Desalination 308 (2013) 198–208

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

New directions in nanofiltration applications — Are nanofibers the right materials as membranes in desalination?

Sundarrajan Subramanian [a,*], Ramakrishna Seeram [b,c,d,**]

[a] Department of Mechanical Engineering, National University of Singapore, 2 Engineering Drive 3, Singapore
[b] NUSNNI, National University of Singapore, 2 Engineering Drive 3, Singapore
[c] Institute of Materials Research and Engineering, Singapore 117602, Singapore
[d] King Saud University, Riyadh 11451, Saudi Arabia

ARTICLE INFO

Article history:
Received 9 April 2012
Received in revised form 1 August 2012
Accepted 2 August 2012
Available online 5 September 2012

Keywords:
Electrospun membranes
Thin film nanofibrous composite membranes
Nanofiltration
Desalination
Electrospinning

ABSTRACT

Various desalination technologies are emerging to tackle the increasing water demand globally. Among them, nanofiltration (NF) has recently received an increased attention in the literature to desalt low salt content water. The developments of new membrane materials and novel processes have shown that NF can be potentially applied in the desalination due to enhanced flux, lower operational pressure and energy savings. Nanotechnology based products such as nanoparticles and nanofibers have been introduced to enhance the properties and performance of the membranes derived from conventional polymeric membrane materials and conventional phase inversion processes. When mid-layer made up of electrospun nanofibrous membranes (ENMs) produced by electrospinning has been applied in the thin film composite (TFC) configuration in NF application; higher permeate fluxes than conventional membranes were achieved. This has been ascribed to the high porosity, low transmembrane pressure and interconnected pore structure of ENMs. The ENMs as such or after mixing with nanoparticles are also explored in the area of membrane distillation for seawater desalination. In this article, recent developments of ENMs as TFC membranes in NF application and as desalination membranes in the membrane distillation, geothermal water desalination, and capacitive deionization application are summarized here.

1. Introduction

The increase in the population and increasing need for better quality of people's life has contributed in the higher demand for fresh water and energy resources. This has forced the researchers to look for alternative sources. Various government organizations report that about 1.2 billion people will be short of access to clean fresh water and about 66% of the world's population may live in water stressed countries by 2025 [1–4]. Some of the alternative sources that have been studied to tackle the fresh water scarcity are the treatment of brackish water, waste water [5,6] and seawater into clean water. Among them, desalination technology, which converts seawater into clean water, has been regarded as an effective approach due to their abundance in nature.

Various desalination technologies such as membrane distillation (MD), electrodialysis (ED), RO, freeze desalination (FD), ion exchange (IX), and NF have been developed. Among them, RO has been widely used to remove high salt content in the seawater (for e.g. NaCl rejection of >98%) and most commonly used for the production of drinking water. NF has been developed to desalt low salt content water such as brackish water. NF membranes have the capability to remove sodium chloride rejections of 20–80% with higher rejection capacity toward multivalent ions such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}. NF is now emerging as a viable alternative to conventional water treatment technologies, because it can operate at lower pressures, provide high flux and more energy efficient than RO systems. It has been shown that double the permeate flow can be obtained with NF when compared to RO and by the replacement of RO with NF membranes about 20% electric power can be saved [7].

In order to reduce the resistance and enhance the flux of the NF and RO membranes, thin film composite (TFC) membranes consist of a thin top layer (acting as a separation layer) coated onto a developed support membrane. A three layer composite structure of thin film nanocomposite (TFNC) membrane is shown in Fig. 1a and a cross section of the same is given in Fig. 1b. The TFC membranes comprise three fundamental layers: (1) top ultra-thin selective barrier layer (which bridges and overcoats the surface pores of the middle porous layer), (2) middle porous support and (3) bottom non-woven fabric. Layers (1) and (2) can be carefully altered to produce the optimal separation performance. Although layer (3) does not influence the separation characteristics, it has been used to provide mechanical strength during handling. Some of the advantages of TFC membranes

* Corresponding author. Tel.: +65 6516 4272; fax: +65 67730339.
** Correspondence to: S. Ramakrishna, NUSNNI, National University of Singapore, 2 Engineering Drive 3, Singapore. Tel.: +65 6516 4272; fax: +65 67730339.
E-mail addresses: mpesunda@nus.edu.sg (S. Subramanian), mpesr@nus.edu.sg (R. Seeram).

0011-9164/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2012.08.014

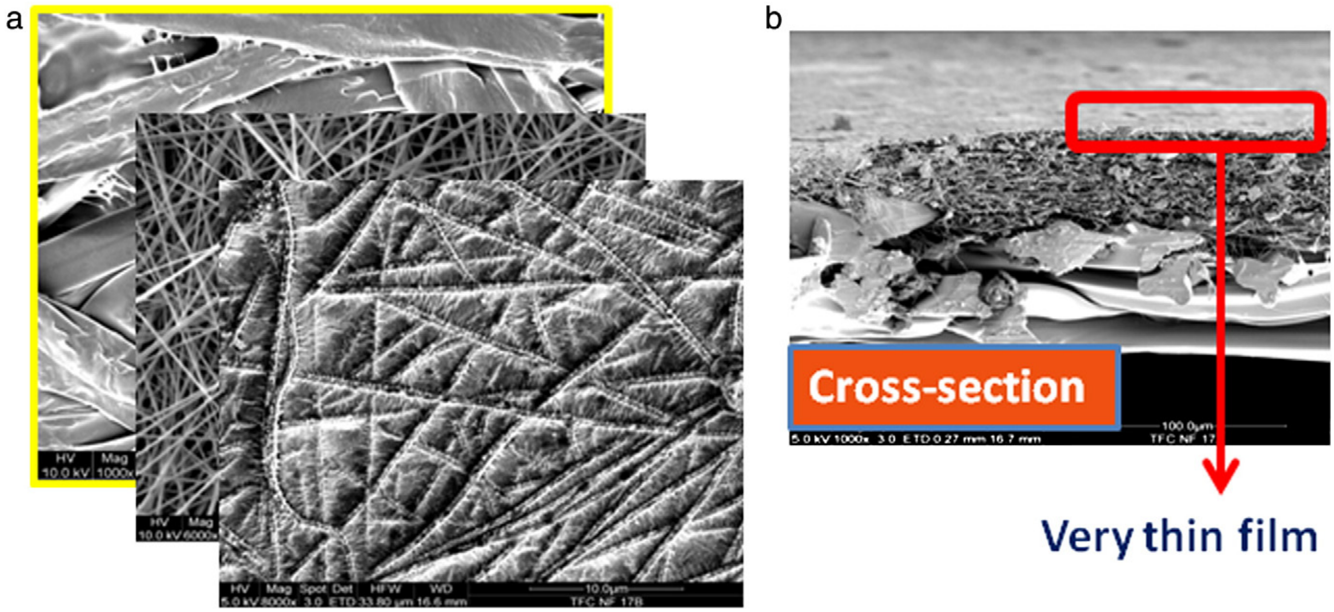

Fig. 1. A three tier architecture of TFNC membrane (a) and its cross sectional view.

are (1) ability to produce varying thicknesses of thin top layer and support layers, and (2) optimization of these two layers with respect to structure, stability and performance. Although, improved water flux and solute rejection were achieved by TFC membranes, they are prone to fouling, non-selective and energy consuming. Hence, innovations in TFC membrane materials were developed (a) to increase the water permeability for energy savings, (b) improvement in selectivity by membrane design, and (3) fouling resistance surfaces.

Hence, in order to achieve the above desirable properties, some of the new concepts were introduced by various groups in the literature. Nanotechnology based products have rapidly growing interest, in the case of water treatment membranes, as they exceed the conventional TFC membrane performance. For instance, thin film nanocomposite (TFN) membranes were fabricated by dipping the ultrafiltration (UF) membrane in metaphenylene diamine (MPD) solution followed by interfacial polymerization of trimesoyl chloride (TMC) solution containing zeolite A nanoparticles. The developed TFN membranes exhibited water permeability and rejection values comparable to that of commercial RO membranes and pure water flux was almost double than that of conventional TFC membranes. This has been ascribed to the formation of highly hydrophilic surfaces and pores by zeolite nanoparticles [8].

Nanofibers are one of the nanotechnology products widely used in various fields such as textiles, biomedicine, tissue engineering, water and air purifications [9–12]. Recent research conducted in Stony Brook University by Chu's group [13,14], in our laboratory at NUS [15,16] and other labs has shown that when the mid-layer made up of ENMs has been applied in the TFC configuration in NF application; higher fluxes than conventional UF membranes were achieved and this new class of membranes is termed as TFNC membranes. We have also demonstrated the applicability of ENMs in air gap membrane distillation (AGMD) for the first time in the literature [17]. Very recently, clay nanoparticles blended with PVDF ENM for direct contact membrane distillation (DCMD) process were studied by Prince et al. [18].

In this paper, the role of ENMs as a support membrane and overall performance of the resulting TFNC membranes in NF application is concisely reviewed. Various properties such as surface architecture, pore-size and thickness of the ENM layer to influence the separation of salt and flux are summarized. The ability of ENMs as such and clay incorporated nanocomposite ENMs in the salt rejection of APMD, DCMD, and geothermal water desalination processes is also presented.

2. Advantages and disadvantages of conventional filter media

The main advantages of non-woven filter media are the presence of fibrous network, which provides a high internal surface area and hence enormous dirt loading capacity when compared to phase-inversed membranes. Hence non-wovens are (i) predominantly used as a pre-filter to remove most of the contaminants in the separation units such as NF and RO membranes and also (ii) used as a backing material during liquid filtration.

However, non-woven media have certain limitations. The present non-woven media can remove particles between 10 and 200 μm in diameter due to the considerably larger average pore-size generated by the micron size fiber. Apart from this, particles are easily trapped and lodged within the tortuous path of the non-woven media. Hence, they are not easily cleanable and reusability is not a viable option and particle retention rates are not defined precisely as with membranes or woven filters. In addition, a thicker fibrous layer is required to reduce the overall average pore-size of the media to separate particles less than 10μm in diameter. This has resulted in a decline in flux. However, non-woven media are mechanically robust and hence it is widely used as a substrate to support porous membranes.

3. ENMs as next generation fibrous media in water treatment applications

In the liquid filtration applications, it is necessary for the filter to separate bacteria, viruses and particulate [19]. Although this need is increasingly met by membrane processes, low throughputs of these processes have driven the material scientists to explore the highly porous media with finer fibers.

With the latest buzz of nanotechnology, it is now viable to produce ENMs with finer diameter. Hence, it is anticipated that the limitations of non-woven filter media discussed above can be reduced or overcome [12,20] by ENMs based pre-filters. In the area of water filtration technology, ENMs are gaining increased attention in the literature.