CHAPTER 8

Prospects and State-of-the-Art of Carbon Nanotube Membranes in Desalination Processes

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1. INTRODUCTION

Over the years the world has witnessed a shift toward research efforts aimed at the exploitation of unconventional and untapped water sources such as wastewater, seawater, and brackish ground water in order to meet the growing global water demand.

By undergoing various treatment stages, these untapped water sources can be converted into potable water and are regarded as "new" water sources. Among all of these sources, seawater offers a very attractive alternative source for freshwater since it can potentially provide an abundant and unlimited supply for various human, agricultural, and industrial needs provided the salt gets removed in a sustainable manner.

Desalination technologies are used to convert undesirable and salty seawater into potable and useable water [1]. Seawater desalination using membrane-based processes, particularly reverse osmosis (RO) membranes, are highly favored over thermally based processes, especially in energy-stressed countries, because of their lower energy consumption [2,3]. Thermally based desalination processes rely on the use of heat because of the need to evaporate water prior to condensation [4]. On the contrary, in RO desalination technologies, pressure is applied to force water molecules to permeate through a semipermeable membrane while preventing the passage of salts. Therefore seawater desalination using RO membranes remains an energy-efficient reference point and a standard of comparison for newer or evolving desalination technologies [2].

One of the greatest issues existing in both seawater and brackish water desalination using currently available RO membranes is the lack of sustainable, robust, energy-efficient, and cost–effective membranes [5]. Indeed, this is a challenging task that requires innovative solutions with feasible implementations. Before attempting to correct these challenges, it is important to have adequate knowledge and understanding of the minimum amount of energy required to separate pure water from seawater. For example, the theoretical minimum energy of desalination for seawater at 35,000 ppm salt concentration and at a typical recovery of 50% was 1.06 kWh/m in 2011 [2]. This provides a benchmark for comparison with recently crafted technologies and helps guide future efforts aimed at reducing the energy demand for desalination processes [2].

Nanotechnology enabled or simply nano-enabled membranes are increasingly gaining popularity as promising candidates for desalination applications. These nano-enabled membranes rely on the incorporation of various types of nanomaterials onto conventional polymeric membranes used in desalination or other processes such as ultrafiltration. The main aim of using nanomaterials is to overcome the challenges that conventional membranes used in water desalination are often faced with, such as high fouling propensity, trade-off between their selectivity and permeability, as well their high energy consumption during the desalination process [5]. In particular, carbon nanotube (CNT)-incorporated polymeric membranes are one of the most widely studied nano-enabled membranes. CNTs consist of single or multiple layers of graphene sheets rolled into a tubular structure and can have diameters ranging from 1 to 2 nm for single-walled CNTs (SWCNTs) or 2–25 nm for multiwalled CNTs (MWCNTs) [6]. They are known to possess a unique combination of structural and physicochemical properties owing to their nanoscale dimensions: high volume-to-surface ratio, small inner diameters, antimicrobial properties, frictionless surfaces for rapid fluid flow, and many others [7].

The incorporation of CNTs onto polymeric membranes has shown to result in membranes with (i) improved mechanical and thermal stability, (ii) excellent hydrophilic and antifouling properties, (iii) controllable pore size diameters, and (iv) improved selectivity and permeability [8–10]. Currently, there are different views in the research area involving the use of newly emerging CNT-based membranes in desalination processes. These diverse views are centered on whether CNT-based membranes; particularly, the vertically aligned (VA) CNT membranes are capable of reducing the energy needs of the desalination processes owing to their ultrahigh water permeabilities [3]. The ultrahigh water permeability of CNT membranes is believed to help reduce the amount of pressure or energy needed to drive pure water molecules across the semipermeable membrane, whereas the energy consumption of a desalination process is determined by the need to bring the feed volume to a pressure equal to the osmotic pressure of the concentrate [2]. This factor suggests that regardless of how permeable a membrane may be, the applied pressure cannot be reduced to below the osmotic pressure of the concentrate or, more precisely, the osmotic pressure of the boundary layer forming at the membrane surface.

Furthermore, it should be emphasized that operating at high water fluxes generally leads to high membrane fouling; that is, at high fluxes, the effective concentration of the solutes or foulants near the membrane surface increases. Subsequently, the rate of foulant deposition on the membrane surface increases [11], which is a result of the greater permeation drag force that is experienced by the foulant toward the membrane surface [12,13]. Therefore, the ultrahigh permeability characteristic of CNT membranes could assist in the reduction of capital costs needed to run the desalination process, because of the reduced membrane area that will be required to achieve maximum water flux while rejecting the transportation of salts. It is, however, important to accentuate that flux is not "everything" since there are many other membrane systems that function better when operated at lower fluxes.

CNT-based membranes may be leveraged in RO membrane material modification to overcome the issue of fouling or biofouling. Biofouling, which is caused by growth of biofilm on the surface of a thin film composite (TFC) membrane, hinders the performance of the membrane, thus limiting the membranes' prolonged use. Biological foulants such as bacteria, fungi, and algae grow in large quantities on the membrane surface, thereby inhibiting permeation through the membrane surface [14]. On the other hand, the use of strong oxidizing agents such chlorine and ozone to remove the adsorbed biofilm may be detrimental to the membrane's structure as they are capable of degrading the polyamide layer on TFC membranes [1,15]. Another limitation of conventional TFC RO membranes involves the ultimate trade-off between permeability and selectivity; i.e., it is practically impossible to further increase the membrane's selectivity without compromising permeability.

CNT-based membranes possess antibacterial properties that are beneficial in combating biofouling upon direct contact with microorganisms. However, the antimicrobial mechanism of CNTs is not yet fully understood. Many authors present conflicting

and diverse mechanistic models. For example, Vecitus et al., proposed a three-step mechanism for SWCNTs that includes three sequential steps: (i) initial contact between SWCNTs and bacteria, (ii) perturbation of the membrane cell, and (iii) electronic structure–dependent bacterial oxidation [16]. Several reports and reviews have been documented reporting on the use of CNTs in mitigating fouling in TFC RO membranes [17–20]. However, most of these studies were tested only on bench-scale systems. There is therefore still a need for further development and upscaling of CNT membrane processes to accurately determine their benefits. Furthermore, membrane scientists argue that biocidal properties alone do not demonstrate that a membrane has a low fouling propensity. For instance, in a staged array membrane configuration, the destroyed microbes may necessitate an additional step for membrane cleaning.

The issue of selectivity-permeability trade-off could be avoided in CNT membranes due to the ability of selectively adding functional group moieties at the CNT pore openings that are capable of rejecting salt ions while maintaining ultrafast water transport inside the nanotubes [21,22]. Such gate-keeper-controlled chemical interactions are unique for CNT-based membranes, as first demonstrated by Hinds et al. [21]. The addition of biotin functional groups at the CNT opening, for example reduced the $Ru(NH_3)_6^{3+}$ flux by a factor of 5.5, and this was further reduced by a factor of 15 when streptavidin was added to the biotin tether [21]. This result formed the basis for the separation or restriction of ionic flow from a solution containing an analyte of interest, and it can be used as a guiding tool for further control of pore dimensions.

A number of studies on the potentiality of VA–CNT membranes in desalination processes have been based on molecular dynamic (MD) simulations and very few report on their experimental feasibility. This is particularly so because of the complexities encountered in synthesis procedures for aligned CNT membranes, which are the most promising candidates, rather than mixed-matrix CNT membranes, for desalination based on the findings from simulation studies. These issue are discussed in deeper detail later in this chapter.

With such challenges, a great deal of work lies ahead before full realization and exploitation of CNT-based membranes for desalination applications. This chapter presents an overview of the manufacture, physicochemical properties, and effective application of carbon nanotube (CNT) membranes in desalination technologies. Ultimately, the chapter seeks to summarize the current knowledge pertinent to CNT exploitation in desalination, explain the extent to which the fluid transport properties and chemical functionalities in CNTs necessitate high water fluxes, and describe the controllable salt rejection required for desalination. Factors that influence the cost of CNT membranes, which ultimately translates to the cost of desalination using CNT membranes, are also discussed. Last and maybe most important, the sustainability of CNT membranes as a solution to current desalination problems is evaluated.

2. TYPES OF CNTs USED IN MEMBRANE FABRICATION

2.1 CNT Configurations

Since their discovery in 1991 by Iijima [23], carbon nanotubes have been widely studied and applied in various disciplines, including in the water treatment field as adsorbent materials or in membrane modification for the removal of a wide range of organic and inorganic pollutants from water and wastewater [24–27]. This interest is due to a unique combination of the structural and physicochemical properties of carbon nanotubes: high volume–to–surface ratio, small inner diameters, antimicrobial properties, frictionless surfaces for rapid fluid flow, and many others [7]. CNTs are commonly classified as SWCNTs or MWCNTs based on the number of cylindrical graphene sheets organized around the hollow nanotube core (Fig. 1). SWCNTs consist of a single layer of graphene sheet rolled into a tubular structure and have diameters in the range of ~1 to 2 nm, whereas MWCNTs consist of multiple layers of graphene sheets with diameter sizes in the range of ~2 to 25 nm [6]. Most research on CNT–incorporated membranes focuses on MWCNTs and very rarely on SWCNTs, even though these possess the smallest outer diameters. This is because MWCNTs are generally easy to prepare and align using conventional chemical vapor deposition (CVD) methods, and their manufacturing costs are lower than those of SWCNTs. This means that MWCNTs can be produced in the large quantities necessary for industrial–scale applications.
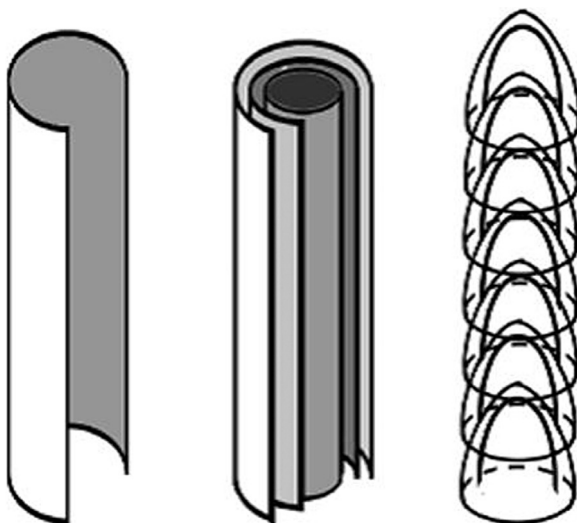

Fig. 1 Sketches depicting structures of (A) SWCNT, (B) MWCNT, and (C) N-CNT (bamboo-shaped CNT). *(Reproduced with permission from S. van Dommele, Nitrogen Doped Carbon Nanotubes: Synthesis, Characterization and Catalysis, Utrecht University, 2008).*

Researchers have attempted to use heteroatom-doped CNTs in the form of nitrogen-doped carbon nanotubes (N-CNTs) for polymer blend membrane modifications. N-CNTs are typically produced by either postsynthesis modification of CNTs with a nitrogen-containing compound such as acetonitrile, melamine, and many others or by in situ incorporation of nitrogen during CNT growth [28]. The use of N-CNTs was intended to improve the compatibility and interaction between CNTs and the polymer material such as (PES) [29]. Performance results of this N-CNT/PES membrane revealed a superior compatibility between the N-CNTs and PES because of the high surface reactivity of N-CNTs compared with pristine CNTs. The differences in the structure of various forms of CNTs commonly used in membrane modification are shown in Fig. 1. These include CNTs with typical tubular configurations and unique "bamboo-shaped" orientations.

Although the use of SWCNTs in membranes would be ideal for sea and brackish water desalination because of their intriguingly small inner diameters, the challenge of aligning SWCNTs vertically remains a serious hindrance [30,31].

MWCNTs are also less expensive to manufacture than their single-walled counterparts; therefore MWCNTs can be produced in large quantities. However, the inner diameters of most MWCNTs range between 3 and 10 nm [32], which means that they fall short of molecular separation applications where extremely small diameters would be more beneficial in achieving effective and efficient separation of molecular species.

Park et al. [32] sought to substitute commercial UF membranes with VA-CNT membranes in water-purification applications. The authors discovered that the solute rejection of membranes was difficult to increase or control because the MWCNTs' inner diameters were difficult to reduce further. Notwithstanding the concerns raised earlier, SWCNTs with diameters close to 1 nm were suggested as a probable solution for increasing salt rejection, provided that they undergo surface modifications to further reduce their pore size to just below 0.6 nm. This is because a hydrated Na^+ is about 0.716 nm and Cl^- 0.664 nm in size.

2.2 CNT Tip Functionalization and Alignment

Functional group moieties can be introduced with ease onto the VA-CNT membranes. In particular, the CNT tips functionalized to reduce or control their pore size diameters. Park et al. [32] functionalized CNT tips of VA-CNT membranes with methacrylate groups by graft polymerization to "gate" the transport of solute compounds [33]. The modified membranes showed better water flux and antifouling properties than the commercial UF membranes. In addition, the solute rejection potential was greatly improved vis-à-vis the control VA-CNT membranes.

Consequently, the use of SWCNTs as membranes is of great interest because of their intriguingly small inner diameters (1–2 nm) that can be useful for sea and brackish water desalination. However, as mentioned before, the challenge of aligning SWCNTs

vertically remains a serious hindrance in their use as membrane filters. Filtration methods have previously been used successfully to align MWCNTs vertically. Recently, the same approach was adopted for the alignment of SWCNTs. Indeed, when shear forces are applied, they propagate the alignment of CNTs perpendicular to the filter substrate in the direction of flow [31].

Kim et al. [30] prepared VA-CNT membranes using a combination of methods, namely filtration and self-assembly of SWCNTs. In their study, functionalized SWCNTs were dispersed in tetrahydrofuran (THF) (Fig. 2, Step 1), and the suspension was filtered through a filtering media such as a polytetrafluoroethylene (PTFE) filter (in Step 2). Their findings showed that the filtration method used facilitated the vertical alignment of CNTs on a porous substrate and that the gas mixture transport through the prepared membranes was much faster than those predicted by Knudsen diffusion.

As shown in Fig. 2 Step 3, the aligned SWCNT/filter is then spin–coated with a dilute solution of a high–mechanical–strength polymer to seal the structure, while allowing most of the nanotube ends to be slightly exposed above the polymer surface [30]. However, microscopic analyses of these membranes revealed that the SWCNTs are encapsulated with additional graphite layers, which signals that during the fabrication process, they are transformed from SWCNTs into MWCNTs. Alternatively, a polymer suspension containing CNTs can be injected into a molded cavity, a die, or a nanochannel to
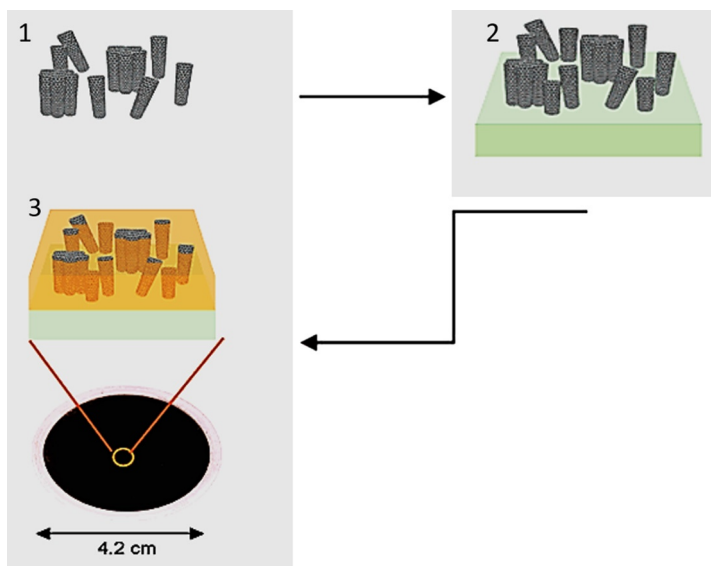

Fig. 2 Schematic representation of the fabrication of VA-CNT membranes by the filtration method. *(Reproduced with permission from S. Kim, J.R. Jinschek, H. Chen, D.S. Sholl, E. Marand, Scalable fabrication of carbon nanotube/polymer nanocomposite membranes for high flux gas transport, Nano Lett. 7 (2007) 2806–2811).*

form a shape of interest. In this way, the CNTs will then change orientation by virtue of the flow that is induced by the shear forces applied [31].

3. TYPES OF CNT COMPOSITE MEMBRANES

CNT–incorporated membranes are promising tools for the treatment of conventional and emerging contaminants in water as well as for sea and brackish water desalination using RO systems. This option is due to the presence of nanoporous channels that allow for the passage of large volumes of water while rejecting the permeation of "unwanted" species/ions. These CNT-based membranes and in particular the VA–CNT membrane systems have an enormous potential to improve the selectivity of RO membranes that are commonly used in seawater desalination processes, owing to their dynamic molecular sieving and separation mechanism [18].

There are two common types of CNT-based membranes: CNT mixed-matrix membranes (CNT MMMs), which are typically mixed matrices of CNTs and flexible polymers, and VA–CNT membranes, which could either be CNT "straws" protruding from a nonporous polymer or high-density, aligned CNT arrays.

Fig. 3 shows the typical differences in the structures, water transport, and solute rejection of the two types of CNT membranes presented in this chapter. In the VA–CNT membranes, the CNTs are arranged in an upright position (perpendicular) to the membrane surface. On the contrary, for mixed composite CNT membranes, CNTs are dispersed in the matrix forming part of the membrane's top layer, thereby contributing to the hydrophilic and surface properties.

In latter sections, the differences of these CNT membrane types and the correlations between the structural morphologies and permeation properties thereof will be probed and their water transport and solute rejection capacities investigated. We will also explore their environmental sustainability and commercial availability.
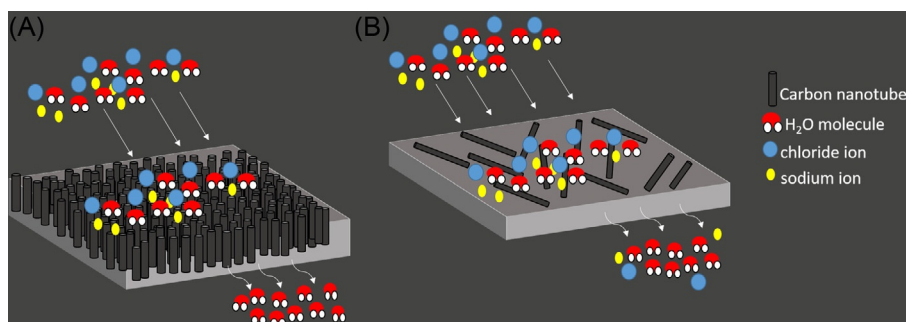

Fig. 3 Water transport and solute rejection of CNT membranes through (A) vertically aligned CNT membranes and (B) CNT mixed-matrix membranes.

4. FABRICATION PROCESSES FOR CNT MEMBRANES FOR DESALINATION

Table 1 depicts the different fabrication techniques for CNT-based membranes normally utilized in a desalination process. Work carried out by different workers fabricating CNT membranes is compared and contrasted with respect to manufacturing process, support material used, CNT alignment or nonalignment, characterization tools used, and performance properties. For the VA–CNT membranes, the process normally entails synthesis of VA–CNT arrays on a suitable substrate by making use of the conventional CVD method prior to the addition of an impermeable polymer such as polystyrene (as a support). On the other hand, the preparation of CNT MMMs involves the dispersion of CNTs in a solvent and mixing with a suitable polymer prior to casting the solution on a plate typically by a phase inversion method [35].
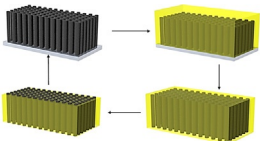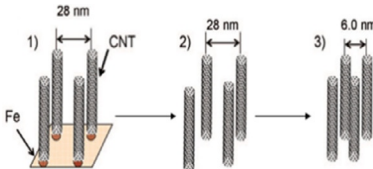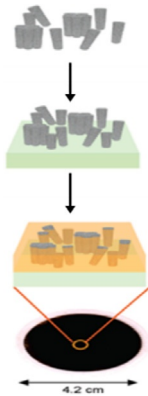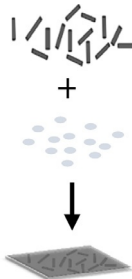
Although tremendous progress has been made in the lab-scale production of CNT MMMs, experimental work involving the fabrication of VA–CNT membranes is still in its infancy because the production systems are challenging and onerous. These issues are dealt with appropriately in later sections of this chapter.

Several reviews dedicated to CNT-based membranes (MMMs and VA–CNT membranes) and their potentiality in desalination applications have been documented. For example, Das et al. [34] comprehensively reviewed the potential role of CNT membranes in seawater and brackish water desalination. The function of CNTs in the membrane technology arena was analyzed by looking at the studies focusing on the fabrication and functionalization of CNT membranes for desalination purposes and how CNT membranes compare in properties and performance behavior with conventional membrane processes. These differences are tabulated in Table 2 and indicate that unlike CNT MMMs (in which CNTs are mixed in either a MF, UF, or NF membrane matrix), VA–CNT membranes are a unique membrane type because of their outstanding properties, including among others, ultrafast water transport and self–cleaning properties.

CNTs have the ability to be selectivity functionalized at their pore openings to enhance their salt rejection capacities and their ability to remove various micropollutants present in water. Thus CNT membranes have been envisaged as potential candidates to replace both RO and NF membranes, because CNT membranes offer minimal energy consumption by lowering the applied pressure to drive desalting of solutions [34]. However, no single method is capable of alleviating the global water pollution problems on its own, which means that the existing water-treatment technologies are not sufficient to provide 100% pure water. Therefore a combination of methods, including those that have advanced from nanotechnology through the use of carbon nanotube membranes, can be a more viable approach.

Manawi and coworkers [36] recently assessed the potentiality of carbon-based nanomaterials (including CNTs, graphene, graphene oxide, carbon nanofibers, MXene, carbide-derived carbon, and fullerenes) in membrane fabrication for water treatment and desalination. CNTs, in particular, were identified as promising candidates to overcome the issues of fouling (and in particular biofouling) that membranes used in RO

Table 1 Different fabrication techniques for CNT membranes

	Polymer infiltration/ encapsulation Hinds et al. [21]	Liquid-induced densification Yu et al. [34]	Self-assembly and filtration method Kim et al. [30].	Phase inversion mixed-matrix method Celik et al. [8].
CNT membrane type	VA-CNT membrane	VA-CNT membrane	VA-CNT membrane	CNT MMM
Manufacture	CNT arrays grown on a silicon wafer substrate Polystyrene infiltrated onto the CNT array Spin-coating and removal of excess polymer HF acid used etch off CNT film from substrate Water-plasma oxidation to open CNT tips	CNT forest grown by water–assisted CVD method Water-etching to detach CNT arrays N-hexane introduced into as-grown CNT arrays and dried CNTs collapse near to packing into a rigid body upon liquid evaporation	SWCNTs prepared by arc discharge method and treated with H_2SO_4/HNO_3 acid mixture Amine functionalized SWCNTs dispersed in THF Dope solution filtered through a PTFE membrane filter	MWCNTs treated in H_2SO_4/HNO_3 acid mixture MWCNTs sonicated in NMP followed by addition of PES Dope solution casted on glass plate and immersed in coagulation bath

Support	Polystyrene	None	Polytetrafluoroethylene	None
CNT configuration	Vertically aligned	Vertically aligned	Partial alignment	Nonaligned
Characterization	SEM, HRTEM, porometer, electrochemical measurements and others.	TEM, SEM, N_2 desorption experiments and others.	HRTEM, permeation of gas mixtures and others.	SEM, FTIR, contact angle goniometer, cross–flow filtration experiments and others.
Performance	Presence of CNTs increases conductivity of the membrane. Attachment of biotin/ streptavidin moiety on the CNT tip allows gating or sieving of $Ru(NH_3)_6^{3+}$ ions.	Densely packed SWCNTs observed from SEM. N_2 gas diffusion is two orders of magnitude higher than predicted by Knudsen and three to seven orders of magnitude higher than for composite membranes.	Rapid gas transport through the CNT membranes that deviates from Knudsen diffusion.	Inclusion of CNTs into the PES membrane increases membrane roughness, surface hydrophilicity, pure water flux, and porosity.

Table 2 Properties of different membrane processes used in water treatment

	MF	UF	NF	RO	VA-CNT	Ref.
Pore size (nm)	>50–500	2–50	<2	0.3–0.6	0.6–10	[21,34,36]
Operating pressure (bar)	0.1–2	<5	3–15	29–100	0.7–2	[32,37,38]
Permeability (L/m^2 h bar)	>1000	10–1000	1.5–30	0.05–15	>1000	[33,37,39]
MWCO (Da)	>300,000	1000–1,000,000	100–1000	100	100	[33,40,41]
Membrane thickness (μm)	50–100	150–300	~0.05	0.1–0.2	0.6–10	[30,42]
%NaCl rejection	–	–	20–80	95 to >99	100	[34,37]
Resistance to fouling and biofouling	Poor. Resistance to fouling can be improved through membrane surface modification with hydrophilic additives.	Poor. Resistance to fouling can be improved through membrane surface modification with hydrophilic additives.	Poor. Resistance to fouling can be improved through membrane surface modification with hydrophilic additives.	Poor. Resistance to fouling can be improved through membrane surface modification with hydrophilic additives.	Very good. CNTs possess antimicrobial properties. Resistance can be further enhanced with membrane surface functionalization.	[18,43]
Application	Removal of solid particles, protozoa, and bacteria.	Removal of viruses and colloids.	Removal of multivalent ions, proteins, dissolved organic matter, and hardness.	Removal of monovalent ions, desalination, water reuse, ultrapure water.	Removal of organic micropollutants and desalination application.	[7,32,37,44]

Adapted from R. Das, M.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z.Z. Chowdhury, Carbon nanotube membranes for water purification: a bright future in water desalination, Desalination 336 (2014) 97–109.

desalination processes are often faced with. This is due to the CNTs ability to effectively destroy bacterial cells upon direct contact. Furthermore, VA–CNT membranes were highlighted to be potentially useful in water desalination because of their remarkably fast fluid transport properties. In as much as high-salt rejection is desired during seawater or brackish water desalination, the desalination process used must still be able to generate reasonable pure water flux on the other side of the semipermeable membrane. Indeed, Elimelech and coworkers [2] caution against the use of ultrahigh permeating membranes in seawater RO desalination processes because concentration polarization as well as membrane fouling are exacerbated at high water fluxes [32]. For VA–CNT membranes to be effectively used for seawater desalination, a redesign of membrane modules will be required such that the preceding factors are taken into account.

Goh et al. [6] wrote a comprehensive review that raises some important questions about the potentiality of nanomaterials in desalination membrane modifications. Questions about whether CNT polymeric membranes will be able to offer high performance and affordable desalination solutions were raised. Ultimately, this review encourages a thorough examination of all research areas and priori focus points before commercialization of this technology, such as looking at economic and environmental concerns with regard to the use of nano-enabled or, better yet, CNT-based polymeric membranes. Toward the end of their review, the authors encouraged environmentalists to work closely with material scientists in understanding and raising awareness of environmental hazards that these nano-enabled membranes may pose for humans.

Ahn et al. [3] documented the fabrication methods for CNT-based membranes and speculated on their potential use in desalination processes. The fundamental differences between the two CNT membrane types are presented in Table 3. Clearly, the limitations

Table 3 Comparison of VA-CNT membranes and mixed matrix CNT membranes

VA-CNT membranes	Mixed-matrix CNT membrane
CNTs are vertically aligned within the membrane	CNTs are irregularly arranged within the polymer matrix
CNTs are densely packed together	Composite layers with polymer membrane and nonwoven support
Water flux through the membrane is extremely fast	Water flux through the membrane is reasonably fast
Functional groups can be conveniently attached at the CNT tips or on the membrane surface to prevent fouling	Low (or anti) fouling membranes
Complex fabrication procedures, less cost-effective	Fabrication processes are convenient, simple, and readily commercializable
May need specially adjusted operation system	Operation similar to that of conventional membrane processes

Adapted from C.H. Ahn, Y. Baek, C. Lee, S.O. Kim, S. Kim, S. Lee, S.-H. Kim, S.S. Bae, J. Park, J. Yoon, Carbon nanotube-based membranes: fabrication and application to desalination, J. Ind. Eng. Chem. 18 (2012) 1551–1559.

that hinder the popularity and commercialization of VA-CNT membranes mainly include the complex fabrication processes used, which makes scaling up of these membranes a challenge. For this reason, more efforts have been directed toward the exploitation of mixed-matrix types of CNT membranes, even though they possess more moderate water fluxes than VA-CNT membranes. In addition, CNT MMMs are made using fabrication procedures that are relatively simple, and therefore CNT MMMs are more likely to be commercialized sooner [3].

5. SOLUTE TRANSPORT PROPERTIES OF CNT MEMBRANES

Molecular dynamic (MD) simulation has been one of the fundamental tools used by researchers to gain insights into the transport behavior of water molecules inside confined CNT channels [37]. As mentioned earlier in this chapter, recent research work involving the use of CNT membranes for desalination has mainly been based on simulation studies. The properties and behavior of fluids when confined at nanolength scales greatly differ from their behavior in bulk form. For example, in the macroscopic world, it would be unexpected for water (a polar compound) to be able to enter and interact with the constricted and hydrophobic CNT pores [38]. However, the first MD simulation studies by Hummer and coworkers showed that despite their hydrophobic nature, SWCNTs can be rapidly filled and emptied with water molecules (forming a column of five water molecules in length inside a nanotube) [39]. Furthermore, the filling and emptying of the CNTs with water molecules can be properly controlled such that water molecules do not remain constricted inside the tubes [39].

One other notable feature associated with CNT fluid transport, as reported by Hummer et al. [39], is that of the changes in the structural configuration of water molecules when inside a confined CNT channel. Inside the channel, the hydrogen-bonded and methodically linked water molecules or simply "water wires" are formed, as depicted in Fig. 4. The formation of these ordered one-dimensional hydrogen-bonded water wires inside the CNTs and at the CNT openings highly resembles those that are formed during water transport by biological channels such as transmembrane protein aquaporins [40,41]. Other similarities between CNT channels and the biological aquaporin channels include their hydrophobic interiors or linings that enable near frictionless and fast water transport [40,42]. Kalra et al. [43] used MD simulation to study molecular transport of water through CNT membranes under the influence of an osmotic gradient. The authors demonstrated that the flow rates within the CNT pores are extremely fast and independent of the length of the nanotubes. It was found that the flow inside these nanotubes was almost frictionless and was restricted only by the events at the entry and exit points of the CNT pores. Nonetheless, the flow rates remain comparable with those of transmembrane aquaporins [43].
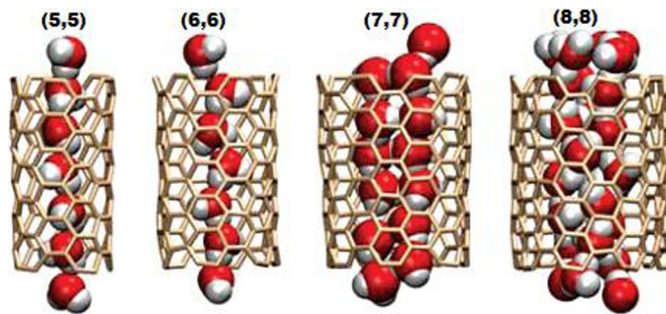
Fig. 4 Molecular dynamic simulation depicting water configuration or formation of "water wires" in differently sized armchair carbon nanotubes. *(Reproduced from B. Corry, Designing carbon nanotube membranes for efficient water desalination, J. Phys. Chem. B 112 (2008) 1427–1434).*

Several macroscopic equations have been used to explain the relationship between fluid flow or transport rate and the pore radius of the CNTs. One of these models is the nonslip Hagen-Poiseuille equation, which can be represented in Eq. (1) as

$$Q_{HP} = \frac{\pi \left(\frac{d}{2}\right)^4}{8\mu L} \cdot \frac{\Delta P}{L} \tag{1}$$

where Q_{HP} represents the volumetric flow rate, ΔP is the pressure difference across the tube length (L), μ is the viscosity of water, and d is the pore diameter. This equation assumes that fluid flow inside the CNT tubes is laminar and that there is no slip at the boundary layer (i.e., the fluid velocity at the CNT walls is zero) [45]. However, several studies on nanosized hydrophobic pores, such as those of CNT membranes, have shown major deviations from this assumption, with flow enhancements that are orders of magnitude higher than predicted by the continuum Hagen-Poiseuille model.

MD studies on CNT pores reveal that water molecules move freely with large slip inside the CNT walls because of the atomically smooth and hydrophobic interiors of CNTs [44]. The slip length, which is merely the distance that the velocity profile can be extrapolated with to reach zero, is normally used when describing the slip flow of molecules inside CNT walls (Fig. 5).

When Hagen-Poiseuille formalism in Eq. (1) is corrected to include slip–flow conditions, it can be represented in Eq. (2) as

$$Q_{Slip} = \frac{\pi \left(\frac{d}{2}\right)^4 + 4 \left(\frac{d}{2}\right)^3 \cdot L_S}{8\mu L} \cdot \frac{\Delta P}{L} \tag{2}$$

where L_S is the slip length, which is given in Eq. (3) as

$$L_S = \frac{U_{wall}}{dU/dr} \tag{3}$$
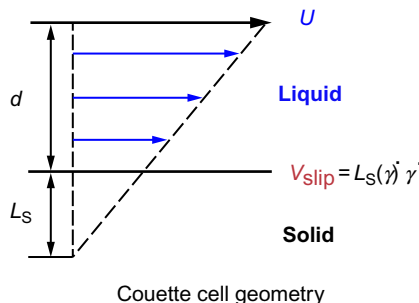
Couette cell geometry

Fig. 5 Illustration of slip length at the liquid/solid interface. *(Reproduced from N.V. Priezjev, A.A. Darhuber, S.M. Troian, Slip behavior in liquid films on surfaces of patterned wettability: comparison between continuum and molecular dynamics simulations, Phys. Rev. E 71 (2005) 041608).*

where U_{wall} is the axial velocity at the wall, and dU/dr is the radial velocity gradient at the wall.

Holt et al. [45] applied the slip-flow formalism (Eq. 2) to determine the flow through sub–2-nm CNT membranes. The slip lengths were found to be hundreds of nanometres larger than the pores size and were on the order of the overall size of the system [45]. When the same equation was used to calculate slip length for polycarbonate membranes with 15 nm pore sizes, the slip length was about 5 nm. These findings therefore suggest that slip-flow formalism cannot be used to describe flow through CNT pores in the 1–2 nm size regimes because of confinements in length and partial wetting of the CNT surface [37].

The extremely fast water transport of CNT membranes is therefore favorable for filtration purposes such as NF and RO. However, in the case of RO desalination, the efficiency of the process is determined by three critical factors: capital costs, energy costs, and system operation costs [40]. While there are many speculations about the CNT membranes' potential to greatly reduce the energy costs of RO desalination processes, the minimum energy required to pump water through a semipermeable membrane is governed by the solution's osmotic pressure, that is, osmotic pressure difference between seawater and freshwater [46]. Nonetheless, the high water fluxes of CNT membranes can greatly reduce the primary costs because of the small membrane area required to achieved maximum flux [46]. However, these fluxes do not necessarily affect the energy consumption of the desalination process [46].

In a MD simulation study, Corry [42] simulated water conduction and suitability of differently sized CNTs with armchair-type chirality (5,5), (6,6), (7,7), and (8,8) in water desalination applications. CNT performance was evaluated by calculating salt rejection efficiency (Table 4) [35]. The numbers denoted within parentheses describe the chirality and metallicity of the carbon nanotubes investigated, that is, the manner in which the grapheme sheet was rolled up to form a carbon nanotube [47]. The armchair configuration describes the shape of the hexagons making up the tube as one moves around

Table 4 Water and ion conductance of nanotubes under 209 MPa pressure at 250 mM ion concentration

Size	Diameter (Å)		Run lengths (ns)	Conductance pt pns	
	C–C	Internal		H$_2$O	Ions
(5,5)	6.6	3.2	10.00	10.4 ± 0.4	0.0
(6,6)	8.1	4.7	20.00	23.3 ± 0.3	0.0
(7,7)	9.3	5.9	25.00	43.7 ± 0.5	0.007 ± 0.005
(8,8)	10.9	7.5	17.00	81.5 ± 1.2	0.137 ± 0.025
(6,6) long	8.1	4.7	10.00	23.4 ± 0.5	0.0

Reproduced from B. Corry, Designing carbon nanotube membranes for efficient water desalination, J. Phys. Chem. B 112 (2008) 1427–1434.

the body of the nanotube and the metallic nature of SWCNTs. The calculations showed that the CNTs led to salt rejection from 100% for (5,5 and 6,6) to 95% and 58% for the wider tube (7,7 and 8,8). Additionally, when the salt rejection efficiencies of the simulated CNT membranes and those of commonly used RO membranes were compared, the membrane comprising (7,7) nanotubes could be expected to obtain 95% desalination at a flow rate over 1500 times that of existing RO membranes [42]. Therefore, more in-depth studies on overcoming the energy costs of desalination processes using CNT membranes are crucial in order to fully realize their applicability in water purification and desalination applications.

From the preceding discussions, it is evident that the incorporation of VA-CNTs onto polymeric membranes has important implications on their transport and separation properties. This is because CNTs provide, among others, the ease of chemical functionalization and doping, low friction, biocompatibility, and controllable pore sizes necessary for fast water transport and the required solute rejection in desalination processes.

6. CHARACTERIZATION TOOLS FOR CNT-BASED MEMBRANES

6.1 Introduction to Techniques used to Probe CNT Membranes

Characterization of CNT-based membranes is typically achieved using similar techniques to those that are normally used to characterize conventional polymer-based membranes. The techniques used include scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), atomic force microscopy (AFM), streaming potential and surface charge analysis, contact angle analysis, electrochemical impedance spectroscopy (EIS), thermal gravimetric analysis (TGA), attenuated total reflection–Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy, and many others [48]. It is of vital importance that the different techniques used for the analyses correlate with one another for effective clarification of the morphology and properties of the prepared membrane.

6.2 Microscopic Investigation of CNT membranes

The incorporation of CNTs into membrane matrices is known to drastically transform the morphology of the membranes [49]. These changes can be detected easily by studying the surface properties as well as the internal structure of the membrane (Fig. 5) [50]. Depending on where the SEM image is taken on the membrane, it is possible to visualize and distinguish between the pores located on the membrane top surface and those located in the membrane sublayer. Depending on the phase inversion kinetics that occur during membrane formation, the membrane sublayer may consist of large finger-like structures (referred to as macrovoids) or it can consists of sponge-like structure made up of many small pores. For example, in order to effectively view the membranes' cross-sectional morphology (or internal structure), the membrane sample must be freeze-fractured in liquid nitrogen followed by coating with either gold or carbon in order to impart electrical conductivity [51]. The addition of CNTs onto the polymer matrices is known to significantly affect a membrane's surface porosity. Celik et al. [8] reported that during the formation of CNT MMMs, the addition of small amounts of CNTs within the PES matrix enhanced the phase separation process, thus giving rise to the formation of larger membrane pore sizes. Furthermore, CNT inclusion has been reported to greatly influence the hydrophilicity, surface roughness, and mechanical strength of the MMMs [52,53].

TEM is also a suitable technique for probing the internal structure of membranes containing nanomaterials such as CNTs. Therefore, information on the membrane thickness, pore sizes, and CNT density is obtainable from TEM analysis. The number of reports in which TEM has been used to structurally investigate the internal morphology of CNT/polymer membranes, particularly CNT MMMs, are very few. This is because the preparation of polymeric samples for TEM analysis tends to be significantly more complex because it involves preparing thin slices of the materials at cryogenic temperatures using a microtome [54]. However, the information obtained from TEM or HRTEM images is valuable and provides information about the dispersion of CNTs in the membrane matrices, their pore sizes, and distribution. TEM could be used to study how chemical functionalization or heteroatomic doping (with either N or P) of CNTs affects dispersion in the membrane [55].

In the analyses of VA–CNT membranes, TEM analysis is commonly the first technique applied, in particular for the as-prepared CNT arrays, prior to polymer infiltration. TEM is capable of probing the internal structure or morphology of these nano-based membranes and can also indicate whether vertical alignment of CNTs has been achieved. SEM is equally widely used to study the topography of VA–CNT membranes. Unlike TEM analysis, SEM examines the surface and produces an image that clearly establishes the alignment of CNTs within the membrane. TEM and SEM images for VA–CNTs and VA–CNT membranes prepared using different methods are shown in Figs. 6 and 7. In Fig. 6, SEM cross-sectional images of PSf membranes prepared from blending different amounts of MWCNTs, are shown. All MWCNT/PSf membranes have similar
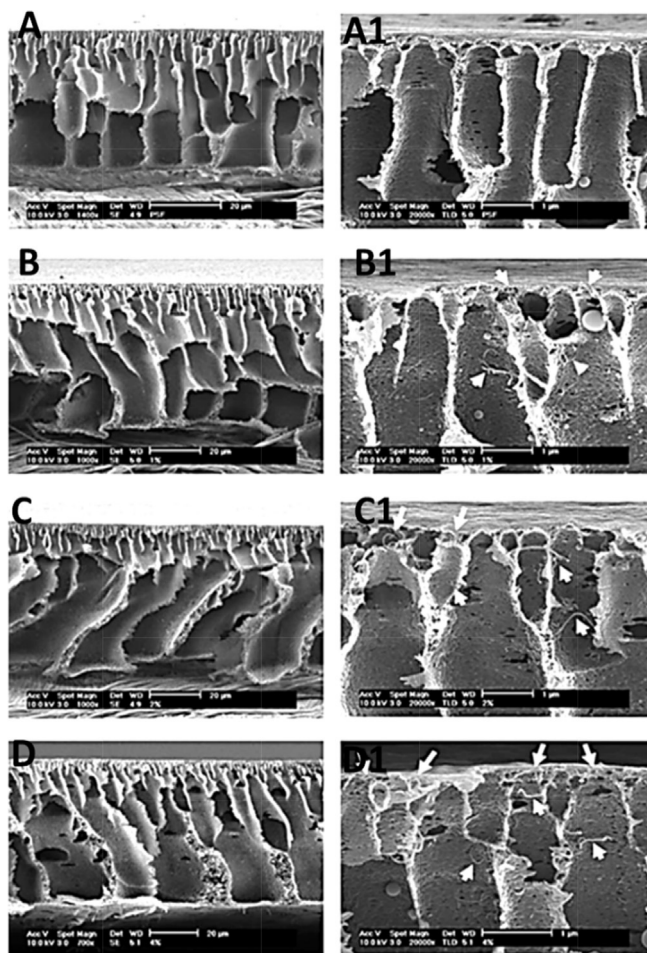
Fig. 6 SEM cross-sectional images of MWCNT/PSf blend membranes with different loadings of MWCNTs; (A) 0 wt%, (B) 1.0 wt% (C) 2.0 wt%, and (D) 4.0 wt%. Images A1 to D1 are high magnification (20000×) images of A to D, showing the presence of MWCNTs in the surface layer of the membrane. *(Reproduced from J.-H. Choi, J. Jegal, W.-N. Kim, Fabrication and characterization of multiwalled carbon nanotubes/polymer blend membranes, J. Membr. Sci. 284 (2006) 406–415).*

substructures with finger–like internal pores. One noticeable difference from their sub–structures is the amount of MWCNTs that have migrated to the membrane top surface, to make the membrane surface hydrophilic. Fig. 7A and B shows SEM and TEM images for a CNT film that possesses a height of about 2.2 mm (obtained under the CVD growth conditions: acetylene/argon composition of 200/500 sccm, growth temperature of 810° C, and ramp rate of 810°C/min). TEM micrographs presented in the figure show two graphene walls as well as patterned CNTs obtained via the nanotemplate method, in which a TEM grid was used as a mask [56]. SEM images of VA–CNTs synthesized on stainless steel meshes are shown in Fig. 8.
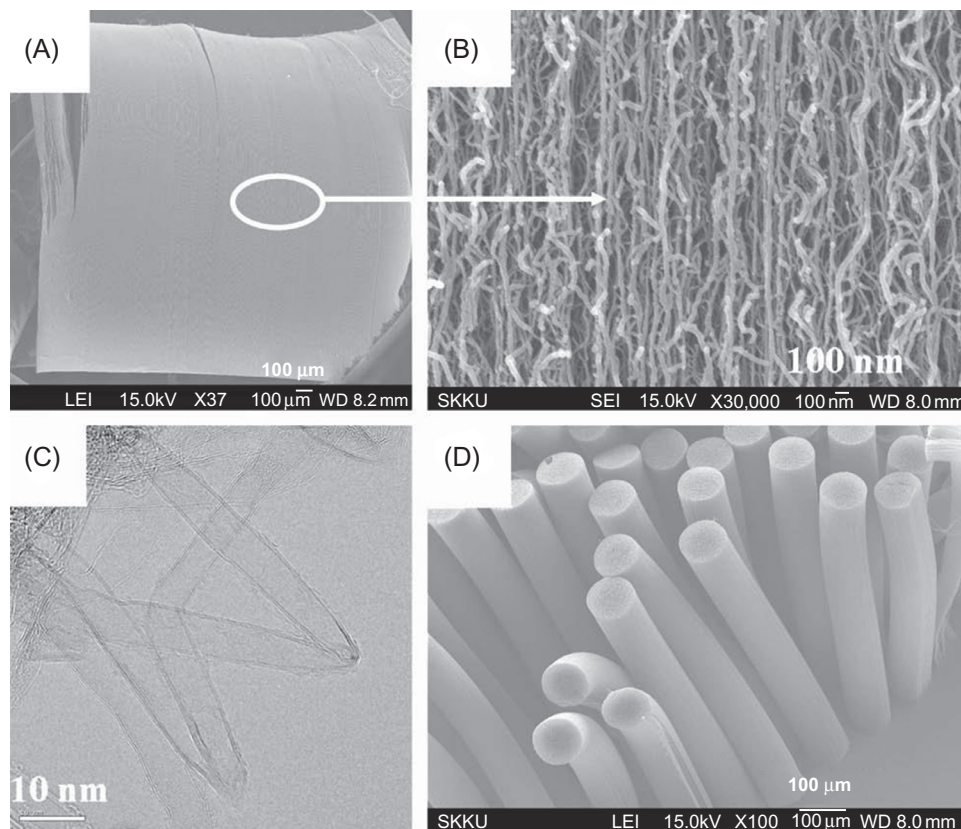
Fig. 7 SEM micrographs for (A) CNT film, (B) the middle of the CNT film, (C) HRTEM micrographs for CNTs, and (D) patterned CNTs using a TEM grid prepared using the nanotemplate method. *(Reproduced from S. Patole, P. Alegaonkar, H.-C. Lee, J.-B. Yoo, Optimization of water assisted chemical vapor deposition parameters for super growth of carbon nanotubes, Carbon 46 (2008) 1987–1993).*

6.3 Mechanical Strength Analysis

The role of CNTs on improving the mechanical strength of MMMs polymeric membranes is widely documented [57,58]. CNT inclusion improves the mechanical strength of MMMs and as such increases the life span of the membranes. Membranes' mechanical-strength properties are typically measured on a microstrain analyzer or Instron analyzer. It is important for a membrane to have a sufficiently high mechanical strength in order to withstand transmembrane pressure during filtration.

These measurements are very important particularly because CNT MMMs are tailor-made for pressure-driven processes. Maphutha et al. [59] showed that excellent mechanical properties can be obtained by the systematic incorporation of CNTs into a membrane material. A CNT composite membrane with polyvinyl alcohol used as a barrier layer was prepared for the purpose of removing oil from wastewater, and a 7.5% concentration of CNTs was found to produce a tensile strength of 119%, 77% in Young's modulus,
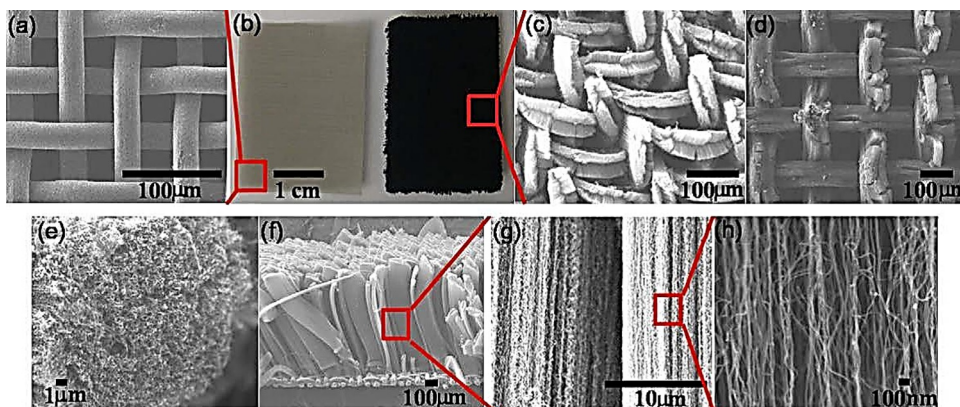
Fig. 8 SEM micrographs of VA-CNT membranes (in different forms) prepared using the filtration method: (A) SEM image of stainless steel mesh; (B) optical images of the mesh before and after the synthesis of VA-CNTs; (C) top surface view of synthesized VA-CNTs; (D) top view of the VA-CNTs with an average length of about 100 μm; (E) magnified, tilted view of the tip of VA-CNTs; (F) cross-sectional image of the VA-CNT filter, and (G, H) magnified SEM images of (F). (A) SEM image of stainless steel mesh; (B) optical images of the mesh before and after the synthesis of VA-CNTs; (C) top surface view of synthesized VA-CNTs; (D) top view of the VA-CNTs with an average length of about 100 μm; (E) magnified, tilted view of the tip of VA-CNTs; (F) cross-sectional image of the VA-CNT filter, and (G, H) magnified SEM images of (F). *(Reproduced from C. Lee, S. Baik, Vertically-aligned carbon nano-tube membrane filters with superhydrophobicity and superoleophilicity, Carbon 48 (2010) 2192–2197).*

and 285% in toughness [59]. Other works have also demonstrated the profits resulting from the use of functionalized CNTs as additives (or fillers) in polymeric membranes. The ultimate tensile strength, mean modulus, and tensile strain were found to increase when small amounts of CNT particles (wt% of 0.02–0.04) were added on suitable polymers [29].

6.4 Contact Angle Analysis

Surface contact angle analysis is used extensively in membrane technology to measure the hydrophilicity, surface energy, and surface tension of polymeric membranes containing CNTs. Contact angle measurements are usually recorded from 10 or more places on the membrane surface, and an average value is reported. This is done in order to obtain reproducible data representative of all the membrane surface properties. The ultimate goal is to fabricate membranes that are highly hydrophilic since they are generally desirable for desalination applications. Such membranes are less susceptible to fouling than their hydrophobic counterparts [50] because of the formation of a strong hydration layer on the membrane surface that prevents the attachment of foulants. Hydrophilicity is achieved by effectively mixing polymers with hydrophilic additives such as highly functionalized CNTs and/or heteroatomic CNTs such as N–doped CNTs [29] and can be predicted easily by a decrease in contact angle values. For example, when acid

functionalized CNTs are incorporated into PES membranes, a decline in the contact angle from >71 degree for bare PES membrane to <60 degree for 4 wt% MWCNT/PES composite membranes results [50].

6.5 AFM Analysis

AFM analysis is a technique for analyzing membrane surfaces and therefore provides information complementary to SEM and TEM analyses on the carbon nanotube-based membrane's surface properties. AFM generally probes the membrane's internal structure and provides information on the membrane's surface roughness characteristics and can also help measure membrane pore sizes. Fig. 9 shows that after the addition of surface-engineered CNTs onto the cellulose acetate/polyethylene glycol polymer matrix (PM), the membrane surface roughness increased along with an increase in CNT loading up to 0.3 wt% (from PM-CNT 1 to PM-CNT 3). However, with further increments to 0.4 wt% (PM-CNT 4), the membrane surface became smoother. The reason for the reduction in surface roughness is due to the reduced electrostatic interaction between the CNTs and the polymer matrix, thus leading to partial positioning of CNTs in the matrix, which then leads to smooth surfaces. As the loading was increased to 0.5 wt%, the surface roughness started to increase again because of the formation of CNT-agglomerated clusters within the membrane matrix. The major issue with very rough membrane surfaces is that they are prone to fouling because of the ease in the attachment of foulants [50]. This is due to the increase in charged sites on the membrane surface.

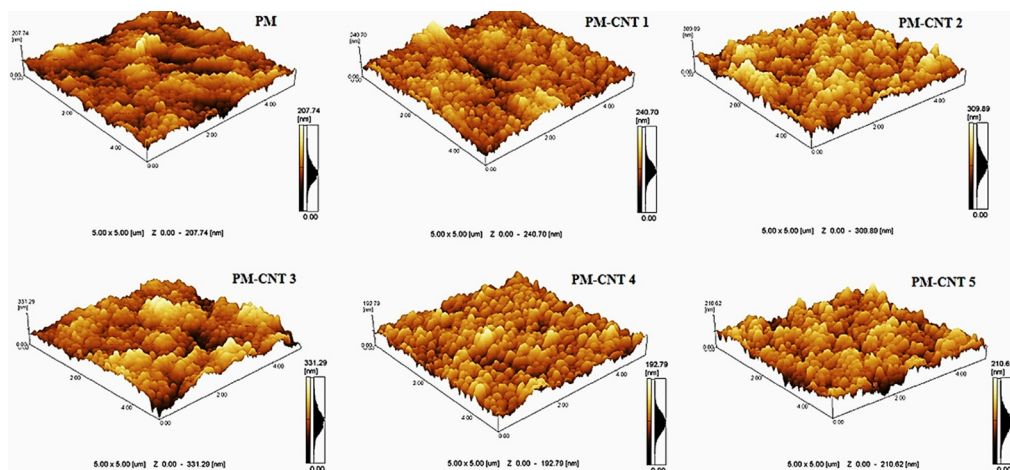**Fig. 9** AFM topographic images depicting changes in surface structure of cellulose acetate/polyethylene glycol polymer matrix (PM). *(Reproduced with permission from A. Sabir, M. Shafiq, A. Islam, A. Sarwar, M.R. Dilshad, A. Shafeeq, M.T.Z. Butt, T. Jamil, Fabrication of tethered carbon nanotubes in cellulose acetate/polyethylene glycol-400 composite membranes for reverse osmosis, Carbohydr. Polym. 132 (2015) 589).*

6.6 Streaming Potential and Surface Charge Analysis

Information relating to the surface charge of CNT polymer membranes is important for understanding how a particular membrane will behave toward targeted pollutants in water, especially charged species/ions. The surface charge of a membrane can be determined via electrokinetic analysis [60]. Electrokinetic occurrence is the interaction between a charged surface and the electrolyte rather than the inherent charge characteristics of the material [61]. In this measurement, zeta potential is measured as a function of pH. The inclusion of CNTs in membranes has a tremendous effect on the surface charge of the membranes. However, the values obtained vary with the concentrations of CNTs added to the membrane and the type of chemical groups and/or heteroatomic species attached on the CNTs.

When the membrane charge is known, the behavior of the pollutants present in water or wastewater toward the membrane surface can be predicted. It has been shown that electrostatic repulsions between the membrane surface and pollutants prevent the occurrence of fouling on the membrane surface [62] suggesting that CNTs can be used as materials for manufacturing membranes that have outstanding antifouling properties.

6.7 Other Characterization Techniques

Other characterization techniques used for membrane analysis include XPS and XRD spectroscopy. XPS is normally used for surface chemical analysis of the CNT membranes and to study the chemical bonding environments within the CNTs and heteroatoms. XRD provides the crystallinity, atomic structure, and crystallite size determination of membranes. Other conventional and unconventional instrumental techniques used to study membranes in general are presented elsewhere [49, 50].

7. ENVIRONMENTAL SUSTAINABILITY OF CNT MEMBRANES

7.1 Energy Demand

The energy demand for a desalination process is set up by the need to bring feed water to a pressure that is equal to the osmotic pressure of the concentrate. Currently, the energy consumed by RO desalination stands at 2 kWh/m^3 at 50% recovery and is far greater than the theoretical minimum energy required for desalination of 1.06 kWh/m^3 [2,33]. The minimum amount of energy required to separate pure water from salty water is equal in magnitude but has an opposite sign to the free energy of mixing, and can be calculated in Eq. (4) as

$$-\mathrm{d}(\Delta G_{\mathrm{mix}}) = -RT \ \ln a_{\mathrm{w}} \mathrm{d}n_{\mathrm{w}} = \pi_{\mathrm{s}} V_{\mathrm{w}} \mathrm{d}n_{\mathrm{w}} \tag{4}$$

where ΔG_{mix} is the free energy of mixing, R is the ideal gas constant, T is the absolute temperature, a_{w} is the activity of water, n_{w} is the number of moles of water, π_{s} is the osmotic pressure of seawater, and V_{w} is the molar volume of water.

The minimum energy can then be calculated from the integration of Eq. 4 as

$$Wo = (-d(\Delta G_{mix})/dn_w)_{P, T} = -RT \ln a_w \tag{5}$$

Although the energy consumption of the RO desalination process has not yet reached the theoretical limit, the use of highly permeable membranes such as CNT-based membranes is expected to alleviate this problem. However, this will not directly influence the reduction of the energy necessary for desalination processes to occur [2]. Nonetheless, fouling-resistant membranes such as CNT-based membranes are beneficial in overcoming the high energy costs associated with high-pressure requirements essential in order to drive pure water molecules through a fouled membrane.

7.2 Disposal

As with other nanoparticles, disposal of CNTs and/or CNT-based membranes is not widely documented, because these materials are relatively new and most researchers and environmentalists are still trying to study their impact on human health and the environment as well as their disposal issues. According to the UK Environment Agency, "any CNT containing waste is considered as hazardous waste unless evidence suggests otherwise" [63]. This signals that the fabrication costs of CNT-based membranes could potentially be driven up (when environmentally benign processes are sought) and especially if these membranes are scaled up. For example, currently the cost of 1.0 g of pristine MWCNTs is greater than $100. Although this seems high, because of their high surface area, very small amounts of CNTs are used as additives in CNT MMM fabrication processes. Furthermore, as newer methods of production are being developed, the price of CNTs is expected to gradually decrease. However, Brehm (2008) at Massachusetts Institute of Technology (MIT) suggested that incorporating environmental objectives during the synthetic stage of novel materials (such as CNTs) can bring drastic change in both industrial and environmental practices, that is, preventing problems rather than reacting to them [64]. This is a viable approach to minimizing CNT toxicity at the source prior to their incorporation onto other materials such as membranes [64] or point-of-use systems such as filters.

Methods that have been suggested for CNT disposal include high-temperature incineration [65] and vitrification or the encapsulation of CNTs into glass or ceramic structures [63]. Vitrification is a relatively new method that is still under development and is therefore considered as an alternative disposal technique for the future [63]. Clearly, more efforts are needed in this area in order to create better solutions for the disposal of CNTs or CNT-based membranes in a sustainable manner. These efforts will require active collaboration among material scientists, industrialists, academics, and environmentalists in order to pinpoint the potential risks associated with these new materials and to come up with better disposal methods [66].

7.3 Toxicity of CNT Membranes

It is clear that CNTs have an enormous potential in water-treatment applications, particularly in membrane technology. However, their large scale application will be realistic only when their nanotoxicity in water or even air is fully understood.

In the recent past, increasing fears have been associated with the escalating use of CNTs in water-treatment applications because of the CNTs' potential to be toxic. Because of their fibric nature, CNTs have been compared to asbestos, a highly pathogenic material [67,68]. Workers have also been concerned that CNTs are extremely light and can therefore easily enter the environment as suspended particulate matter, creating a serious inhalation hazard for human beings and animals [69]. In particular, it has been claimed that MWCNTs can induce frustrated phagocytosis and cytotoxicity as well as pro–inflammatory conditions in macrophages, which could be greater than those of asbestos [70]. This apparent toxicity of CNTs is attributed to their inherent physical and chemical properties, such as their unique nanostructure, diverse composition, and high volume-to-surface ratio [67]. As a result, much work is required to ascertain whether such materials are suitable for drinking water applications.

Indeed, recent studies have demonstrated that different methods of administration could result in different pathologies. For example, SWCNTs and MWCNTs were shown to produce numerous pathological changes when administered in mice through either the lungs or the heart, thereby causing diverse respiratory impairments [69].

Other researchers assessed the pharmacological efficacy, stability, and toxicity of CNTs in vitro and in vivo and found contradictory results [71]. Sanpui et al. [72] demonstrated that the diverse electronic structure of CNTs has an ability to increase the susceptibility of epithelial cells to influenza A H1N1 infection. In addition, others have suggested that CNTs may cause harm to cells by activating many pathways, mostly involving damage to the DNA [73]. The toxicity of CNTs on aquatic life, bacterium, and higher plants is being probed as well [74]. Nevertheless, specific types of CNT modifications, such as substitutional doping and efficient surface functionalization, can greatly minimize CNT toxicity. These modifications represent promising progress towards their much needed use in desalination. It is important to note that there is a likely possibility for CNTs to be released from CNT MMMs or VA–CNT membranes and leach directly into water, even though CNTs are embedded on highly stable supports. In particular, some irregularities may cause CNTs to leach into water and ultimately into the environment during desalination processes; therefore precautionary measures are required [67].

It is evident that the toxicity of CNTs in water or the environment is not fully understood, and published reports often produce conflicting deductions. Therefore comprehensive and systematic studies still need to be carried out on this subject. The critical factors that should be considered are the CNT structural morphology (shape and size), surface properties, biodurability, purity, method of production, and modification [75]. Furthermore, CNT toxicity depends on parameters such as exposure conditions, model

or test organism, CNT type and source, dispersion state (sonication), modification strategies, medium, and concentration [76,77]. Once all these factors have been adequately addressed, CNTs could be safely used in water-treatment processes. A research group from Pharmacy School of University College London, recently demonstrated that the CNTs can be produced as risk-free materials only if their surface can be chemically modified and their length shortened by chemical treatment. In their research paper, they emphasized that only those measures can shorten the length of CNTs and ensure that they are stably suspended in biological fluids without agglomeration so that risk-free materials can be produced [78].

CNTs cannot be added directly to water for treatment purposes like commodity chemicals can, because doing so can potentially present new hazards to the health of humans and the environment [79]. Furthermore, additional separation or recovery processes can be necessary to recover the used CNT materials. Therefore, the incorporation of CNTs within the polymeric membrane materials may prove to be more eco-friendly, thus guaranteeing future industrial-scale application of CNT-based membranes in desalination processes.

7.4 Commercial Viability of CNT Membrane Desalination Processes

Although desalination processes have been identified as a potential solution to global water scarcity [80], the economic implications associated with these processes, in general, are too high for underdeveloped and developing countries. The typical construction of desalination plants requires a massive capital expenditure. In addition, the daily operational costs of pumping water from the sea into a desalination plant require a high amount of energy. Since seawater desalination is a highly specialized field, personnel working on these projects are usually highly skilled engineers and normally salaried competitively. As such, input costs in these projects are astronomical. Over the past decade, attempts to lower the cost of desalination in developed countries have proved successful, with the price of desalinated water reaching $2.10/m^3 [81]. According to a review by Ghaffour et al. (2013), the parameters that influence the total capital and operational costs of a desalination plant include electric power availability, desalination process configuration, plant size and its component design, raw water quality and required water quality and other consumables. In a CNT membrane desalination plant, the parameters are expected to be similar. However, the CNT cost parameter is factored in separately. Therefore, in order for CNT membranes to be fully adopted in desalination processes, the cost per volume of saline water treated by these membranes would need to be the same or even lower than the current costs of desalination processes. Cost is always the dominating and deciding factor in the end.

Polymeric membranes used for seawater desalination have evolved over time. By 1969 cellulose acetate (CA) membranes had immerged as the best membranes for

desalination purposes [82]. However, the quest for desalination membranes with high flux and high rejection capacities has been a continuous endeavor. Indeed, the incorporation of carbon nanomaterials, in particular CNTs or the fabrication of VA-CNT membranes, is being applied to lower the cost of seawater desalination. The incorporation of CNTs into polymeric membranes has been shown to produce remarkably enhanced membrane properties such as flux, recovery, antifouling, and salt rejection [5]. It is expected that CNTs will lead to lower energy requirements when pumping seawater across a membrane in order to get fresh water. Fouling of membranes is reported to drive up the energy costs, as a result of the requirements of high pressures necessary to drive pure water molecules across a fouled membrane. Therefore, the inclusion of carbon nanomaterials in membranes to be used for desalination processes, is envisaged to eliminate the deposition of micro-organisms on the membrane surfaces which can contribute to membrane fouling [83]. As such, the presence of CNTs on polymeric membranes brings about properties that can render the membranes energy-efficient. Fig. 10 describes the potential performance and commercial viability of CNT membranes with reference to other nano-enabled membranes such as inorganic nanomaterials incorporating membranes, aquaporins, ceramics, and other nanostructured membranes [45]. Indeed, VA-CNT membranes have highly enhanced performance prediction (closer to aquaporins) yet very far from commercialization.
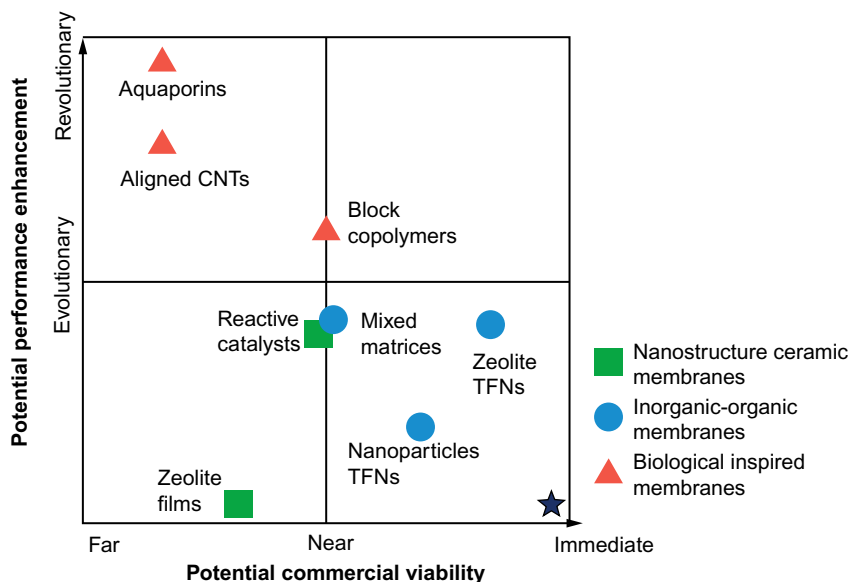

Fig. 10 Potential performance versus commercial viability of nanotechnology-enabled membrane. *(Reproduced with permission from M.M. Pendergast, E.M.V. Hoek, A review of water treatment membrane nanotechnologies, Energy Environ. Sci. 4 (2010) 1946–1971).*

The use of integrated systems has been shown to be one of the ways by which energy costs can be minimized. Seawater has high osmotic pressure because of the presence of divalent ions, for example. By subjecting the seawater feed through a prefiltration stage, the effect of lowering the osmotic pressure of the feed can be explored [84,85]. The ability to fabricate membranes with improved surface properties by incorporating CNTs will further reduce the capital expenditure required for the running of desalination plants. Researchers have already projected that the use of CNT membranes in a desalination plant would offer a significant cost reduction up to 22% and chemical cost savings of up to 76% [86]. Therefore the use of CNT technologies to bring down costs will be at center stage of cutting edge research until the scientific community considers the safety measures discussed in previous sections or provide proof that the potable water generated using CNT membranes is safe and acceptable.

8. CHALLENGES AND FUTURE PERSPECTIVES

CNT membranes are perceived as robust and ideal materials for the generation of fresh water during filtration and desalination processes. This perception is propelled by advances made in the growth of CNTs of various morphologies (e.g., size, shape, and geometry). The mm-long VA-CNTs provide new openings for the transportation of water molecules through tubes. However, CNT-based membranes exhibit several obstacles that must first be addressed before they can be utilized effectively in desalination processes.

The conventional methods for the production of CNTs (such as CVD) have insurmountable shortcomings [50]. One such disadvantage is that CNT manufacturing processes and in particular those for producing VA-CNTs have not yet been scaled up [35]. In addition, when alternative methods such as arc-discharge and laser ablation are utilized in CNT synthesis on an industrial scale, the process becomes very costly. The distinctive properties of CNTs can be useful when these nanomaterials have been homogenously dispersed in a polymer solution [87]. Inherently, CNTs tend to pack up into undesirable bundles or clusters because of the presence of van der Waals interactions within the CNT lattice, which can further compromise the mechanical strength of CNT membranes [88].

However, the "unbundling" of CNTs can be achieved through (i) covalent modifications via the attachment of functional substituents, for example $-COOH$, $-OH$, and $-NH_2$, (ii) noncovalent modification via wrapping of water-soluble linear polymers around the CNTs [89], and (iii) by mixing CNTs under shear force such as ultrasonication [90]. Although CNT functionalization is a challenging and laborious exercise, it leads to more stable surface modification, which is vital in attaining CNTs that can be dispersed with ease in the membrane matrices [10]. The tendency of CNTs to agglomerate during solution-casting processes remains another overarching obstacle.

The practice of chemically functionalizing or substitutional doping CNTs assists in obtaining membranes with excellent surface properties [86]. To keep the fabrication costs of CNT membranes minimal, further research is needed to seek low-cost, simple, and efficient ways of functionalizing and/or dispersing CNTs in membrane matrices. Therefore further research to find ways of simplifying the engineering processes and to understand the membrane science should continue to be pursued.

Membrane fouling is an inevitable occurrence where the application of CNT polymer membranes in water treatment is concerned. The degree of fouling is further influenced by the conditions of the feed water that is undergoing treatment [10]. Even though CNTs possess antimicrobial properties that may be beneficial in averting biofilm formation on a membrane surface, the big issue still remains for staged array membrane configurations and on the influence of the destroyed microorganisms on subsequent membrane filtration steps. Furthermore, having CNTs in mixed-matrix membrane configuration remains questionable and is said to render all the attractive and desirable features of CNTs useless because the majority of the CNT mass is buried in the bulk polymer matrix [17]. The probability of CNTs leaching out from a polymer membrane is another issue requiring attention, especially in cases where dispersion and chemical bonding has not been achieved [46]. Therefore, if CNT polymer membranes are to be endorsed for future large-scale operations in water-treatment processes, the leaching aspect of nanomaterials into the water source must be thoroughly addressed and inhibited.

As mentioned in the previous sections, VA-CNT membranes have better prospects than CNT MMMs when it comes to their performance in desalination processes and the diversity of application. However, their fabrication processes may be a limiting factor in that they hinder widespread exploitation as a result of the complexities in the process and thus incapability of producing reproducible membrane samples. Even though fluxes through the individual nanotube are high, fluxes per unit cm^2 area are limited because of the low porosity of CNTs. This is a serious limitation for their applications. Another great challenge in VA-CNT membranes is the alignment of large numbers of CNTs with well-controlled morphology and geometry across the entire membrane structure. For instance, during polymer infiltration step, it is difficult to find a conformal deposition process that will be able to conform to the spaces between the VA-CNT arrays and adequately fill these spaces, without tempering with the alignment of CNTs. Researchers need to design an etching process that will selectively open the nanotube ends without producing voids in the membrane structure. The challenge is to remove impurities within the VA-CNTs while maintaining the nanotube's original integrity.

Because they are tiny particles instead of ions or molecules for which a system of risk assessment already exists, CNTs face distinctive challenges for risk assessment and management [91]. A deep understanding of these materials is still required in order to

prevent and eliminate the probability of hazards emanating from these materials in water treatment [91]. This level of understanding will significantly help to exponentially increase research and development activities of membranes containing CNT nanomaterials.

VA-CNT membranes provide new prospects for the transportation of liquids and separation of unwanted species. Clearly, the potential for CNT membranes is enormous. The key question that remains is, can these CNT materials be commercialized for large-scale applications? Commercialization of these materials is important because CNT-polymer membranes possess enhanced selectivities. In contrast to conventional polymeric membranes, CNT polymer membranes have outstanding advantages, such as higher flux and higher salt rejection [86]. In view of these outstanding properties, a drive toward commercialization of these materials (which are energy-efficient and less susceptible to fouling) should be undertaken. Over the past decade, challenges pertaining to the application of CNTs revolved around the high cost of CNTs. However, the cost has since dropped from $200 per gram in 1999 to between $50 and $100 per gram in 2013, making it affordable to use CNTs in different materials [92]. The affordability of CNTs would make the scaling up of CNT polymer membranes a possible task [93]. The realization of the ultrafast transport of molecules within tubes of CNT-membranes is critical at this stage.

9. CONCLUSIONS

The merits and challenges associated with the use of CNTs in membrane systems for desalination applications were systematically analyzed. Over the past decade, considerable efforts were made toward the development of membranes containing carbon nanomaterials to overcome fouling, high-energy demand, unselective separation of dissolved contaminants, and low permeation. Clearly, the use of CNTs in membrane systems is on the rise and will continue to be investigated, and provided health concerns can be alleviated, attempts will be made to implement them on an industrial scale in the foreseeable future.

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