Electrospun Membranes for Environmental Protection

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Abstract. Electrospinning is a much-used process for making nano-sized fibres as a result of its simplicity and versatility and of unique mechanical and thermodynamic properties of the obtained nanofibres. Electrospun membranes, which have a porous structure characterized by high uniformity and porosity, find applications in many membrane processes, ranging from membrane distillation to reverse osmosis. The paper reviews electrospun membranes applications in environmental protection, focusing on water and wastewater treatment and air purification. Recent progress and prospects for future development are highlighted.

1. Introduction
Nanostructure science is an interdisciplinary area of science activity that has changed the way materials are produced, offering a large new field of functionalities that can be accessed [1-5]. Nanoscale materials science has revolutionized progress in many areas, overturning many of the traditional approaches [6,7]. Nanotechnology-based materials are often used in filtration processes, as the use of submicron materials results in better filter effectiveness, at the same pressure drop in interception and inertial impaction regimes, as compared with coarser filtration materials.

Between the many existing techniques for nanofibres producing (drawing, template synthesis, phase separation, self-assembly) [8-12], electrospinning proved to be one of the most important, as it is simple and capable of providing highly porous structures of non-woven nanofibres with uniform pore size. The large specific surface area of nanofiber membranes permits a very effective adsorption of impurities from the air or water, contributing to their high filtration efficiency [13-17]. Also, this kind of membranes operates at lower energy and henceforth with lower costs [18-22]. In consequence, electrospun membranes, which were used for the first time in filtration in early 1980, became more and more used in many air and water purification applications [23-26].

2. Fundamentals of electrospinning
The principle of the electrospinning process is simple: an electrical potential is applied between a polymer solution or melt and an electrically conducting collecting surface. Under the applied voltage the droplet is gradually transforming its shape into a conical shape known as the Taylor Cone, from which ultrafine nanofibers emerge and are collected, on the collector [27, 28].

A requirement for the polymer solution to be electrospun is its viscoelasticity; a spinnable polymer solution has to be semi-dilute and highly entangled [29]. The process comprises three stages: jet initiation, its extension and finally nanofiber formation [30, 31]. From the point of view of how the jet decomposes into droplets, three types of instability are distinguished (Figure 1):
• axial-symmetric instability, which is controlled by the superficial tension (non-conductive) or by the electrostatic forces (conductive); this instability leads to drop formation;
• non-axial-symmetric instability (bending, conductive), which is governed by electrostatic forces; this type of instability is responsible for the process of jet elongation (thinning);
• „whipping” type instability, which produces random spreading of the jet and even its fracture into short fibers; this type of instability is produced by the increased charge density and polymer flow rate.

![Diagram](image)

Figure 1. The simulation of instability phenomenon:
1 - linear jet zone; 2 - zone of first instability axial-symmetric;
3 - trajectory of the jet leaving the needle; 4 - halving angle for the trajectory cone; 5 - second zone of instability; 6 - third zone of instability; 7 - jet axis.

Various morphologies of the nanospun nanofibers can be obtained by varying the process parameters and the polymer solution properties. This way nonwoven nanofibrous membranes with highly porous structures can be produced [32].

3. Main applications of nanofiber electrospun membranes
The principle of the majority of membrane separation processes is the selective filtration of influent through pores of different sizes. The special features of electrospun nanofibre membranes, namely high specific surface, high porosity, fine tunable pore size, interconnected open-pore structure and high permeability to gas and fluid [33], make them very suitable for such treatments.

3.1. Water and wastewater treatment
Membrane technologies for drinking water treatment have concerned much interest because of their many advantages, such as moderately low operational costs and high efficiency. Electrospun nanofiber membranes from polyvinylidene fluoride, which have piezoelectric properties, are efficient in preventing fouling, offering this way high water productivity and maintenance of flux [34].

Chitosan - polycaprolactone nanofibrous membranes have been used for antibacterial water filtration, significantly reducing Staphylococcus aureus while supporting a water flux of ∼7000L/h/m with 100% removal of 300 nm particulates, in condition of full membrane integrity [35]. Membranes from a network of ultra-fine cellulose nanofibres infused into a scaffold from electrospun polycrylonitrile nanofibres on a melt-blown polyethylene terephthalate non-woven substrate have been used for water purification, displayed very good retention abilities for simultaneous bacteria and viruses, while maintaining high permeation flux [36]. Membranes from nanofibres are used in many phases of the wastewater treatment: in pre-filtering treatments that remove contaminants that could affect further processes (such as ultrafiltration or nanofiltration), in removing of fine particles and bacteria, in wastewater colour removal, in removal of heavy metal ions such as chromium, nickel,
copper, lead, cadmium and even in biological treatments. Membranes made of electrospun nanofibrous polysulfone and Nylon 6 have been used as pre-filters, showing good capacity to remove over 95% of particles with dimensions in the range of 7 - 10 µm without permanent fouling [37, 38].

Many types of electrospun nanofiber membranes proved to be effective in Cu(II) adsorption. Membranes from electrospun fibroin / Cellulose Acetate (80/20) nanofibres were used to adsorb Cu(II) ions in an aqueous solution after ethanol treatment, reaching a value of 22.8 mg/g Cu2+ [39]. Electrospun keratose / fibroin blend membranes exhibited better copper ion adsorption capacities compared to common fibrous filters [40]. A blend of polyvinyl alcohol / tetraethyl orthosilicate / aminopropyl triethoxysilane was electrospun and the obtained membranes were used for uranium (VI) adsorption from aqueous solutions, reaching a maximum adsorption capacity of 168.1 mg/g at pH of 4.5 and temperature of 45 °C [41]. Electrospun nanofibre membrane made of thiol-functionalized poly (vinyl alcohol) / SiO2 showed high Cu2+ adsorption, which was maintained through six recycling processes [42]. Membranes from electrospun keratin nanofibers were tested for the Cu(II), Ni(II), and Co(II) metal ion removal, and their selectivity was found to decrease in the order Cu(II) > Ni(II) > Co(II). The experiments revealed a good adsorption capacity for Cu(II) ions, even with the coexistence of Co(II) and Ni(II) metal cations [43]. An adsorbent made by intercalation ethylene diamine tetraacetic acid in layered double hydroxides, followed by encapsulation into polyacrylonitrile polymer matrix using electrospinning showed a 93% copper removal efficiency when the initial Cu(II) concentration was 64 mg/L, with the adsorbent dosage of 1.50 g/L. The study concludes that the adsorption of Cu(II) is a result of a chelation process by interlayer ethylene diamine tetraacetic acid, a powerful chelating agent [44]. Cellulose electrospun nanofibers were modified with oxolone-2,5-dione, enhancing this way the surface area of the nanofiber mat and helping in detecting heavy metals like cadmium and lead [45].

Many electrospun membranes have been tested for colour removal in wastewater. Membranes made of electrospun keratin nanofibrous acted like adsorbents for Methylene Blue by means of a chemisorption process which occurred by ion exchange [46]. Electrospun polyhydroxyalkanoate film was used as adsorbent agent for Malachite Green, a triarylmethane dye. Titanium dioxide photocatalysts have been incorporated into the film to achieve, besides adsorption, a photocatalytic degradation effect, achieving complete discoloration in 45 min under solar irradiation [47]. Electrospun nanofiber membranes from polysulfone, polyvinylidene fluoride and polyethylene have been used in membrane bioreactors treating molasses wastewater, showing performances comparable to the commercial membranes [48].

3.2. Desalination

As drinking water resources become more and more scarce, desalination turned out to be an important method to convert the salted water of oceans and seas into potable water. Two basic technologies are used to remove salts from ocean water: thermal evaporation and membrane separation. Desalination, the process of extracting mineral components (mainly sodium chloride) from saline water, is often obtained using membrane processes such as reverse osmosis and nanofiltration. The principle of these processes is the following: salted water is forced through a membrane that permits only water molecules to pass, blocking salt (or other minerals) molecules. Mats from electrospun polyacrylonitrile nanofibers have been used as support layer for thin film composite nanofiltration membranes. These membranes were tested in desalting a saline solution (2000 ppm concentration), and was found that as the fibre size decreased, the salt elimination increased, but at the expense of permeate flux [49]. It was also found that the optimum concentration of polyacrylonitrile for the electrospinning of fibres was 8% wt.

Electrospun nanofibrous membranes that show higher hydrophilicity and lower surface roughness are best for pressure-driven membrane processes, while hydrophobicity is an essential feature for membranes used in the membrane distillation process, a thermal-membrane desalination technology using low-grade or waste-grade heat [50]. The principle of membrane distillation is the following: hydrophobic membranes separate the liquid phase from the vapour phase within the membrane pores,
and only the vapours are able to pass through the membrane, while the liquid feed including dissolved components, is retained by the membrane. Membranes form electrospun polycrylonitrile nanofibres were turned from hydrophilic to hydrophobic by surface fluorination, without altering the morphology and structure of the membranes. It was found that if fibre orientation is opposite to the flow direction, the desalination performance is affected in terms of permeate flux.

Membranes from electrospun polyelectrolyte nanofibres, which have been subjected to a heat-press post-treatment to improve their integrity and enhance water permeation flux, have been used for membrane distillation. These membranes showed a steady water permeation flux of about 21 kg m\(^{-2}\) h\(^{-1}\) for 15 h when using a 3.5 wt % NaCl solution [51]. Composite membranes from electrospun nanofibres of poly (vinylidene fluoride) and poly (vinylidene fluoride-co-hexafluoroproplene) were used in a direct contact membrane distillation. It was found that after 12 hours of treatment, the salt rejection was 99.9888 % for the first type of membrane and 99.9901 % for the second one. The permeate flux of the second composite membrane is 4.28 kg/ m\(^2\)

3.3. Air filtration
One of the most important sources of air pollution are the fine particles (less than 2.5 mm in diameter), which are a main cause of acute and chronic effects on human health [53]. This is why air filtration technology is of great importance. Numerous fibrous membrane based on a various range of fibres are used in diverse filtration applications. Many of these are made of electrospun nanofibers, as they have some features that make them suitable for air filtration area, such as high specific surface area and open porosity, together with an interconnected porous structure [54]. Electrospun polyamide 6 nanofibres have been deposited onto a nonwoven viscose substrate to make protective clothing against nanoparticulate, showing up to 80% retention of 20 nm size particles and over 50% retention of 200 nm size nanoparticles [55]. Other membranes were obtained from electrospun nanofibres of polyamide 6, obtained from a solution of polymer solved in formic acids. These membranes, that have a thickness of 71 µm, proved to have good filtration potential for the microparticles with 0.3 µm diameter, in conditions of very good dimensional stability [56].

Nanoparticles such as MgO, TiO\(_2\), Al\(_2\)O\(_3\) and other oxides have been incorporated into nanofibers to obtain membranes for air filtration applications. Membranes obtained by depositing various metal oxide nanoparticles using liquid phase deposition and electrospraying techniques on the surface of nanofibers made by electrospinning of poly(ethylene terephthalate) with cellulose acetate proved to have potential as filter media in protective clothing and air filter applications [57]. Membranes made of nonwoven polypropylene covered by a polyvinyl alcohol were effective in eliminating organic polar compounds, ethers and compounds containing carbonyl groups from gas [58]. Transparent air filter for indoor air protection have been obtained by using electrospun polymer nanofibers. These filters with ~90% transparency show high air flow and high effectiveness as air filters (over 95% removal of PM2.5 under extreme hazardous air-quality conditions) [59]. Electrospun nanofibre membranes from waste high-impact polystyrene were applied as air filtration media, showing an efficiency greater than 99.999%, which was equivalent to that of the HEPA filter [60]. Electrospun biodegradable polylactide air filter membranes showed a higher dust capture efficiency [61].

4. Conclusions
Electrospinning is a versatile method of producing nanofibrous porous membranes using a wide range of polymers. By choosing the polymer and the solvent, as well as the parameters of the electrospinning process, the morphology of the resulting membranes can be determined. The use of electrospun nanofibre membranes in filtering processes is the result of their special characteristics, namely the high surface-to-mass ratio, the high pore interconnectivity and the uniform distribution of their dimensions. In addition, the number of applications of these membranes is greatly enhanced by their
functionalization by changing the surface chemistry of the membrane. The paper first briefly reviews the principles of electrospinning, and then summarizes the latest developments in the use of membranes as a water filtration medium (drinking or waste) and air. The contribution of electrospun nanofibre membrane processes to desalination processes is also presented.

5. References
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