ENMs will be the new target materials to improve upon the physical

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<sup>2</sup> <https://www.bccresearch.com/market-research/nanotechnology/nanofibers-technology-market-nan043b.html>

properties and limit fouling of single polymeric melts. Having a more uniform pore-size and reliability for the nanofibers is also a necessity.

The ENMs are but one way for water filtration and desalination, as other thin film purifying media is also beneficial. Alternatively, aquaporins have the ability to transport water across membrane channels, and unwanted particles or ions can be excluded. The aquaporins are integrated into a membrane to promote high water flux along with the usage of various stabilizing agents to avert protein aggregations in the aqueous media. Much emerging biochemistry has come from aquaporin proteins studies for water filtration, such as the recently developed propargyl  $\beta$ -sheet peptide with aquaporin proteins in the matrix [137], moreover a commercially available option driven by forward osmosis already exists [138]. Photocatalysis for creating multifunctional membranes and nanofibers that can have environmental and economical benefits [139]. Wastewater can be treated by  $\text{TiO}_2$  nanofibers mixed with carbon quantum dots [140]. It has also been shown that functionalized graphene sheets are also valid for water purification treatment [141].

Although these methods are useful, it remains to be seen how adaptable their synthetic methods and material throughput can withstand the future water filtration demands, as ENMs can be easier to produce, but do fall victim to the challenges listed. ENMs are also applicable in materials composites, cosmetics, aerospace engineering and science, energy and healthcare sectors as well as air and gas filtrations [142]. There are still many areas of improvement for reach and development of ENMs as briefly outlined here that can lead to innovative new ideas stemming from engineering and sciences in both materials as well as environmental sectors. Creating a more extensive database for ENMs is particularly useful to further the field in both industry and academia. The water treatment domain seems, however, the most predominant for ENMs research because of the vast kinds of electrospun components that can be incorporated into the polymer membranes so efficiently, creating a vast array of materials for many kinds of filtration techniques worldwide.

## 11. 6 Conclusions

In summary, different kinds of polymers, blends and modification techniques for ENMs were discussed and their benefits, challenges and future needs were also established. This chapter is meant for developing and giving an overview of the concept behind electrospinning for making polymer nanofiber membranes in terms of water filtration purposes, regarding generating clean and potable water both from desalination and wastewater sources. Those that are deemed excellent ENMs will provide high surface area to volume ratios for excellent filtration efficacy. Both adsorption and filtration type membranes could potentially be used for the same purpose. Various kinds of toxic metal ions, organic dyes and other water contaminants have been shown to have efficient removal from aqueous solutions. Different filtration mechanisms are discussed and overviewed. There are 8 primary polymers used for conventional ENMs that can be modified based on procedure, parameters and mixing – changing ENM properties and characteristics for the desired water filtration application. Bio-based polymers are also usable but required doping to make them less hydrophilic in nature to withstand long-term water treatment. The ENMs have been shown to be quite versatile for water treatment applications.

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