Carbon nanotube membranes for water purification: A bright future in water desalination

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HIGHLIGHTS

- Carbon nanotube (CNT) membranes for next generation water desalination
- Tip-functionalized nonpolar CNT-interior facilitates water influx and rejects salts.
- These robust, antibacterial and antifouling CNT-membranes remove most pollutants.

GRAPHICAL ABSTRACT
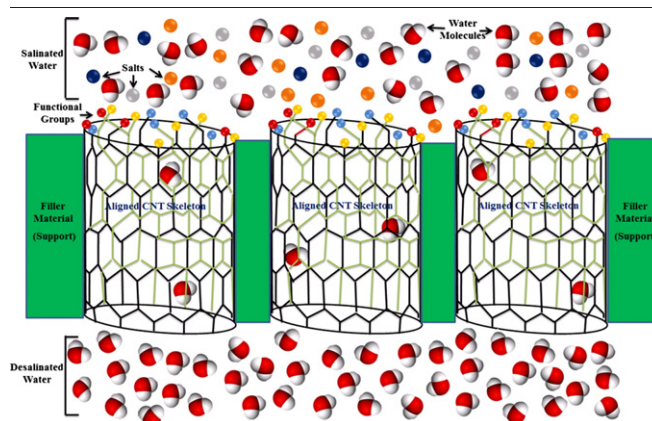
ARTICLE INFO

ABSTRACT

Water pollutants have huge impacts on the entire living systems including terrestrial, aquatic, and aerial flora and fauna. In addition to conventional priority, and newly emerging micro/nano-pollutants, increasing global warming and consequent climate changes are posing major threats to the fresh water availability. Global warming and climate change are constantly increasing the salinity level of both land and sea water, dwindling the availability of existing fresh water for household, agriculture and industry. This has made it urgent to invent an appropriate water treatment technology that not only removes macro-, micro- and nano-pollutants but also desalinates water to a significant extent. Tip-functionalized nonpolar interior home of carbon nanotubes (CNTs) provides strong invitation to polar water molecules and rejects salts and pollutants. Low energy consumption, antifouling and self-cleaning functions have made CNT membranes extraordinary over the conventional ones. We comprehensively reviewed here molecular modeling and experimental aspects of CNT-membrane fabrication and functionalization for the desalination of both sea and brackish water. We present here the current problems and future challenges in water treatments. The article is potentially important for the hydrologists, membrane technologists, environmentalists and industrialists working in the field of water purification technologies to eradicate fresh water crisis in near future.

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Contents

1. Introduction

Climate changes due to increasing global warming are bringing variation in natural systems, leading to ice-melting, sea level rise, soil, and fresh water submergence and increasing evaporation. These are collectively making the fresh, and sea water saltier and rapidly dwindling the availability of existing fresh water. While it is difficult to control or significantly reduce global warming, climate changes, fresh water salination and other forms of water pollutions; the lack of cost-effective water purification technology has already aggravated the crisis of clean and safe water for the rapidly growing population. This issue is extremely serious and has been posing a big threat to global health, economic growth, sustainability and social progress. Thus, a cost-effective water purification technology is a need of the day and its failure might further endanger the life process and ecofriendly human existence at the global scale.

To address the undeniable need of pure water, various water treatment technologies have been proposed and applied at experimental and field levels. These technologies are commonly fall into primary (screening, filtration, centrifugation, separation, sedimentation, coagulation and flocculation); secondary (aerobic and anaerobic treatments); and tertiary (distillation, crystallization, evaporation, solvent extraction, oxidation, precipitation, ion exchange, reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), adsorption, electrolysis and electrodialysis) level water treatment technologies [23]. However, the most of these technologies are not capable of fixing water pollutants in an effective way. Some methods are energy and operationally intensive and thus are not affordable at a commercial scale. Adsorption techniques are easy and simple but cannot desalinate salty water [91]. In this respect, membrane technologies have got some attention because of their interesting inherent features. Membranes do not need chemical additives, thermal inputs and spent media regeneration making them more popular over other water treatment technologies [66]. In fact, the advent of membrane technologies has given immeasurable facilities and opportunities to purify water even at the ionic levels. Membrane filtration allows the passes of water solvent but rejects solutes, gases, fluids and various particles present in the polluted water. Currently, several membrane separation techniques such as RO, NF, UF, MF, distillation, dialysis and electrodialysis are available. Among them, RO, NF, UF and MF are pressure driven membrane processes which are frequently applied in water treatment plants [41]. Both the sea and brackish water can be desalinated using a RO process [24] and around 19% of the world's desalination plants have successfully installed the RO membrane [34].

However, like other membrane technologies, RO also needs the input of high-pressure and consequent energy. Energy consumption costs approximately one half of the total cost in the RO process and

thus contribute significantly to the emission of greenhouse gases [8]. For example, RO needs 3.4 kWh/m^3 electricity for sea water desalination [20,70]. This energy requirement has significantly dampened the popularity of the pressure driven membrane technologies at commercial premises. Furthermore, pollutant precipitation reduces the lifetime and modules of the membranes and causes fouling and pore blocking [68]. Additionally, membrane technologies are less robust and incapable of self-cleaning function, necessitating the chemical treatments for cleaning and recycling. Some recently invented membranes such as forward osmosis (FO), membrane distillation, and capacitive deionization are promising in desalination but are not commercially and practically available [24]. This situation has compelled scientists to search for novel membranes such as carbon nanotubes (CNTs) for cost-effective water purification and desalination technologies.

Well-aligned CNT can serve as robust pores in membranes for water desalination and decontamination applications [19]. The hollow CNT structure provides frictionless transport of water molecules, and this makes them suitable for the development of high fluxing separation techniques. Appropriate pore diameters can constitute energy barriers at the channel entries, rejecting salt ions and permitting water through the nanotube hollows [10]. It is also possible to modify CNT pores to selectively sense and reject ions [4]. Thus, CNT membrane can be used as a 'gate keeper' for size controlled separation of multiple pollutants. Besides, it has antifouling, self-cleaning and reusable functions. This review is the state-of-the-art developments in the utilization of CNTs for desalination technology in a holistic manner. Efforts have been made to demonstrate gold rush possibility of potential CNT membranes to resolve both the seawater and brackish water desalination. Additionally, molecular simulation studies to understand the friction less movement of water molecules through CNT-nanochannels, membrane fabrication, functionalization and influencing factors are extensively presented. The major problems and future challenges of CNTs based membrane technologies are also comprehensively discussed.

2. Threats to water treatment

The rapid changes in human lifestyles over the years have consistently added different notorious anthropogenic pollutants in the aquatic systems. Eradication of these newly emerging deleterious pollutants is either impossible or difficult using the classical water purification systems. Major threats to common water purification systems are summarized in Fig. 1. It clearly reflects that a single method is insufficient to remove all pollutants from water. The pathogen removal processes of conventional water treatment plants may affect effluent water quality (turbidity, pH, temperature) and decrease pathogen sensing ability. Certain bacteria in treated water may release toxins, which may seriously affect the overall quality of water during the treatment process.

Ultraviolet Treatment	Distillation	Chemical Transformation	Coagulation & Flocculation	Biological Treatment
1. No residual effect 2. Cannot remove heavy metals & other non-living contaminants 3. Expensive 4. Inactivated by water cloudiness & turbidity	1. Most contaminants remain behind 2. Requires a large amount of energy & water 3. Pollutants with bp <100^{0}C cannot remove	1. Excess reagents needed 2. Product may be a low-quality mixture & cannot be released to the environment 3. Inactive in harsh conditions 4. Not highly selective	1. Critical to proper functioning 2. Complex & less efficient process 3. Requires alkaline additives to achieve optimum pH	1. Sensitivity of microorganisms to environmental factors & difficult to control 2. Intermediates irreversibly damage the microbial cells 3. Costly and time consuming

Threats to Water Purification

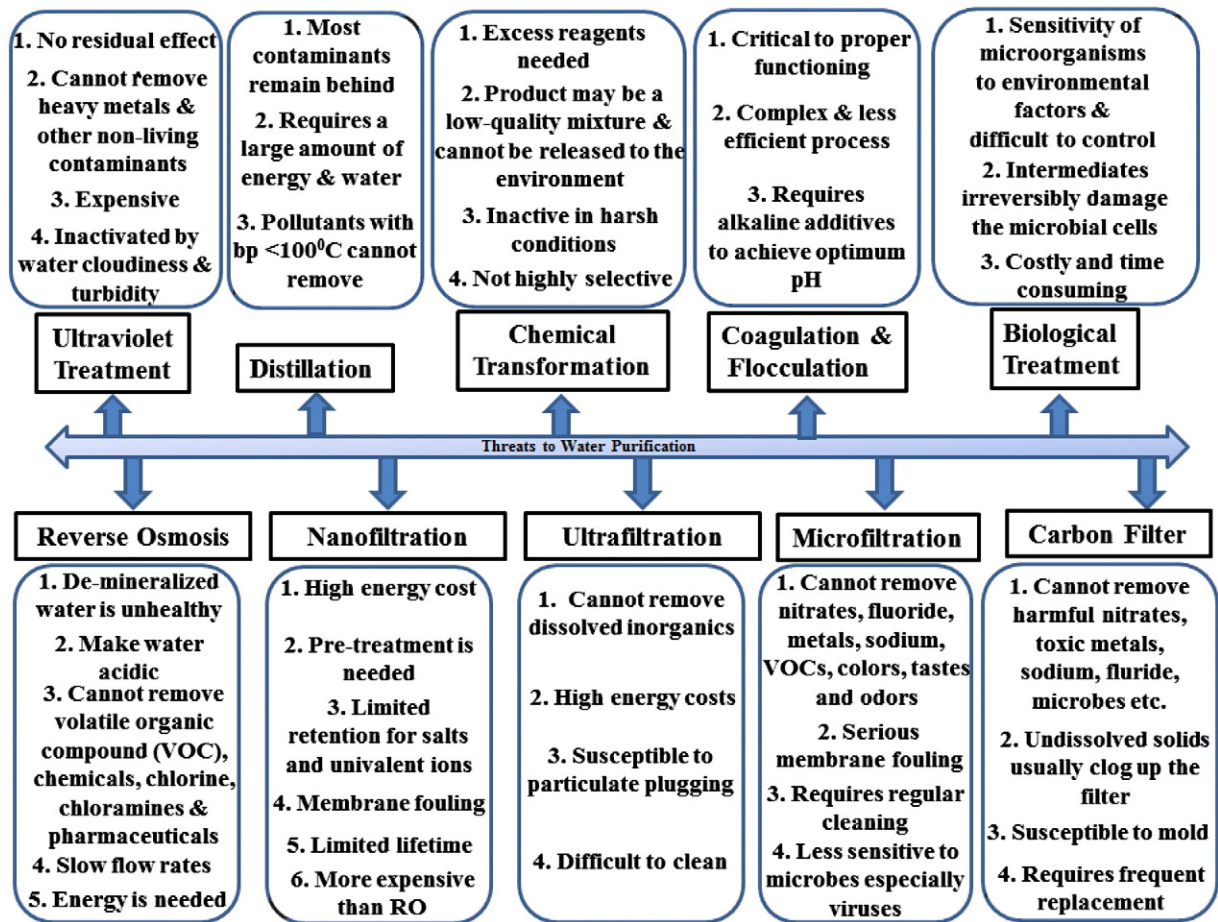| Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration	Carbon Filter
1. De-mineralized water is unhealthy 2. Make water acidic 3. Cannot remove volatile organic compound (VOC), chemicals, chlorine, chloramines & pharmaceuticals 4. Slow flow rates 5. Energy is needed	1. High energy cost 2. Pre-treatment is needed 3. Limited retention for salts and univalent ions 4. Membrane fouling 5. Limited lifetime 6. More expensive than RO	1. Cannot remove dissolved inorganics 2. High energy costs 3. Susceptible to particulate plugging 4. Difficult to clean	1. Cannot remove nitrates, fluoride, metals, sodium, VOCs, colors, tastes and odors 2. Serious membrane fouling 3. Requires regular cleaning 4. Less sensitive to microbes especially viruses	1. Cannot remove harmful nitrates, toxic metals, sodium, fluride, microbes etc. 2. Undissolved solids usually clog up the filter 3. Susceptible to mold 4. Requires frequent replacement

Fig. 1. Some major threats to conventional water purification systems.

For example, cyanobacteria releases microcystin toxin in water while undergoing the treatment process. Low concentration and small dimensions of pollutants are difficult to sense and mitigate. Finally, high operating costs limit their field-level applications [85]. The presence of water contaminant in water treatment plants also decreases the efficiency of the treatment plants. In view of these facts, the existing techniques are not sufficiently effective to give 100% pure and safe water to qualify the waste water discharge criteria.

3. Nanotechnology for water treatment

The advent of nanotechnology has given immeasurable opportunities to purify water even at ionic state. The various nanostructured materials have been fabricated with features such as high aspect ratio, reactivity, and tunable pore volume, electrostatic, hydrophilic and hydrophobic interactions which are useful in adsorption, catalysis, sensing and optoelectronics. Nanoscale metals (silver, titanium, gold and iron) and their oxides have been widely used in environmental mitigation. Silver nanoparticles are effective in disinfecting biological pollutants such as bacteria, viruses and fungi [41]. Titanium nanoparticles have been used in micropollutants transforming redox reactions [42]. Photocatalyst nano-TiO_2 can degrade phenolic recalcitrant compounds, microbial and odorous chemicals into harmless species [9,63]. Most of the nanomaterials have increased surface porosity, which improves salt rejection and avoids macrovoid formation [24]. Nanomaterials have played important roles in degrading various recalcitrant dyes, and halogenated compounds and removal of heavy metals with disinfecting microbes. Gold and iron nanoparticles are especially suitable for removing inorganic heavy metals from surface and waste

waters [41]. Nanomaterials are not only effective in disintegrating various pollutants, but also they are active in bimetallic coupling with other metals and metal oxides which synergistically improve pollution catalysis. Various nanomaterials can be used to make composite membranes. This enhances salt retention ability, curtails costs, land area and energy for desalination. For example, zeolite nanoparticles are mixed with polymer matrix to form thin film RO membrane [21,37]. It increases water transport and >99.7% salt retention ability [37]. Silica nanoparticles were doped with RO polymer matrices for water desalination [38]. It improved polymeric networks, pore diameters and transport properties. CNTs and graphene were used for adsorption based desalination because of their extraordinary adsorption capacities [54,80].

Although nanmoaterials are appreciated in water desalination, they are not free from limitations. Drawbacks include thermal instability, requirement of high pressure, fouling, pollutant precipitation, pore blocking, low influx, slow reaction, formation of toxic intermediates, formation of freshly synthesized ion particles and aggregation on storage. Low chances of reusability and unknown risks to eco-systems are also major concerns [41]. Several hurdles such as insufficient data quality on long time operation, stability and scaling up have to be resolved prior to commercialization [24]. Thus, a reliable, safe, sensitive and cost-effective water treatment technology has become the hardest currency for water purification and desalination.

4. Carbon nanotube in membranes technology

CNTs are composed of cylindrical graphite sheets (allotropic form of carbon) rolled up in a tube like structure with the appearance of lattice-work fence [81]. Single-walled carbon nanotubes (SWCNTs) have

cylindrical shape consisting of a single shell of graphene. On the other hand, multi-walled carbon nanotubes (MWCNTs) are composed of multiple layers of graphene sheets. Both SWCNTs and MWCNTs have been used for direct water desalination [16,53,64] or indirectly to remove trouble making compounds that complicate the desalination processes [39]. CNTs are fascinating in advanced membrane technologies for water desalination since they provide low energy solution for water treatment. CNT-membranes provide near frictionless water flow through them with the retention of a broad spectrum of water pollutants. The inner hollow cavity of CNTs provides a great possibility for desalinating water. The high aspect ratios, smooth hydrophobic walls and inner pore diameter of CNTs allow ultraefficient transport of water molecules. Some prototypes of CNT based membranes are shown in Fig. 2 and the fundamental aspects of CNTs are discussed in the subsequent subsections.

4.1. Water transport through CNT hollow tubes

The smooth and hydrophobic inner core of the hollow CNTs can allow the uninterrupted and spontaneous passage of water molecules with very little absorption (Fig. 3A).

The specially aligned CNTs are of special interest for the construction of CNT membranes. The pore diameter has special effects on the water passages through the membranes consisting of aligned CNTs. Majumder et al. [55] observed frictionless movement of water molecules with high velocities from 9.5 to 43.0 cm s^{-1}/bar speed through a 7 nm diameter membrane pore. The flow rates were four to five times faster than those of conventional fluid flow of between 0.00015 and 0.00057 cm s^{-1}/bar). Molecular simulation dynamics showed that the water conductance of the (7, 7) and (8, 8) tubes are roughly double and quadruple that of the (6, 6) tube, respectively [10]. Though a single water chain forms in both the (5, 5) and (6, 6) tubes, the permeability of the former is a little under half the latter due to the fact that water chains only form across the narrower pore half of the time [10]. Thus, CNT types and conformation play significant roles in water passage and permeability.

The equation of motions nicely describes water transport through CNT membranes as a function of time. Motion reflects dynamics and kinematics of water molecules passing through the tubular structures. Dynamics employs forces, and energy whereas kinematics describes displacement, initial velocity, final velocity, acceleration and time. The
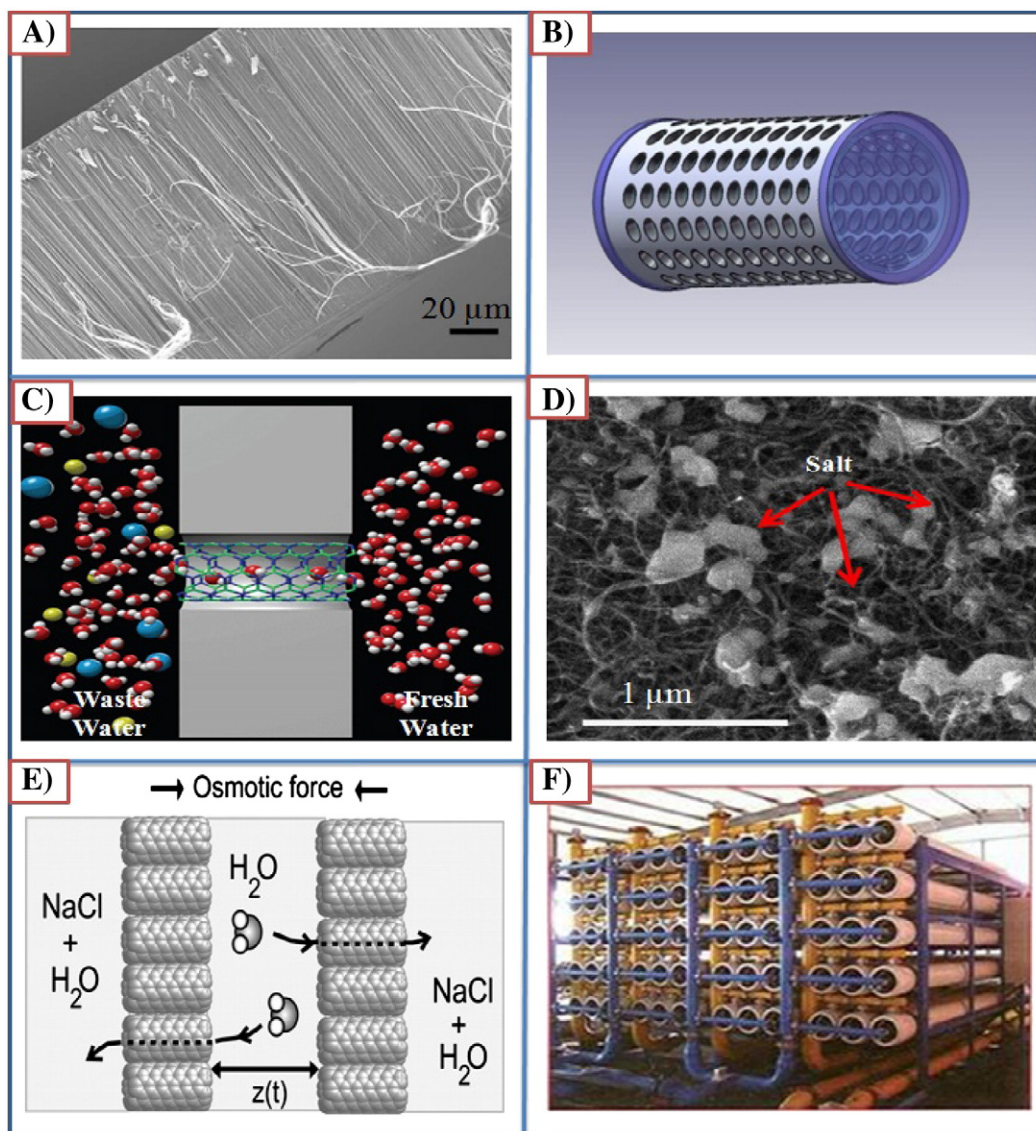
Fig. 2. Structures of some CNT membranes. Shown are (A) cross-sectional scanning electron microscope (SEM) image of a pristine CNT membrane; (B) CNT based water filter with cylindrical geometry; (C) movement of water molecules through a CNT channel; (D) SEM image of scattered NaCl nanocrystals on CNT membrane surface; (E) movement of pure water molecules through CNT-membrane in osmotically imbalanced compartments, and (F) engineered CNT membranes in industrial set up. The figures are adapted with permissions from [28,43,45,78,91].
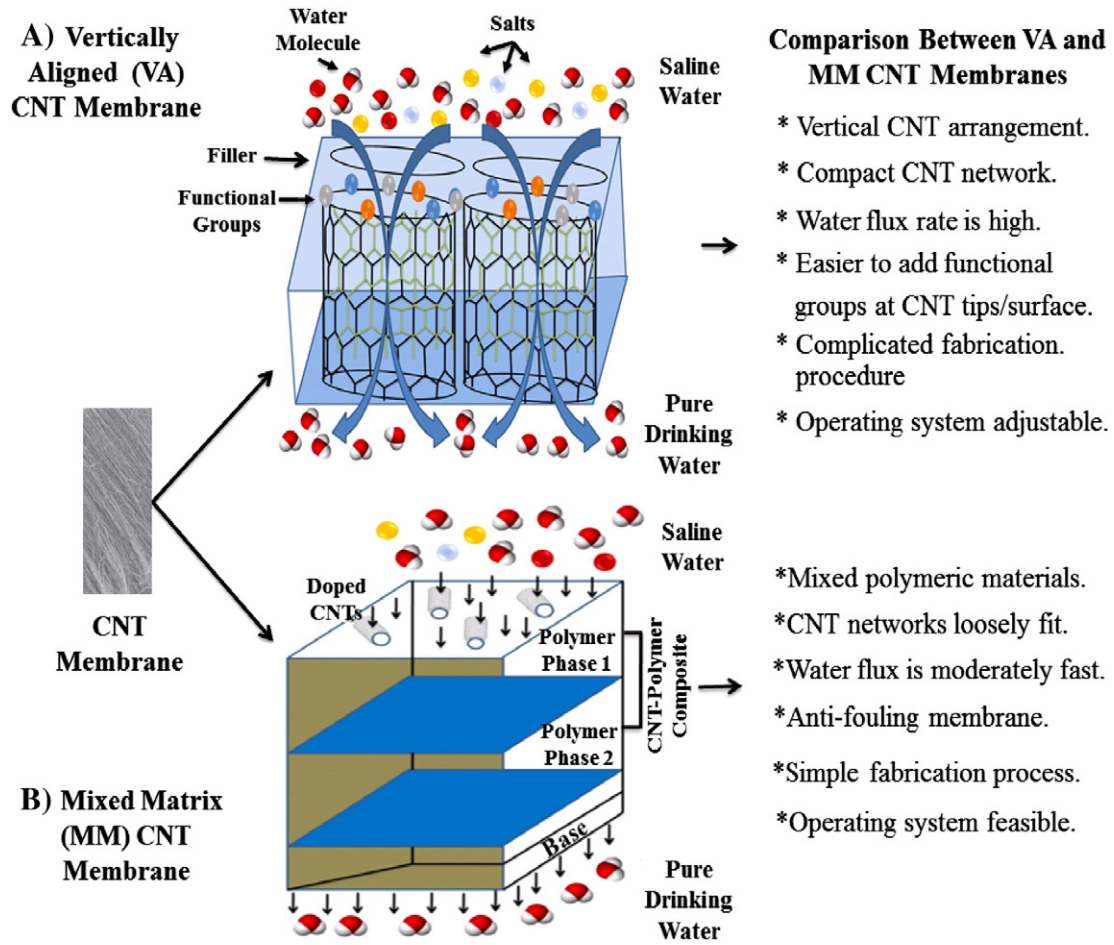
Fig. 3. A prototype of CNT membrane. Shown are trapping of salts and movement of water molecules from salinated water through SWCNT (A) and mixed matrix CNT (B) membranes.

motion of water flow through CNT structure often follows Fickian motion [71], which describes all motions in a disorderly mass passing through the CNTs. However, the secondary movement of water molecules through a narrow 1D channel follows a single file mechanism in which they are hindered from passing each other [48]. The diffusion of water molecules through hollow CNTs is a highly coordinated movement and could be better described by the ballistic motion of water chains [1,71]. Fickian, single file and ballistic motions act as three different isotherms to describe the nature of water molecules passing through CNTs and can be explained by Eqs. (1)–(3).

$$dr^2 \propto Ddt \tag{1}$$

$$dr^2 \propto Fdt^{1/2} \tag{2}$$

$$dr^2 \propto Bdt^2 \tag{3}$$

Where, dr^2 means square displacement; D, F and B imply proportionality coefficient; dt represents time. From Eq. (1), it is possible to describe water diffusion through CNTs by measuring self-diffusion coefficient (D) from the mean square displacement (dr^2) of water molecules as a function of time. Eq. (2) may be used to get single file mobility of water molecules through hollow nanotube, and is dependent on pore size, connectivity and pore–fluid interactions [71]. The mechanism of water diffusion could be well understood by ballistic motion (Eq. (3)) where water molecules have small interactions with CNTs [27,28]. In general, water does not follow the simple fluidics mechanics [82]. Ahn et al. [1] used the term "Nanofluidics" instead of simple fluidics to simulate water movement through nanotube structure. The fluid passes

through a nanochannel has a slip [29] which is sliding of water nanofluids with nanochannel having no change in friction force. Hagen–Poiseuille equation can be used to understand this mechanics using a Slip-Flow condition given in Eq. (4):

$$Q_{slip} = \frac{\pi (d/2)^4 + 4(d/2)^3 . Ls(d)}{8 \mu} . \frac{\Delta p}{L} \tag{4}$$

Where, Q_{slip}, means slip length of water fluxing into nanochannel; d, implies nanochannel diameter; Δp, presents pressure differences at both open ends of nanochannel; μ, considers water viscosity; L, postulates nanochannel length, and Ls (d) infers slip length. It can be measured by Eq. (5).

$$Ls(d) = L_{s,\infty} + \frac{C}{d^3} \tag{5}$$

CNTs are made by graphene layer and have slip length ($L_{s,\infty}$), 30 nm. C, indicates fitting parameter and d, specifies diffusion coefficient of water molecules (0.9423×10^{-9} m^2/s for a 2.1 nm diameter nanotube) [71]. This motion mechanism is not only associated with water diffusion through CNT membranes, but also applicable for oil and gas transports through the most of nanochannel membranes [35,49].

4.2. Fabrication and functionalization of CNT membranes

CNT membrane performances often rely on its processing and fabrication methods. Currently, two types of nanotube membranes are available: (i) vertically aligned (VA) and (ii) mixed matrix (MM) CNT membranes [1] (Fig. 3). The VA-CNT membranes are synthesized by

arranging perpendicular CNTs with supportive filler contents between the tubes. These membranes are high molecular sieves with intercalated filler matrix such as polymer between them (Fig. 3A). The fillers may be epoxy, silicon nitride and others with no water permeability. The VA-CNT membrane was first introduced by Hinds et al. [30] with polystyrene as filler material between CNTs. The fabrication procedure was simple but the pore sizes were irregular. The membrane could not retain Ru $(NH_3)_6^{3+}$ ions initially following H_2O plasma and HCl treatments, respectively. However, functionalization of CNT core with negatively charged carboxylate groups trapped the positively charged Ru $(NH_3)_6^{3+}$ ions [30]. Biotin and streptavidin attachment onto the functionalized CNT membranes reduced ion transport by 5.5–15 times [30]. Such functionalized membranes worked as gatekeeper-controlled chemical separators or an ion-channel mimetic sensor. Holt et al. [31] introduced micro-electromechanical method for synthesizing VA-CNT membranes with stimulated nanofluidic functions. They incorporated silicon nitride (Si_3N_4) fillers between the nanotube spaces to inhibit water flow between the nanotube gaps and create stress to stimulate water flow through the tube. The water flux was increased by >3 folds over other no-slip, and hydrodynamic flow and enhanced ion selectivity than MWCNT membranes. The membrane transported $Ru^{2+}(bipyr)_3$ species with sizes up to 1.3 nm but blocked 2 nm Au particles, suggesting that their pore sizes were between 1.3 and 2 nm. High selectivity to multiple variants, high water fluxing and low energy consumption was obtained using these membranes.

The synthesis of homogeneous CNT membranes is challenging [1]. The chemical vapor deposition (CVD) is probably the best method to synthesize VA-CNT membranes [12]. The use of catalysts in CVD method makes uniform CNT membranes of 20–50 nm in diameter and 5–10 μm in length [32]. The fabrication process of VA-CNT membrane is illustrated in Fig. 4.

On the other hand, a MM-CNT membrane consists of several layers of polymers or other composite materials (Fig. 3B). Such membrane can be easily fabricated with reduced cost and was introduced by Zimmerman et al. [93] to overcome the disadvantages of polymeric membranes for gas purification. However, this membrane has significantly strengthened the water purification ability of the existing membranes. Membrane fouling and pollutant precipitation are major problems in separation technology. Irregular pore size, deleterious micropollutants, influent water quality and pH variations decrease membrane capacities. Precipitation takes place in membranes when water pollutants exceed their solubility limit in water. Additionally, fouling creates defects in membrane pores causing pore blocking and complicating membrane regeneration. MM-CNT membranes could be a great solution to overcome the bottlenecks of current separation technologies. Choi et al. [13] have used MM-CNT membranes to improve filtration capacity of ultrafiltration membranes. It increases water permeability, solutes retention and mechanical robustness of the membrane [91]. The major findings in this field are summarized in Table 1.

4.3. Functionalization

Functionalization of CNT membranes is often a precondition for CNT-based water purification. Pristine CNTs often aggregate which significantly deceases water flux and pollutant rejection capacities of the membranes. CNTs are generally contaminated with metal catalysts, impurities and physical heterogeneities [58]. Additionally, CNTs are capped into hemisphere like fullerene type curvature during synthesis and purification [51]. These capped CNTs are unzipped into open tips which could be oxidized into specific functional groups to trap selective pollutants. Functionalization can add positive ($-NH_3^+$), negative ($-COO^-$, sulfonic acids) and hydrophobic (aromatic rings) groups
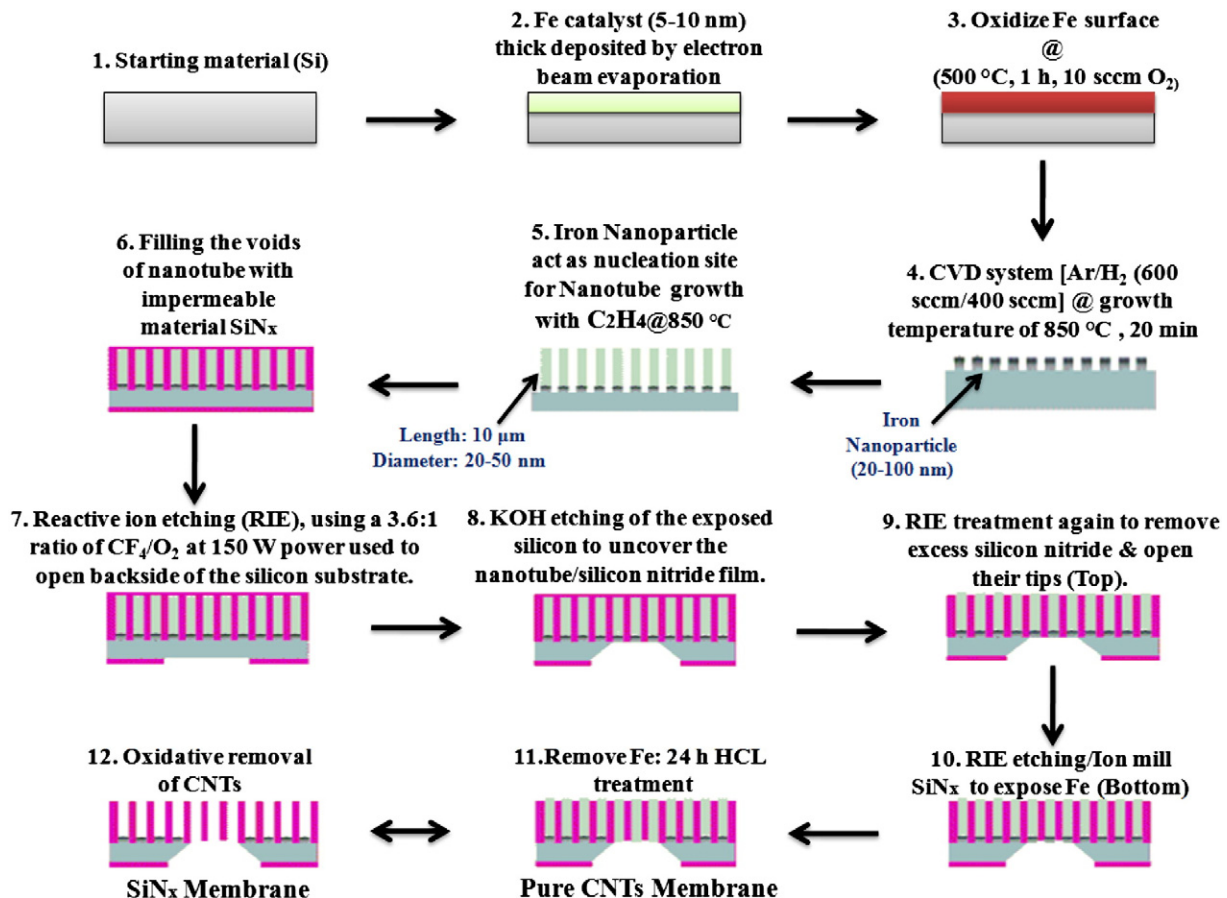

Fig. 4. Process flow for the fabrication of VA-CNT membrane (redrawn with permission from [32]).

Table 1
Potentiality of vertically aligned (VA) and mixed matrix (MM) CNT membranes.

| Membrane types	Substrate/Filler	Major observations	References
VA	Polystyrene	• Have potentiality in chemical separations and sensing. • Modest interaction of the ion with the CNT tips and the core is secured.	[30]
VA	–	• Removed heavy metals and hydrocarbons. • Filtered E. coli and poliovirus (~25 nm).	[72]
VA	SiN$_x$	• Water flux rate was 2.4×10^{-8} mol/m^{2}s. • Bamboo shaped CNTs can be used in separation and chemical sensing.	[32]
VA	Si$_3$N$_4$	• Water flow exceeded >3 orders. • Pores (<2 nm) enhanced ion selectivity and water permeability.	[31]
VA	–	• Nanotube filter separated diesel and water layers. • Cleaned oil spill.	[49]
VA	Epoxy resin	• Increased water permeability.	[17]
VA	Polyethyleneimine	• Degraded recalcitrant contaminants upon functionalization.	[87]
MM	Polysulfonate	• Increased hydrophilicity. • Increased water permeability, up to 2 wt.%. • Decreased solute rejection, up to 2 wt.%. • Decreased permeability and increased rejection at 4 wt.%.	[13]
MM	Polysulfonate	• Increased surface roughness. • Altered surface hydrophilicity. • Increased mechanical stability.	[5]
MM	Poly (vinylidene fluoride)	• Eliminated E. coli cells (~2 μm) through size exclusion. • Inactivated 80% of the bacteria within 20 min contact time. • Removed viruses with great extent.	[6]
MM	Polyamide–polysulfone	• Increased water permeability. • Enhanced bacterial cytotoxicity (60%/h). • Decreased biofouling during operation.	[83]
MM	Polyethersulfone	• Increased water refluxing capacity. • Greater antifouling activity against whey proteins.	[18]
MM	Poly (methyl methacrylate)	• Increased water flux (62%) with improved selectivity and sensitivity. • Retained Na$_2$SO$_4$ (99%).	[73]
MM	Polyvinyl-N-carbazole	• Cytotoxic for Gram-positive and Gram-negative bacteria (~80–90%). • Removed virus (~2.5 logs). • Cost-effective method.	[3]
MM	Polysulfone	• Increased fouling resistance.	[44]
MM	Polysulfone	• Increased water flux (60% to 100%). • Retained solutes and resistant to protein fouling.	[90]
MM	Polysulfone	• Enhanced thermal stability. • Increased heavy metals rejection.	[74]
MM	Polyethersulfone	• Increased water fluxing without aggressive chemical cleaning. • Excellent antifouling properties rendered membranes suitable for recycling use.	[50]
MM	Polysulfone	• Increased water flux (160%).	[2]
MM	Polyvinylidene fluoride	• Reduced fouling tendency. • Improved self-cleaning ability. • Retained salts (R (Na$_2$SO$_4$) > R (MgSO$_4$) > R (NaCl)).	[56]
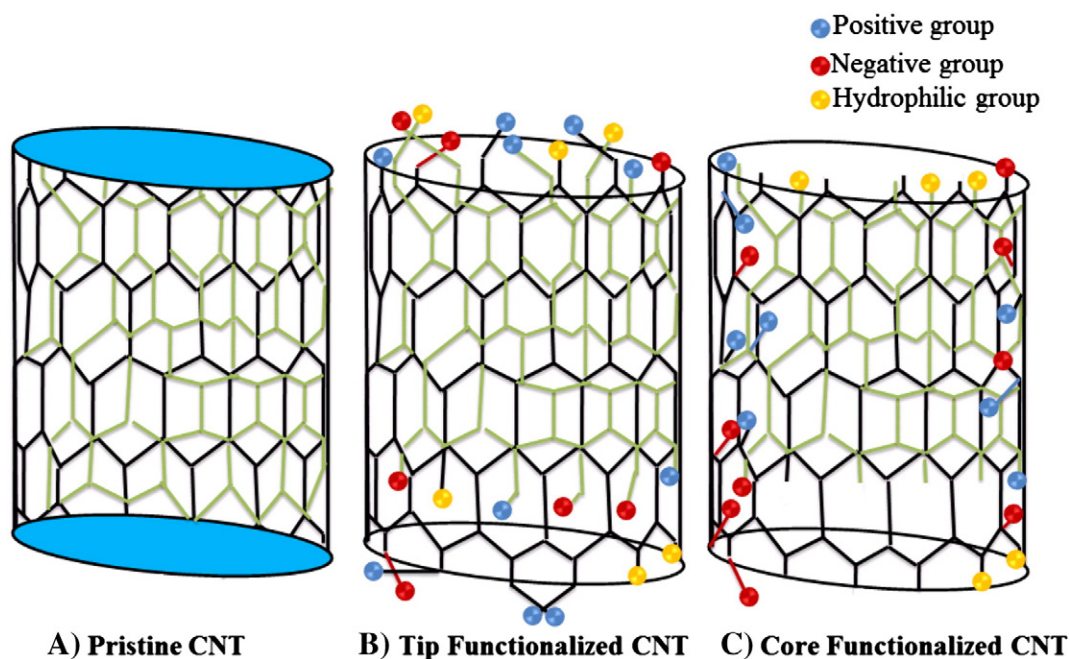
Fig. 5. Functionalization of CNT membranes.

on CNT surfaces [24,45]. These make CNT membranes selective for particular pollutant retention and increase water influx through the nanotube hole. Functionalized CNT membranes show good water permeability, mechanical and thermal stability, fouling resistance, pollutant degradation and self-cleaning functions [68]. Tip functionalized CNT membranes have selective functional groups on the nanotube mouth and the core functionalized CNT have functionalities at the sidewall or interior core (Fig. 5). Both types demonstrate increase water fluxing and selective rejection of pollutant [59]. Functionalization decreases energy consumption through increased permeability and physical adjustability [24]. CNT membranes can also be decorated with various nanoparticles such as Cu, Ag, Au, Pt, Pd, TiO_2, polymers, and biomolecules (pollutant degradative enzymes, DNA and proteins) which have attractive membrane properties and thus broadened CNT membranes application in water desalination [86].

4.4. Factors controlling CNT membranes quality

CNT membrane is a novel excellent membrane technology, but several factors are hindering their commercialization. High-density CNT membranes with uniform pore distribution can control the crowning fate of the membrane. The CNT forest density controls total surface area, pore volume and hydrophobicity of hollow tube membranes and thus is directly proportional to water permeability and desalination capacity. The CNT packing density in epoxy matrix was evaluated by comparing the water refluxing rate in VA-CNT membranes on epoxy support with (6.75×10^{-2}) and without (1.21×10^{-1} ml/cm^2 · min) compression [17] (Fig. 6). In addition, it was postulated that water permeability may be increased by 4 folds if CNT friction could be increased by 1–20 wt.% [14]. The close distance of CNTs may stimulate aggregation and precipitation because of van der Waal's forces [1]. Suitable filler material in the interstitial space of CNTs in membrane can decrease agglomeration by keeping CNTs in perpendicular orientation. Modification of CNT exterior surfaces can improve the trapping of filler materials into CNT interstitial spaces. Mixtures of organic and inorganic fillers can keep individual nanotube in well-aligned CNT membrane. Attachment of functional

groups via acidic, basic, and oxidizing agent creates binding sites for multiple filler materials and hence increases miscibility. Functionalization also controls pore size and diameter which are suitable for fabricating uniform CNT membranes for optimum water desalination.

Pore size and diameter play important roles in water desalination. Molecular modeling of VA-CNT membranes demonstrates that salt rejection capacity significantly decreases with increasing pore diameter (0.32 < 0.49 < 0.59 < 0.75 nm pore rejects 100% ≥ 100% >95% >58% salt, respectively [10,11]. Typical RO and NF membranes have pore diameters 0.6–0.8 and >1 nm, respectively [46]. Thus, to occupy the position of RO membrane, CNT membranes should be ~0.6 nm in diameter [1]. The density, pore architectures and thickness of CNTs drastically affect membrane morphology, water permeability and desalinating ability of the CNT membranes. The membrane thickness and water permeability inversely relate with each other [92]. Increasing membrane thickness decreases water flux and selectivity. Peer observation is necessary to grow aligned CNTs by a suitable membrane synthesis process. Low temperature oxidation reduces the catalytic efficiency of Fe catalysts, yielding low density CNT forests [32]. Adjusting oxidation temperature at 800°C in Ar/H$_2$ atmosphere produces fine nucleation sites for nanotube growth. CNT tip opening and making filler impermeable are rate limiting steps in developing defects free CNT membranes in etching process. Corrosive etching treatment further damages the tubes, producing rough CNT surfaces. Therefore, it is necessary to optimize all sensitive parameters to fabricate an ideal CNT membrane for water purification and desalination.

4.5. Potentiality of CNT membranes

The potentiality of CNT membranes to replace RO, NF and UF membranes is depicted in Fig. 7 and comparative advantages are discussed in Table 2 and Section 5. The nanoporous surfaces of CNT membranes are suitable for rejecting micropollutants and ions in liquid phase. The hydrophobic hollow structures encourage friction less movement of water molecules without the need of any energy-driven force to push water molecules through hollow tubes. The cytotoxic effects of CNT membranes decrease biofouling and increase
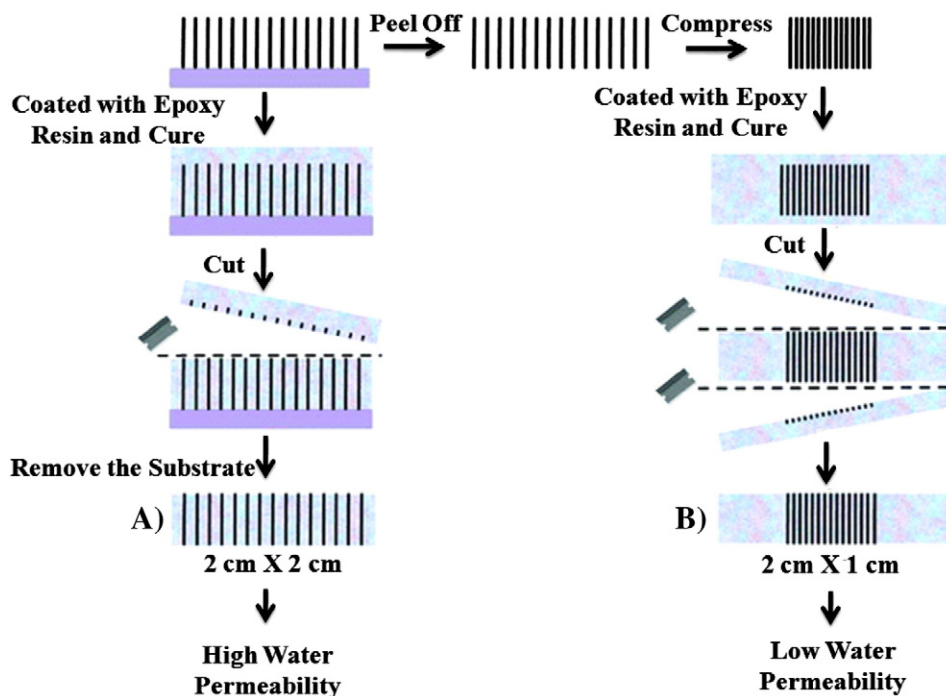

Fig. 6. Schematic representation of CNT membrane preparation with (A) and without (B) mechanical compression (redesigned and adapted with permission from [17] for better understanding).
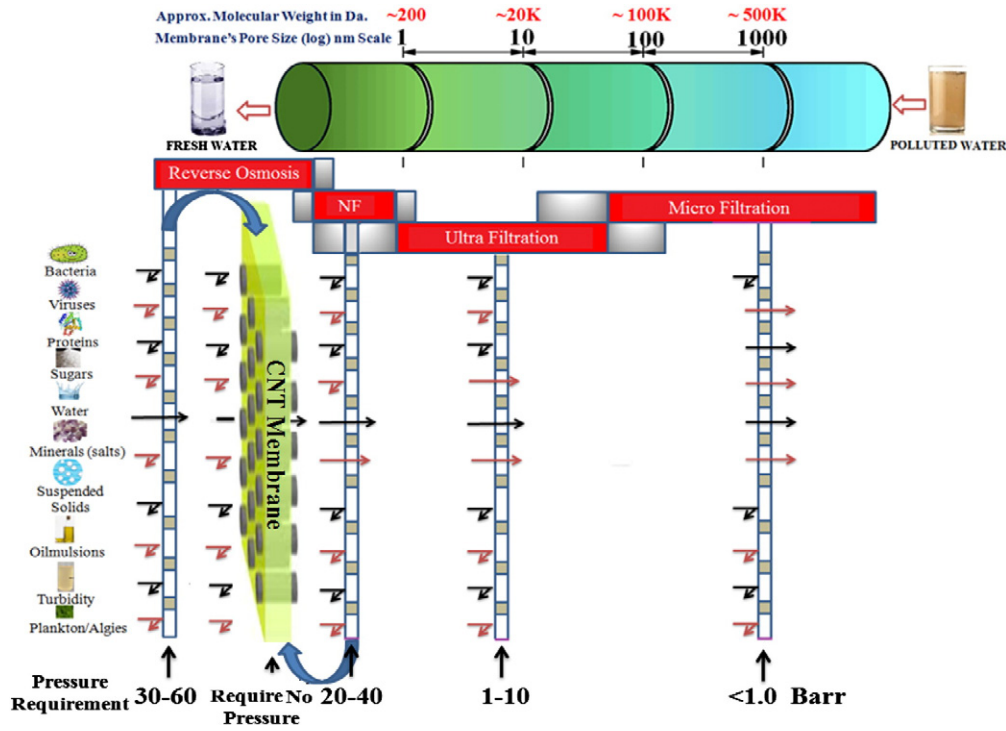
Fig. 7. Diagrammatic representation of major membrane filtration methods.

membrane life by killing and removing pathogens. Fabrication and functionalization of CNT membranes selectively reject particular pollutant from water mixture [45,86]. Finally, CNT membranes can be made highly reusable, less complex, durable, scalable, and eco-friendly without the need of complicated chemical transformation.

5. Comparison of CNTs based membrane with other conventional membranes

The features of currently available membrane technologies are diagrammatically presented in Fig. 7. The dense porous architectures of RO and NF membranes require pressure to force the water molecules

Table 2
Comparative features of major membrane technologies.

Feature	CNT membrane	RO	NF	UF	MF	References
Definition	It is an open tip single hollow structure or polymer composite arranged perpendicularly with impermeable filler matrices.	A process which applies transmembrane pressure to cause selective movement of solvent against the osmotic pressure difference.	A separation process in which particles and dissolved macromolecules smaller than 2 nm are rejected.	A process whereby a solution containing a solute of >1–100 nm in diameter is removed from the solvent.	A separation process in which particles and dissolved macromolecules larger than 100 nm are rejected.	[36]
Specific application	Desalination and selective removal of specific pollutant from complex mixtures.	Desalination, water reuse and ultrapure water production.	Hardness, heavy metals, and dissolved organic matter removal.	Virus and colloid removal.	Suspended solids, protozoa, and bacteria removal.	[7,66,84]
Materials	CNTs and polymers in VA and MM–CNT membranes.	Organic polymers such as, polyamide, polysulfone and polyether sulfone.	Organic polymers like polyamide, polyester and other porous polymers.	Polysulfone, acrylic, cellulose and others.	Polypropylene, polysulfone, polyurethane and so on.	[30,31,33,52,67,77,89]
Pore types and sizes (nm)	Micropores (0.1–2)	Micropores (0.3–0.6)	Micropores (<2)	Mesopores (2–50)	Macropores (>50–500)	[31,47,84]
Thickness (μm)	2–6	~0.1–0.2	~0.05	150–300	50–100	[25,31,60]
Water permeability (mPa^{-1} s^{-1})	~7 × 10^{-7}	~3 × 10^{-12}	~40 × 10^{-12}	~0.5 × 10^{-10}	–	[25,31,66]
Solute rejection ability	Good	Good	Good	Moderate	Poor	[10,25,66]
Self-cleaning capability	Capable with or without functionalization.	Only with functionalization.	Only with functionalization especially at ceramic reactive membranes.	Only with functionalization especially at ceramic reactive membranes.	Only with functionalization especially at ceramic reactive membrane.	[50,56,57,66,75]
Tunable selectivity	Mixed matrix only	Mixed matrix only	Mixed matrix only	Mixed matrix with ceramic reactivity	Mixed matrix with ceramic reactivity	[66]
Membrane fouling	No	Yes	Yes	Yes	Yes	[1,66,68]
Operating pressure (barr)	Negligible	30–60	20–40	1–10	<1.0	[88]

to pass through them. UF and MF membranes consume less energy but retain only suspended particles. In contrast, CNT membranes have the ability to replace both RO and UF membranes with little or no consumption of energy [1]. The hydrophobic hollow tubes of CNTs provide strong invitation to polar water molecules. The nanoscale pore diameter rejects salts and retains ions. The pollutant rejection mechanisms of major membranes are given in Fig. 7 and important features and differences among major membranes are summarized in Table 2.

Table 2 clearly reflects that the choice of the membrane type depends on its functionality, low energy burning, robustness, water permeability, self-cleaning ability and superior contaminant rejection capability. CNT membranes have already demonstrated good water permeability and salt rejection, making them fascinating for desalination applications [1,30,55]. Aligned CNT membranes also provide better water permeability than that of the existing polymeric seawater reverse osmosis (PSWRO) membranes. Pendergast and Hoek [66]) presented a theoretical projection of aligned CNT membranes with PSWRO for desalination application (Fig. 8A). The authors used available data of aligned CNT and popular PSWRO membranes to construct a theoretical projection. The X axis presents fractional content of CNTs used and the maximum density found [31]. The density of CNTs was measured to be ~2.5 × 10^{11} cm^{-2} from several similar transmission electron microscope (TEM) images [31]. The Y axis depicts mean water permeability and the best permeability was quadruple for armchair CNTs (6, 6) [10]. It is worth to mention here, armchair CNTs (5, 5) and (6, 6) are in good position to reject ions, whereas larger CNTs (7, 7) and (8, 8) are not entertained in this way [10]. Cohen-Tanugi and Grossman [15] have recommended the use of CNT membranes as a replacement of RO in order to separate water from salts. The decorated membrane has been proven to be ultimate RO membrane [61] and has potentiality to overcome the limitations of other conventional water purification technologies (Fig. 8 B).

The salt rejection ability of CNT membranes often gets similar performance of commercial NF membrane [1]. Holt et al. [31] have synthesized CNT membrane with pore diameter less than 2 nm, which enhanced ion selectivity and superior to conventional polycarbonate membranes in water permeability. The researchers are now trying to achieve CNT with pore diameter >1 nm, as the membrane can retain most of the solute particles. In addition, it can be possible to remove small ionic solutes from water even with high affinity and great selectivity by changing CNT surface properties [22]. For example, altering of CNT surface charges causes the removal of Na^{++}. This group has achieved nearly 100% removal of salt K_3Fe(CN)_6 using carboxyl functional CNT arrays. It creates an electrostatic repulsion field at tips and

excludes salt ions successfully. Chan et al. [14] have simulated and fabricated CNT membranes (diameter 1.5 nm) with two zwitter ions at tip ends and achieved 100% ion rejection, which is 0% in nonfunctionalized membrane. About 20% ion rejection was associated with five –COOH groups at tip ends of CNT membranes. The combination effect of such type may be due to the steric hindrance effects generated from functional groups present and also presence of electrostatic cloud at nanotube ends. Corry [11] has successfully removed about 100% Na^{++} and Cl^{-} using functionalized CNTs containing –COOH, –NH_3 and –OH groups. Such type of CNT membranes can be used as charged based NF membranes [45]. Ratto et al. [69] have patented a CNT membrane with ion rejection efficiency of greater than 99%, which indicated tremendous potentiality of CNT membranes in water desalination. Very recently, Yang et al. [91] have modified CNTs by plasma treatment and found that the adsorption capacity for salt has exceeded 400% by wt. This ability is two orders of magnitude higher than activated carbon based materials for water desalination.

6. Current hurdles and future challenges

The CNT membranes have chance to be pioneer in membrane technology for water purification provided some critical issues are effectively addressed. The first hurdle is the complicated methods for the synthesis of CNTs with uniform pore size and distribution [79]. The current CVD method is often unable to synthesize size-controlled pores with uniform distribution. Bottom up approach could be used for synthesizing well-controlled CNT-chirality with desired pore diameters and structural integrity [65]. However, the method is expensive and time consuming, making them unsuitable for industrial production. The second complication might be the reduction of pore size and diameter of the CNT membranes. Smaller pores with better desalination properties can be possible with only SWCNTs and double-walled carbon nanotubes (DWCNTs) grown on epoxy or mixed composite matrices. However, both S/DWCNTs are expensive and hence the large-scale and sustainable synthesis of such membranes is not commercially feasible. MWCNTs demonstrate better water permeability [17] and the price of this membrane might be significantly cheaper than S/DWCNT-membranes. Such type of membranes could be used in place of ultrafiltration with a pore size of 2–50 nm [45]. Table 3 describes the relationship of nanotube pore diameters with their respective desalination efficiencies. It points out that nanotubes with larger pore diameters have less ion rejection efficiencies if they are not functionalized. On the other hand, nanotubes with smaller pore diameters retain small ions and deliver good quality potable water.
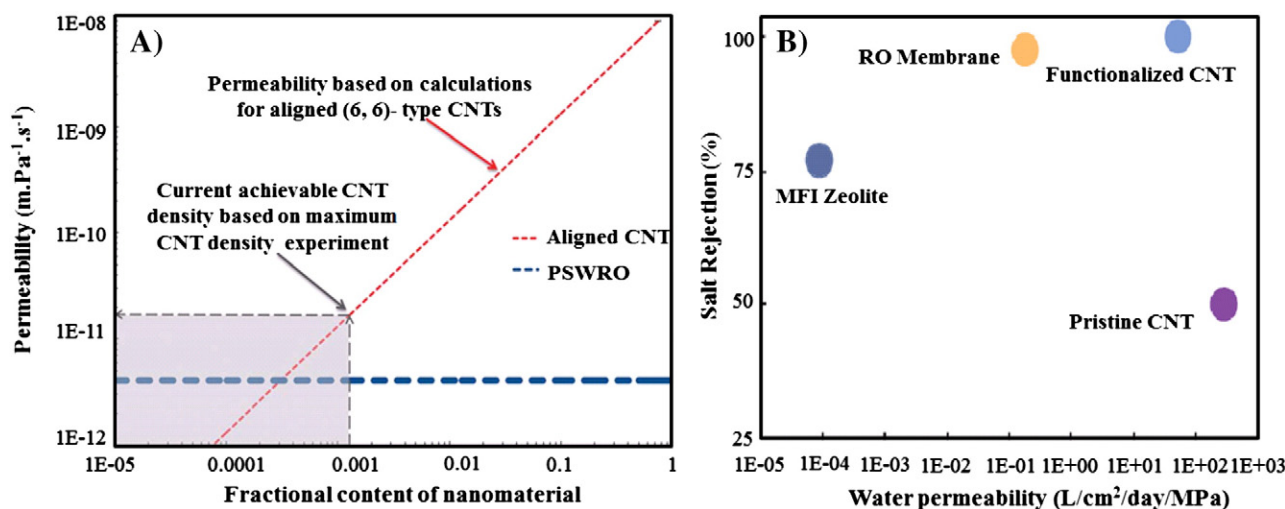

Fig. 8. Theoretical projection of the possibilities for aligned CNT membranes *versus* current PSRO membranes (A) [66]. Performance chart of functionalized CNTs and existing technologies (B) [61]. (Adapted with permissions from [61,66]).

Table 3
Efficiency of CNT membranes in water desalination with respect to their pore diameter.

Pore diameters (nm)	Type of ions reject	Efficiency (%)	References
1.6	K^+, Cl^-	40–60	[22]
0.8	Na^{++}, Cl^-	90	[69]
0.32	Na^{++}, Cl^-	100	[10]
0.49	Na^{++}, Cl^-	100	
0.59	Na^{++}, Cl^-	95	
0.75	Na^{++}, Cl^-	58	
0.69	Na^{++}, Cl^-	84	[26]
0.96	Na^{++}, Cl^-	84	
1.2	Na^{++}, Cl^-	83	
1.5	Na^{++}, Cl^-	83	
1.8	Na^{++}, Cl^-	82	
0.6	Na^{++}	90	[76]
	Cl^-	95	
	K^+	96	
0.5	Na^{++}	95	
	Cl^-	100	
	K^+	99	
0.4	Na^{++}	100	
	Cl^-	100	
	K^+	100	
1.5	Na^{++}, Cl^-	98	[14]
1.1	Na^{++}	28	[11]
	Cl^-	86	
0.4	Na^{++}	100	[40]
0.6	Na^{++}	100	
0.7	Na^{++}	100	
0.8	Na^{++}	100	
1.0	Na^{++}	35	
1.4	Na^{++}	5	

Although each membrane technology has its own merits and demerits, the CNT membranes have been evolved as an ideal water purification technology. It has displayed revolutionary performances and has the potential to be commercially viable in near future. The commercial availability of the CNT membranes must meet certain criteria such as water permeability, desalination capacity, solute selectivity, robustness, antifouling, energy savings, material costs, scalability and compatibility with industrial settings. The third obstruction might be the CNT growth with proper alignment. Difficulties were observed to grow CNT membranes on 12–13 orders of magnitude of aligned CNTs per sq. cm [44]. Any irregularities in membrane shape might produce deleterious effects on water passage and salt rejections. The use of suitable filler polymer materials in nanotube's intermolecular spaces might help proper CNT alignments and enhancement of functions. The fourth difficulty is to add desired functional groups at CNT tips. The atomic structures of the nanotube networks are very sensitive to various wet chemical treatments and hence sometimes it changes CNTs structural properties and even destroys CNT walls, reducing nanotubes water fluxing and solute retention capacities [45]. The closed tip ends of CNTs must be opened or unzipped by appropriate wet chemical treatments for fast water transport. Selective oxidizing agents could be used to open CNT closed tips followed by adding hydrophilic functionalities which have increased affinity for water entering into the tube and eventually enhanced ion selectivity. Once water molecules enter into the nanotube holes, the interior hydrophobic wall of CNTs stimulates water transport at ultra-high speed (>100 Lm^{-2} h^{-1}) [1,31]. However, according to Corry [11], the functional groups may create steric blockage by the ions that are attracted and saturated at the CNT tip ends. The affinity between functional groups and water molecules may promote the temporarily pause of water molecules around the functionalized regions. Thus, the functionalization is a rate limiting step which must be carefully optimized to tune the CNT-membrane permeability to water molecules and solutes.

The fifth hurdle to limit CNT membrane applications is their cost of using SWCNTs. To the best of our knowledge, MWCNTs cannot be used to synthesize CNT membranes with sub-nanometer pore diameter.

Few-walled carbon nanotubes (FWCNTs) are effective for >1 nm pore diameter membrane. However, the synthesis of S/FWCNTs is not straightforward. CNT doping to other polymers or matrices might be an alternative choice for cost reduction. Several groups have used mesoscopic structuring by co-blending CNT and polymer membranes [3,5,6,13,18,44,50,73,74,83,90]. This could be useful to make more stable and thinner CNT membranes with reduced flow resistance. An alternative choice might be to start an experimental program based on sorption and breakthrough curves to demonstrate energy saving potential and sufficient purification effect. Such evidences are grossly omitted by many literatures published on this field.

Other minor problems are associated with the presence of impure particles in pristine CNTs like carbonaceous, contaminated metal catalysts, ash and amorphous carbon which should be eliminated prior to use in membrane fabrication. During comprehensive literature reviews, it was observed that most of the water permeability and salt rejection ability of CNT membranes are evaluated through computational modelings rather than experimental evidences. The experimental proof of this *in-silico* approach is in urgent need to evaluate CNT membrane performance at the viable scale. The specificity and selectivity of the membrane should be cheeked in raw tape or surface water where mixtures of contaminants are usually present. For a cationic membrane, a mixture of anionic contaminants can be used to see whether there is any complexion for binding to functional groups of CNT membranes and *vice versa*.

Another confrontation is whether we could consider CNT-membrane as RO, NF and UF membranes. Membrane technologists often classify CNT membranes as RO, FO, NF and UF membranes [1,24,40,45,61] which is confusing and conflicting to the definitions of ISO (International Organization of Standardization). Mueller et al. [62] have classified CNT membranes as nano-enhanced membrane (NEM) because of its enhanced functional roles over other membranes. This classification hitherto of this specialized membrane could be critically reviewed to regulate them at risk estimation and regulations. Eco-safety and health issues are important concerns to be resolved. Although there is least chance of CNTs to escape from membranes, any abnormalities may own leaching of CNT into water and ultimately in environment. Therefore, safety guideline should be developed to find out new policy in this area.

7. Conclusion

The potentiality of CNT membranes in sea and brackish water desalinations is illustrated in great details. Although RO, NF, MF, UF and other membranes have been used to mitigate fresh water crisis, CNT-based membranes have remarkable accomplishments in terms of water permeability, desalination capacity, solute selectivity, robustness, antifouling, energy savings and scalability. CNT-membranes could be used at all levels from the point of generation (POG) to the point of use (POU) treatments. These have potentiality to give potable water instantly and can serve as next generation universal water filter. Molecular modeling reveals frictionless passage of water molecules through highly hydrophobic CNT hollow tubes. It minimizes the use of pressure which is needed in some conventional membranes. Even water uptake can be regulated by changing nanotube structural properties and functionalization of tips and core axis. Thus, these have opened a new avenue to create a gate point separation of pollutants in water purification technology. Microorganisms induced membrane fouling followed by coagulation and pore blocking is a major concern in separation technologies. This challenge can be overcome by using CNT membranes which have antimicrobial activity. CNTs rupture bacterial cell through the production of reactive oxygen species (ROS), disruption of their metabolic pathway and oxidative stress. This has brought a new revolution in membrane technology with self-cleaning power. Functionalization of CNT membranes with other antimicrobial nanoparticles, such as silver nanoparticle and TiO_2, is a great promise for decreasing biofouling and

increasing self-cleaning capacities. Small size and soft condensed architecture of CNT membranes help to auto-arrange themselves without any external input. High water flux with selective salt rejection has raised its demand for water desalination. However, the effective and homogeneous CNT membrane synthesis is still at the premature stage and need further improvement. We hope the best future of CNT membranes for water desalination and purification in near future.

Acknowledgment

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