Modified nanofiltration membrane treatment of saline water: a review

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ABSTRACT

Nanoparticles have received much attention recently due to their unique properties in terms of photoemission, antimicrobial, and catalytic activity. NPs incorporated membranes have gained attention due to their ability to increase membrane permeability, mechanical properties, hydrophilicity, and selectivity in some cases. This review is focuses on the modification on zeolite and carbon nanotube (CNTs) membranes in the treatment of saline water, and factors affecting the desalination process during this modification and how to control and mitigate them. Therefore, the objective of the research is to evaluate the effectiveness of desalination technology based on the modified zeolite and CNTs membranes, the focus point will be the energy-efficient, greener approaches to synthesis and modification of a variety of nanomaterials to meet the present and future challenges.

keywords: Water treatment; Modified nanofiltration; Nanotechnology; Saline water; Water quality; Zeolite membrane, Carbon nanotubes (CNT)

1. Introduction

Potable water production has become a worldwide concern; for many communities, projected population growth, and associated demand exceeds conventional available water resources. The shortage of water supplies for drinking and irrigation purposes is already a very serious problem for the North African countries, the Middle East and several countries in Southeast Asia and Latin America [1]. Desalination has become an important source of drinking water production. Desalination can be defined as any process that removes salts from water [2]. Desalination processes may be used in municipal, industrial, or commercial applications. With improvements in technology, desalination processes are becoming cost-competitive with other methods of producing usable water for our growing needs. The traditional materials and treatment technologies like activated carbon, oxidation, reverse osmosis (RO) membranes and activated sludge are not efficient to care for complex and intricate polluted water consisting of pharmaceuticals, surfactants, various industrial additives, and abundant chemicals professed. The traditional and decade-old water treatment processes are not able to address adequately the removal of toxic chemicals, organic materials, and microorganisms present in raw water. Currently, nanotechnology has been extensively studied by researchers as it offers potential advantages like low cost, reuse, and highly efficient in removing and recovering the pollutants [3]. Various nanomaterials like carbon nanotubes (CNTs), nanomembranes, zeolites, and dendrites, etc., are helping in the development of more proficient treatment processes among the advanced water systems [4]. There are many aspects of nanotechnology that can be used to address the multiple problems of water quality in order to ensure environmental stability. Nanotechnology-based multifunctional and highly efficient processes are providing affordable solutions to water treatments that do not require large infrastructures or centralized systems [3]. Nanoparticles have received much attention recently due to their unique properties in terms of photoemission,

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antimicrobial, and catalytic activity. Nanoparticles incorporated membranes have gained attention due to their ability to increase membrane permeability, mechanical properties, hydrophilicity, and selectivity in some cases. This review is focused on zeolite and CNTs membranes in the treatment of saline water, and factors affecting desalination. Therefore, the objective of the research is to evaluate the effectiveness of desalination technology based on zeolite and CNTs membranes, the focus point will be the variety of nanomaterials to meet the present and future challenges.

2. Desalination technologies

A desalination process essentially separates saline water into two parts one that has a low concentration of salt (treated water or product water), and the other with a much higher concentration than the original feed water, usually referred to as brine concentrate [5]. The two major types of technologies that are used around the world for desalination can be broadly classified as either thermal or membrane [6,7]. Both technologies need the energy to operate and produce fresh water. Within those two broad types, there are sub-categories (processes) using different techniques. The major desalination processes are identified in Table 1.

2.1. Thermal technologies

Thermal technologies, as the name implies, involve the heating of saline water and collecting the condensed vapor (distillate) to produce pure water. Thermal technologies have rarely been used for brackish water desalination, because of the high costs involved. They have however been used for seawater desalination and can be sub-divided into three groups: multi-stage flash distillation (MSF), multi-effect distillation (MED), and adsorption desalination (AD) [8,9].

2.2. Membrane technologies

Membrane technologies; membrane separation processes operate without heating and therefore use less energy than conventional thermal separation processes. Membrane filtration is a pressure-driven process in which membrane acts as selective barriers to restrict the passage of pollutants such as organics, nutrients, turbidity, microorganisms, inorganic metal ions, and other oxygen depleting pollutants, and allows relatively clear water to pass through [9]. With technological advances and the ever-increasing stringency of water quality criteria, membrane processes are becoming a more attractive solution to the challenge of quality water,

Table 1
Desalination technologies and processes

Thermal technology	Membrane technology
Multi-stage flash distillation (MSF)	Electrodialysis (ED)
Multi-effect distillation (MED)	Electrodialysis reversal (EDR)
Adsorption desalination (AD)	Reverse osmosis (RO)

Source: [5].

and water reuse [10]. It can be subdivided into two broad categories: electrodialysis/electrodialysis reversal (ED/EDR), and RO.

3. Nanotechnology

The term nanotechnology describes a range of technologies performed on a nanometer scale with widespread applications as enabling technology in various industries. Nanotechnology is the creation of materials, devices, and systems using individual atoms and molecules. At such a small scale, new physical, chemical, and biological properties become evident [3]. The evolution of nanotechnology has provided new opportunities for using smaller and more regular structures for porous membranes. Artificial sieves with higher precision and greater flexibility than track-etched membranes have been produced, with commensurate at improvements in performance and functionality [11]. These new filters have facilitated the most detailed scientific investigations to date of membrane-performance-related phenomena. In addition, mesoporous materials, such as mesoporous nanoparticles, are useful for species detection, and uptake and controlled release of biomolecules [12].

3.1. Nano membrane processes

Filtration is a process of removing particulate matter from water by forcing the water through a porous media. This porous media can be natural, in the case of sand, gravel, and clay, or it can be a membrane wall made of various materials. Sometimes, large particles are settled before filtration; this is called sedimentation. Typically, pressure-driven membranes are classified according to characteristic pore size or their intended application (Table 2). Currently, membrane technology is commercially available for suspended solids, protozoa, and bacteria removal (microfiltration, MF), for virus and colloid removal (ultrafiltration, UF), for hardness, heavy metals, and dissolved organic matter removal (nanofiltration, NF), and for desalination, water reuse, and ultrapure water production (RO) [13]. While commercially available membranes perform well in many applications, the drive to protect existing water resources and to produce new water resources demands membranes with improved productivity, selectivity, fouling resistance, and stability available at a lower cost and with fewer manufacturing defects. Better membranes require better materials.

3.2. TFC membranes

TFC membranes are semipermeable membranes manufactured principally for use in water purification or water desalination systems. They also have used in chemical applications such as batteries and fuel cells. A thin-film composite (TFC) membrane can be considered as a molecular sieve constructed in the form of a film from two or more layered materials. The three-layer configuration gives the desired properties of high rejection of undesired materials (like salts), high filtration rate, and good mechanical strength. The polyamide top layer is responsible for the high rejection and is chosen primarily for its permeability to water and relative impermeability to various

Table 2
Membrane characterization by pore type and target species

Pore type (size range, nm)	Membrane type (pore size, nm)	Species	Dimensions (nm)
Macropores (>50)	Microfiltration (50–500)	Yeast and fungi	1,000–10,000
		Bacteria	300–10,000
		Oil emulsions	100–10,000
Mesopores (2–50)	Ultrafiltration (2–50)	Colloidal solids	100–1,000
		Viruses	30–300
		Proteins/polysaccharides	3–10
		Humies/nucleic acids	<3
Micropores (0.2–2)	Nanofiltration (≤2)	Common antibiotics	0.6–1.2
	RO (0.3–0.6)	Organic antibiotics	0.3–0.8
	Forward osmosis (0.3–0.6)	Inorganic ions	0.2–0.4
		Water	0.2

Source, [14].

dissolved impurities including salt ions and other small, unfilterable molecules. A major breakthrough in the field of membrane separations was the development of TFC membranes, which comprise an ultra-thin "barrier" layer polymerized in situ over a porous polymeric support membrane [14]. These membranes are often referred to generically as "interfacial composite," "composite," or "TFC" membranes, although TFC® is a registered trademark of Koch Membrane Systems, Inc. in the US and other countries. The major advantage of TFC membranes over integrally skinned asymmetric membranes is that the chemistry, and hence, the performance of the upper selective layer and the porous support layer can be independently selected to optimize the composite membrane performance. In addition, more expensive monomers can be used to form the selective layer without dramatically increasing cost because this region only accounts for a small portion of the total material. The key factors driving the development of TFC membrane materials over the past 40–50 y were the pursuit of high flux, high selectivity RO membranes for seawater desalination. Along the way, low-pressure RO membranes for desalting brackish water and for reclaiming wastewater to nearly ultrapure levels were developed along with NF membranes now used predominantly for water softening and dissolved organic removal. The porous layer is generally formed through phase inversion and the dense layer is applied through interfacial polymerization or coating (dip, spray, and spin) followed by cross-linking. Curing (heat, UV, and chemical) is frequently applied to further the extent of polymer cross-linking, which significantly impacts the stability, permeability, and selectivity of the thin film. TFC RO/NF membranes are most often formed on the surface of a microporous support membrane via interfacial polymerization (i.e., *in situ* polycondensation). A large number of TFC membranes have been successfully developed from different polymers such as polyurea, polyamide (PA), polyurea-amide, polyether-amide, and others most of which have shown excellent selectivity, in particular high salt selectivity and relatively high water permeability for RO applications [15]. Polyamide TFC membranes continue to be employed because they yield good salt rejection while overcoming the relatively low flux of their integrally skinned counterparts. Polysulfone is the most widely used polymer for RO support membranes. Additives such as poly (ethylene glycol) and polyvinylpyrrolidone (PVP) have been made to PSf support membrane casting solutions to increase the porosity of the support membrane skin layer, and thus, the composite membrane permeability. One common goal of post-treatments is to reduce a TFC membrane's propensity for surface fouling. This can be achieved through surface modifications via graft polymerization induced by methods such as plasma exposure, UV-photoinitiation, or redox initiation [14].

3.3. Thin film nanocomposite membranes

Nanoparticle additions have been made to the thin films of TFC RO membranes in order to take advantage of the properties of the nanomaterials. Addition of nanoparticles to interfacial polymerization processes or surface attachment via self-assembly has introduced the concept of thin-film nanocomposite (TFN) membranes, which offer potential benefits of enhanced separation performance, reduced fouling, antimicrobial activity, and other novel functionality [16]. As with TFC membranes, TFN membrane performance can be fine-tuned with nanoparticle additions to the support membrane, the coating film, or both [17]. By casting molecular sieves in the thin film of an RO membrane, where diffusion controls the transport process, the goal is to essentially reach the percolation threshold in the dense selective layer with an individual particle, Fig. 1. Larger nanoparticles produce membranes with highly favorable surface properties, while smaller nanoparticles increased permeability more by increasing the characteristic pore size [14]. All TFN membranes reported are less cross-linked than pure polyamide TFC counterparts, suggesting another potential mechanism by which TFN membrane permeability is enhanced. This work implies that the addition of nanoparticles can be tailored to particular membrane applications with the selection of nanoparticle size and type. Enhanced hydrophilicity, and thus, reduced fouling is a goal of many TFN studies [17].
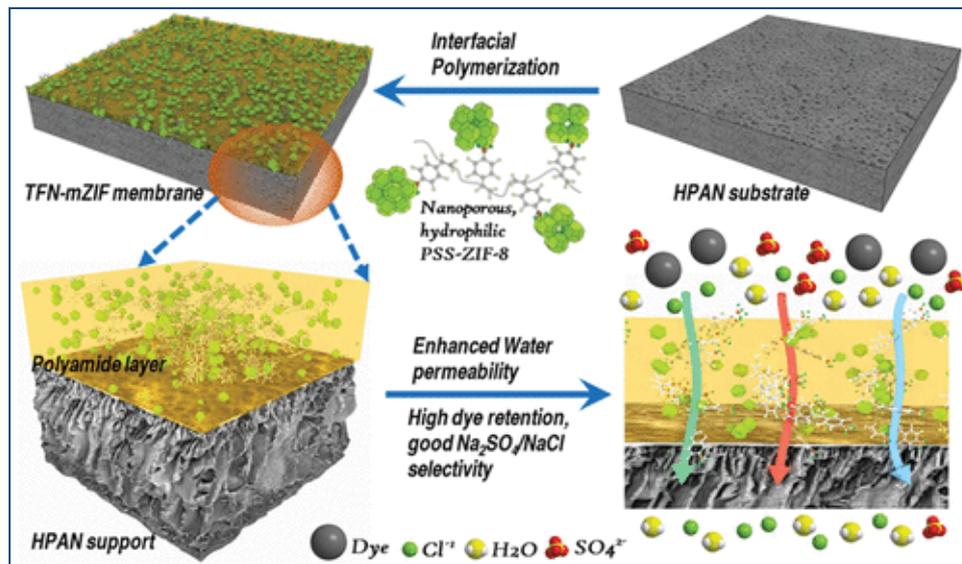
Fig. 1. Schematic of a TFN membrane containing poly (sodium 4 styrenesulfonate; PSS) modified ZIF-8 (mZIF) in a polyamide (PA) layer were constructed. Source, [17].

3.4. Zeolite-coated ceramic membranes

The exact definition of the term "zeolite" is still the subject of discussion. The naming of zeolites in the literature seldom follows a scientific system. If natural analogs exist, the synthetic zeolites are often named after the minerals (e.g., faujasite, mordenite, ferrierite, and offretite). Alternatively, the names given by the discoverers are used. Zeolites are natural minerals that are mined in many parts of the world; most zeolites used commercially are produced synthetically. When developing applications for zeolites, it is important to remember that not all of these minerals are the same. Synthetic zeolites are widely common [18]. In zeolite-based membrane reactors, the membrane normally consists of a thin film of a mesoporous or microporous zeolite on macroporous support, typically α-Al_2O_3, stainless steel or carbon. This thin film may simultaneously serve, (i) as both a catalyst and a permselective membrane, (ii) as a permselective diffusion barrier, or (iii) as an inert non-selective reactant distributor. Permselectivity depends on the size of the permeating molecules relative to the pore size of the membrane, the chemical nature of the permeating molecules and the membrane material, as well as, the adsorption properties of the membrane in a mixture of components with different adsorption characteristics the stronger adsorbing compound will permeate preferentially [19]. A current thrust in ceramic membrane development is to form membranes with water permeability on the range of UF membranes, but solute selectivity like that of NF or RO membranes [20]. In 2001, molecular dynamics simulations showed that zeolite membranes may be applicable for aqueous osmotic separations. Since then, thin zeolite membranes have been studied for RO desalination of brackish water as well as a variety of wastewaters [16]. For RO applications, ceramic alternatives offer a clear advantage of mechanical stability under high pressures and chemical stability to withstand disinfectants. In many wastewater treatment applications, ceramic membranes are more fouling resistant and chemically stable than current polymeric membranes.

Zeolites are naturally occurring aluminosilicate minerals with highly uniform subnanometer and nanometer-scale crystalline structures. Typical zeolite membranes are amorphous silicate, aluminosilicate, or aluminophosphate crystalline structures formed via hydrothermal synthesis [21]. Other synthesis methods include *in situ* layer-by-layer crystallization and dry gel conversion in the presence of a template-water vapor [22]. Aluminosilicate crystals are intrinsically inert, imbuing these membranes with extreme thermal and chemical stability. Zeolite crystals consist of a three-dimensional cross-linked $(Si/Al)O_4$ tetrahedral framework, in which each Al or Si atom occupies the vertex of a network connecting four oxygen atoms. The framework structure contains cavities, see Fig. 2, that allows for the movement and containment of ions and water molecules. The containment of molecules in a given zeolite framework is a function of temperature, water content, ion type, and the ratio of Si to Al atoms in the matrix. Many natural zeolites can be produced synthetically, while additional structures, with no natural occurrence, have been synthesized and are characterized as zeolites based on their structures, such as zeolite-A produced by Linde Corporation [14].

A few common zeolite materials employed in membranes include mobil-type five (MFI-type), sodalite (SOD), and Linde Type A (LTA), shown in Fig. 3. Zeolite ZSM-5 (MFI)—the most commonly applied zeolite in membranes - is composed of a unit cell with the chemical formula $Na_nAl_nSi_{96-n}O_{192} \sim 16H_2O_{(n-3)}$. The MFI structure contains straight channels in one direction and perpendicular sinusoidal channels that are not interconnected [24]. The drawback of employing MFI-type zeolites in porous membranes is that the crystals must be oriented with respect to the permeation direction. The hydrated form of SOD, referred to as hydroxyl sodalite, has also been applied in membrane materials. This mineral has the chemical formula $Na_6Al_6Si_6O_{24} \cdot 8H_2O$ [25]. SODs are
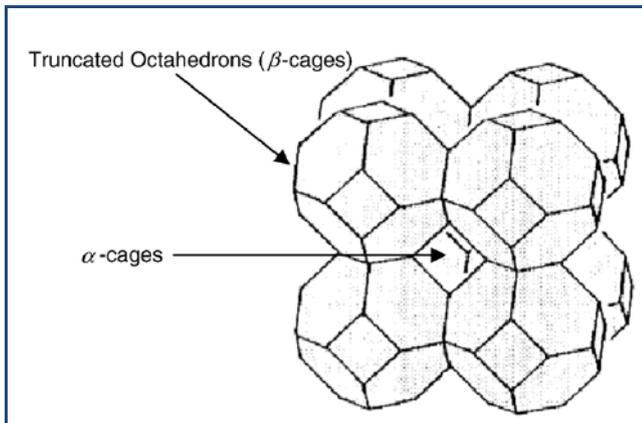
Fig. 2. Repeating unit of zeolite HS. Source, [23].

not mineralogically defined as zeolites, but feldspathoids because in nature salt molecules are contained in their frameworks. The SOD cage, often referred to as the β-cage, is quite common to zeolite structures and when crystalline networks are created with this cage structure zeolitic properties are exhibited. One common example is the zeolite-A (LTA) unit cell, defined by the chemical formula $Na_{12}Al_{12}Si_{12}O_{48}\cdot27H_2O$. The LTA structure is composed of SOD cages (β-cages) connected by truncated cuboctahedron (α-cages), forming an interconnected cage structure [14].

The interconnected inner channel in LTA offers the opportunity for simplified membrane fabrication since crystal alignment is unnecessary. Pore size and framework density are the primary factors of concern when considering zeolites for water separations; pore size determines ion selectivity, and framework density determines water permeability. Atoms other than Si and Al can be substituted into the cage structures of zeolites via ion exchange to imbue alternate charge and structural properties. Since the ability to act as a molecular sieve is due to the channel widths, changing the atoms in the framework, and thus the channel widths will change the sieve properties [18]. Additionally, both the ion and water molecule mobility through a zeolite depends upon the relative density of the framework structure; open porous structures will facilitate less hindered transport. This is indicated by the framework density, defined as the number of Si or Al atoms per 1,000 Å. Framework densities (normalized for ideal Si frameworks) are 18.4, 16.7, and 14.2 for MFI, SOD, and LTA, respectively [16], implying that LTA would be expected to have the largest water mobility. The Si:Al ratio of a zeolite cage is the most important factor affecting chemical stability, hydrophilic properties, and occurrence of intercrystalline defects all primary factors of concern when engineering selective and robust water treatment membranes. An increase in Si:Al ratio implies a decrease in the overall surface charge on the framework [18]. The MFI-type zeolites are capable of a large range of Si:Al ratios, from ~30 in the ZSM-5 form to nearly pure Si for the isomorphous silicate type MFI. Noack et al. [40] find that as the Si:Al ratio decreases in MFI-type zeolites water permeability and selectivity for water increase; however, defects simultaneously increase until a point where selectivity is compromised.

Separations in zeolitic materials occur primarily through molecular sieving, competitive adsorption, or ion exchange [27]. Ions with small hydrated radii diffuse more quickly through zeolite pore structures. Cationic adsorption occurs onto the negatively charged surface of zeolite membranes and may enhance diffusion by establishing a charge gradient. Initially, adsorption occurs onto the pore walls. Inter crystalline molecular sieving occurs when the electrical double layers of these adsorbed ions overlap and inhibit the passage of charged ions [23]. Hydrophilic zeolite membranes previously applied for gas separations are composed of a loose, thick zeolite film through which separation occurs. However, the new RO membranes being developed require an ultra-thin, dense layer and so pains must be taken to form nanoscale zeolite coatings to produce membranes with permeability on par with polymeric RO membranes, Fig. 4 shows some of the membranes support types.

There are ~150 different structures reported by the International Zeolite Association. Among them, only 15 structures have been experimented to fabricate membranes [18]. Table 3 shows a brief description of the structure and pore sizes of a few different zeolites used for membranes. A number of research efforts, with some degree of success, have been directed to finding solutions to the remaining challenges. This review makes an assessment of what has been achieved in the past few years in terms of zeolite membranes that still stand in the way of the successful implementation of zeolite nanomembranes in desalination process of saline water.

3.5. Vertically aligned nanotube membranes-carbon nanotube membranes

CNTs are composed of cylindrical graphite sheets (an allotropic form of carbon) rolled up in a tube-like structure with the appearance of a latticework fence [28]. Single-walled carbon nanotubes (SWCNTs) have cylindrical shape
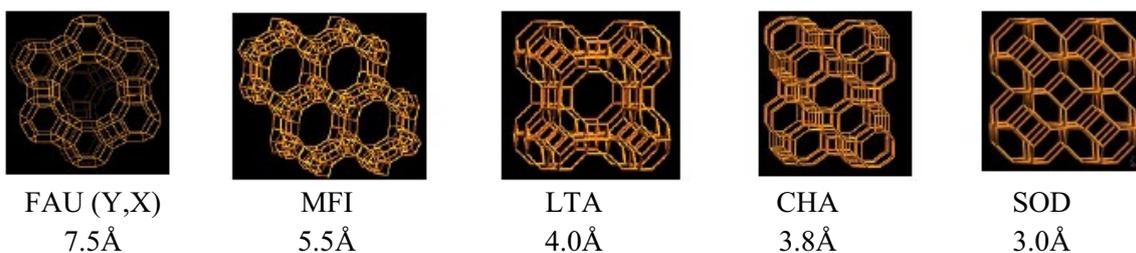

| FAU (Y,X) | MFI | LTA | CHA | SOD |
| 7.5Å | 5.5Å | 4.0Å | 3.8Å | 3.0Å |

Fig. 3. Zeolite types. Source, [26].

Table 3
Brief description of structure and pore sizes of different zeolites used for membranes

Zeolite	Structure	Pore size, channels
NaX, Faujasti (FAU)	Comprised of 12 membered rings. The inner cavity has a diameter of 12 Å and is surrounded by 10 SOD cages	dp = 7.4 Å
T	Intergrowth type zeolite of erionite and offretite	0.36 × 0.51 nm, dp = 0.41 nm
W	Same framework topology as the mineral merlinoite (MER), eight membered ring	Channel dimension 0.31 × 0.35 nm
B-substituted β-zeolite	Three dimensional, 12 ring, interconnected channel	dp = 0.53 × 0.57 and 0.71 × 0.73 nm
SAPO-5	Microporous, non-intersecting tubular channels circumscribed by 12-membered rings	dp = 7.3–8.0 Å
SAPO-44	Chabazite type structure	dp = ~0.43 nm diameter
SAPO-34		dp = ~0.38 nm diameter
NaA	Crystalline aluminosilicate	Channel opening size 0.41 nm
ZIF-8	Sodalite type structure	Large pores of 11.6 Å which are accessible through small apertures of 3.4 Å
L	The channels contain cationic sites, which can interact with negatively charged or polarized molecules	One dimensional pore with an opening 0.71 nm which runs along its c-axis
AlPO-18	Built of AlO_4^{-1} and PO_4^{-1} tetrahedral building units. Three dimensional framework possessing eight membered intersecting channels	dp = 3.8 Å
Isoreeticular zeolite Imidazolate	Metal atoms such as Zn linked through N atoms by ditopic imidazolate ($C_3N_2H_3$ = 1 m) or functionalized IM links to form neutral frameworks	dp = 17.3–7.1 Å
SUZ-4	Framework topology is related to zeolites ferrierite and ZSM-57 and contains straight channel having apertures defined by rings of ten (Si, Al)-O specie; a novel cage may as the site for non-exchangeable potassium ions	Narrow pore size distribution with 97 nm mean diameter and 760 nm long of needle crystal shape
MOF-5	Face centered cubic crystal structure. Each corner is formed by $(Zn_4O)^{6+}$ metal cluster, while each edge is linked by 1,4-benzenedicaboxylate (BDC)	Narrow pore size distribution centered at 1.56 nm
MFI	Intra-crystal	dp = 0.8–1.0 nm
ZIFs	Ordered porous structures with hybrid frameworks consisting of inorganic metal ions or metal clusters coordinated with organic imidazole/imidazolate ligands	dp = 0.02 to 30.1 Å
DDR	Comprised of silicon and oxygen atoms, eight membered ring, clathrasil type (Clathrasis are porous framework silicates with cage like voids)	Aperture of 0.36 × 0.44 nm
MER	Comprises double-eight-rings and γ-cage	dp = 0.27–0.52 nm

Source, [18].

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 [29] or indirectly to remove trouble making compounds that complicate the desalination processes [30]. CNTs are fascinating in advanced membrane technologies for water desalination since they provide a 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 [28]. 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 ultra-efficient transport of water molecules. Some prototypes of CNT based membranes are shown in Fig. 5.

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. 5a. 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.
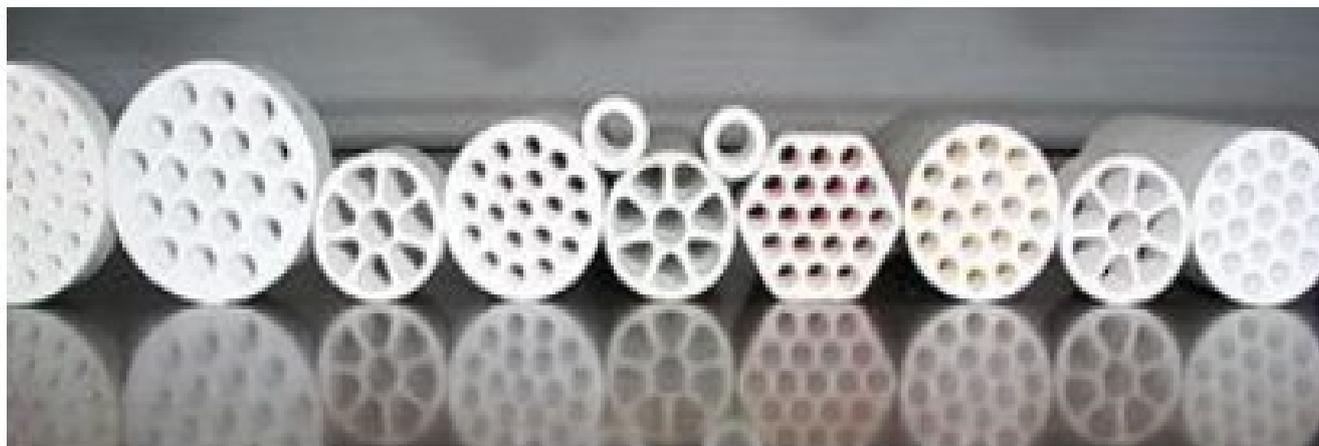
Fig. 4. Zeolite support types. Source, [26].

Majumder et al. [33] observed the 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 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. 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. Thus, CNT types and conformation play significant roles in water passage and permeability.

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 [32]. Additionally, CNTs are capped into hemisphere like fullerene type curvature during synthesis and purification. 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 on CNT surfaces [28]. 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. 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. 6. Both types demonstrate increase water fluxing and selective rejection of pollutants [33]. Functionalization decreases energy consumption through increased permeability and physical adjustability [28]. 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 [34].

The nanoporous surfaces of CNT membranes are suitable for rejecting micropollutants and ions in liquid phase. The hydrophobic hollow structures encourage frictionless 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 membrane life by killing and removing pathogens. Fabrication and functionalization of CNT membranes selectively reject particular pollutants from water mixture [34]. CNT membranes can be made highly reusable, less complex, durable, scalable, and eco-friendly without the need of complicated chemical transformation [28].

4. Modification in nanofiltration membranes

4.1. Zeolite membranes

Pore size and framework density are the primary factors of concern when considering zeolites for water separations; pore size determines ion selectivity and framework density determines water permeability. Atoms other than Si and Al can be substituted into the cage structures of zeolites via ion exchange to imbue alternate charge and structural properties. Since the ability to act as a molecular sieve is due to the channel widths, changing the atoms in the framework, and thus the channel widths will change the sieve properties [35].

Li et al. apply MFI-type zeolite membranes (thickness ~3 μm) for RO desalination (with 0.1 M NaCl feed solution at 2.07 MPa) [35]. Water flux is 0.112 kg m^{-2} h^{-1} with 76.7% Na$^+$ rejection. The membrane is also challenged with a complex solution, more reminiscent of real RO feed waters, and the resulting water flux and rejection are lower (0.058 kg m^{-2} h^{-1} with Na$^+$ rejection of 58.1%). The reduced rejection is attributed to double-layer compression within inter crystal pores of the zeolite material due to the high ionic strength of the feed solution [14].

Another study with similar MFI membranes reports higher flux and rejection values (>95% of Na$^+$ ions) [36].
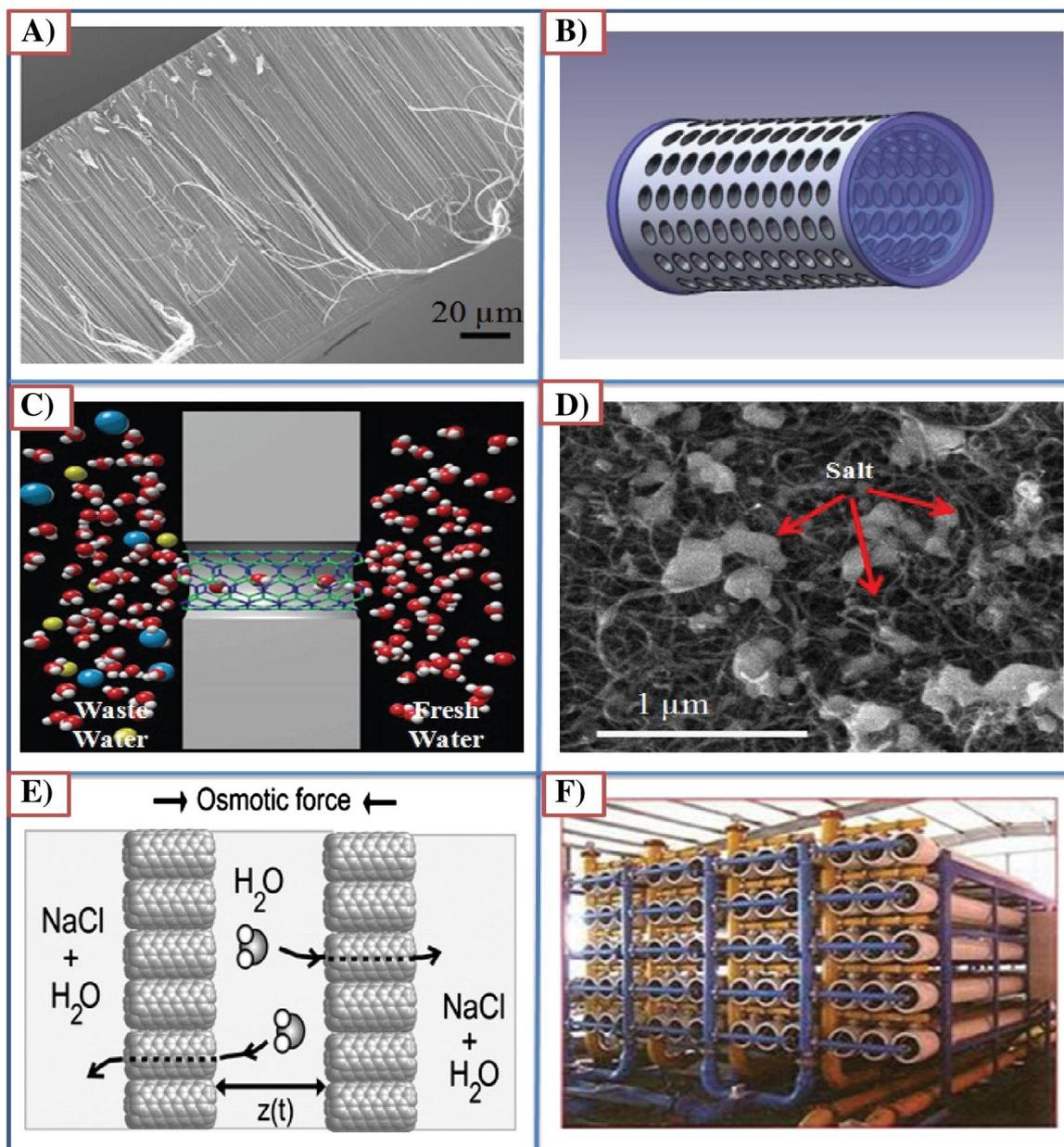
Fig. 5. Structures of some CNT membranes. Shown are (a) cross-sectional scanning electron microscope (SEM) image of a pristine CNT membrane; (b) CNT based water filter with cylindrical geometry; (c) movement of water molecules through a CNT channel; (d) SEM image of scattered NaCl nanocrystals on CNT membrane surface; (e) movement of pure water molecules through CNT-membrane in osmotically imbalanced compartments, and (f) engineered CNT membranes in industrial set up. Source, [28].

Higher trans-membrane pressure increases water permeation and decreases ion permeation, resulting in better separation performance. Higher operating temperature increases both water and salt permeation, but having a larger impact on salt permeation. This is due to the reduced viscosity of the feed solution and increased diffusivity of water molecules and salt ions [28]. The effect of temperature is consistent with that observed for traditional polymeric RO membranes, absent the effects of polymer swelling at higher temperatures. While these membranes served as a proof of concept, higher water flux, and salt rejection are both needed for MFI-based RO membranes to be commercially viable [14].

Duke et al. [37] prepare MFI-type membranes for seawater desalination via template-free secondary growth. Zeolite films are formed over alumina supports by dip coating in a silicalite suspension and grown under hydrothermal conditions. This method improves control over membrane formation and produces fewer defects by decoupling the deposition and crystal growth steps. Alumina content should influence surface hydrophobicity and charge [38]; however, in this study surface charge did not vary with Si:Al ratio [37]. In RO mode (with 0.5 wt.% sea salts at 700 kPa) rejection is highest (50%) in an alumina-free silicate membrane due to strong electrostatic shielding of Na$^+$ ions
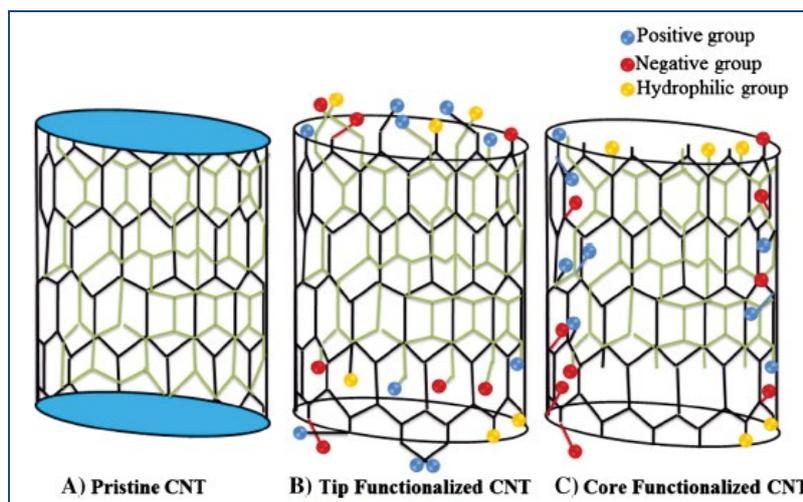
Fig. 6. Functionalization of CNT membranes. (a) Pristine CT, (b) tip functionalized CNT, and (c) core functionalized CNT. Source, [28].

by the monopolar surface, which maintains the ideal double layer for this application. Because the Si:Al ratio allows for tuning of the surface properties and the resultant electrostatic double-layer such membranes could also be tuned for specific ion-selective applications, but further work is needed to fully understand the connection between zeolite chemistry and membrane performance [39,40].

Liu et al. form an α-alumina supported MFI-type zeolite membrane via *in situ* crystallization on the inner surface of tubular ceramic membranes for the removal of organics from produced water [41]. In RO (with 0.1 M NaCl solution at 2.76 MPa) the membranes produce a water flux of 0.35 kg m^{-2} h^{-1} with Na$^+$ rejection of 99.4%. Ion separation occurs via size exclusion of hydrated ions as well as Donnan exclusion at pore entries. When tested for produced water treatment the coated membranes exhibit a water flux of 0.33 kg m^{-2} h^{-1} with an organics rejection of 96.5%. With non-electrolyte solutions, zeolite membrane selectivity is dominated by molecular sieving and so very different rejections are seen for high and low dynamic molecular size compounds. This work produced high salt rejections, but higher permeability must concurrently be achieved for the practical application of these zeolite membranes.

Kumakiri et al. [42] synthesize A-type zeolite membranes via hydrothermal synthesis atop a porous α-alumina substrate. The substrate is seeded with crystals, dipped in an alumina-silica solution, and crystallized at 80°C for 5 h. This process is repeated multiple times until reasonable separation performance is achieved. The membranes tested for performance in RO (with 10 wt.% ethanol feed solution at 1.47 MPa and 30°C) have pure water flux of 0.14 kg m^{-2} h^{-1}. The membrane selectivity for the ethanol/water mixture is 44%. Flux varies linearly with applied pressure, while selectivity is not significantly influenced. Most significantly, the membrane is mechanically stable up to pressures as high as 50 kgf cm^{-2} (4.90 MPa). If the performance of these membranes can be made competitive, their mechanical strength will make them ideal in high-pressure applications.

Kazemimoghadam [23] formed composite polycrystalline hydroxyl SOD membranes atop high porosity tubular mullite supports. The active SOD layer was formed through hydrothermal growth by coating the ceramic support with crystal seeds (~0.4 nm diameter), dipping it in a homogeneous aluminate-silicate gel, and treating it at 100°C to allow crystal growth. The zeolitic membrane was tested for performance as an RO membrane for water treatment at variable trans-membrane pressures (100–300 kPa), feed temperatures (20°C–60°C), and feed rates (0.5–3 L min^{-1}). Flux increased with trans-membrane pressure, temperature (due to resulting lower viscosity), and feed rates (due to enhanced turbulence and hydrodynamic effects). High permeability was achieved (~10–12 m Pa^{-1} s^{-1}), on the order of current polymeric seawater RO membranes; however, no salt rejection data was published. If competitive selectivity can also be achieved, these materials may offer new opportunities for RO membranes in high temperature, pressure, and fouling applications. Specifically, the SOD membranes produced by Kazemimoghadam and Mohammadi [27]. Ten appear to have specific water permeability three orders of magnitude lower than commercial seawater RO membranes. If defect-free zeolite films could be formed with a thickness of 0.2 μm, the resultant membrane would have a water permeability of ~0.5 × 10^{-10}, which is equivalent to a tight polymeric UF membrane. Obviously, this could make zeolite-based RO membranes a viable alternative material for high flux RO membranes, but with dramatically enhanced thermal, mechanical, and chemical stability. The challenge remains improving control over crystal nucleation and growth to ensure defect-free ultra-thin zeolite films, which may require abandoning or substantially modifying traditional hydrothermal synthesis methods.

Both zeolite and catalyst-coated membranes face similar challenges as have always faced ceramic water treatment membranes, that is, high manufacturing cost and low packing density relative to polymeric membranes. An additional hindrance of photocatalytic water treatment is the energy demand for irradiating the surfaces. To minimize this, solar-induced photocatalytic surfaces have been investigated and applied. Reactive surface-mediated photocatalysis for water treatment shows promise, particularly for the

purpose of small-scale production where solar energy can be utilized [45].

Zeolite nanoparticle-based TFN RO membranes attempt to leverage the molecular sieving properties. Jeong et al. [44] cast zeolite-polyamide thin films atop PSf support membranes by dispersing zeolite nanoparticles in the TMC solution prior to interfacial polymerization. Water permeability of zeolite TFN membranes increases as much as 80% over identically cast TFC membranes at the highest TFN particle loading (0.4 wt.%), with rejections consistently above 90%. Pure water permeability increases even for pore-filled zeolites, although permeability increases more for pore-opened zeolites supporting the role of molecular sieving. These results appear to imply a combination of effects contributes to the permeability enhancement born out of zeolite fillers.

Silver-zeolites not only provided more hydrophilic surfaces but also actively inhibit biofouling due to the antimicrobial nature of nanosilver. Lee et al. [45] prepared composite PA thin-film NF membranes with titania (~60 nm) nanoparticles in the skin layer through interfacial polymerization 170. As titania concentration increases toward 5 wt.%, water flux increases and decreases salt rejection, suggesting significant defects formed in the nanocomposite coating film.

Any nanoparticle with water permeability higher than that of the polymer matrix can increase the permeability of the resulting nanocomposite membrane by providing preferential flow paths through the cross-section. Conversely, impermeable nanoparticles can only reduce the water permeability of a membrane because they reducing the area available for permeation through the polymer film. However, impermeable fillers can increase membrane permeability through defect formation, which may also compromise solute rejection. This is a simple analysis, but the concept must be kept in mind as research continues on nanocomposite materials [44].

For certain applications, a loss in permeability may be overcome by the benefits of super-hydrophilic or antimicrobial nanoparticles that significantly reduce membrane fouling, but in generally reduced permeability is not a desirable feature. Cost considerations are also important, while antimicrobial and zeolite nanoparticles are expensive, zeolite TFNs have shown higher flux at extremely low loadings such that the cost increase may be minimal.

4.2. Carbon nanotube membranes

Mixed matrix membranes have been formed with the addition of nanotubes. CNTs exhibit antimicrobial activity; thus, presenting an opportunity for improved disinfection or antifouling membranes. Bundling is often an issue, especially with single-walled CNTs, due to the van der Waals interactions between nanotubes and the fact that they are insoluble in water and organic solvents; this hinders the application for large scale fabrication of membrane materials [46]. Lin et al. [47] recommend functionalizing CNTs with polymer groups that are structurally similar to the bulk polymer matrix to aid nanotube dispersion and homogenous membrane properties.

Krishna et al. [48] coat multi-walled carbon nanotubes (CNTs; known to have the large surface area and substantial photon-generated electron trapping capacity) with titania in order to delay recombination 79. Titania-coated CNTs display two times the inactivation rate of commercially available titania alone when tested on *B. cereus* spores.

Choi et al. [49] cast multi-walled CNT/PSf mixed matrix membranes by nonsolvent induced phase inversion. Nanotubes are pretreated with acid to aid in dispersion throughout the solvent. Surface hydrophilicity of the membranes increases with the presence of CNTs due to the carboxylic acid groups that form on CNT surfaces during acid pretreatment. Pore size increases with nanotube additions up to 1.5 wt.% and then decreases, becoming smaller than pure PSf at 4 wt.%. Water permeability and rejection, however, increased with nanotube additions as high as 4 wt.%, likely because the improved hydrophilicity and resulting anti-fouling ability play the dominant role in membrane performance.

Brunet et al. [50] formed nanotube/polymer membranes by dispersing multi-walled CNTs (4 wt.%) throughout a PSf/PVP polymer matrix via phase inversion. PVP seemed to aid in the dispersion of CNTs throughout the membrane casting solution. Mechanical stability (indicated by the degree of elongation to failure) is enhanced in the mixed matrices with well-dispersed nanotubes; however, the presence of CNT aggregates seems to reduce stability. The blended membranes did not display the desired antimicrobial activity because the contact between organisms and the CNTs stabilized in the polymer matrix is not sufficient to enable inactivation. Future applications may attempt to expose CNTs to solution for antimicrobial applications.

CNTs have attracted attention to novel environmental applications. Brady-Estevez et al. [51] demonstrate the use of CNTs for the removal of viral and bacterial pathogens from water at low-pressure inputs. A thin coating of bundled single-walled CNTs (maximum gap ~0.3 μm) is overlaid on the surface of a PVDF microporous membrane (5 μm pore size). After passing water through the filter all *E. coli* cells (~2 μm) are removed, likely due to size exclusion. More importantly, a fluorescence-based viability test proves that nearly 80% of the bacteria are inactivated after 20 min contact time (an eight-fold increase over the uncoated microporous membrane). This result is confirmed with a metabolic activity test that finds only 6% of the *E. coli* cells are metabolically active following interaction with the filter. Viral pathogen removal is exhibited by passing a suspension containing a model virus, MS2 bacteriophage (~27 nm), through the filter. Size exclusion is not enough to explain the virus removal seen, even with the presence of the nanoporous coating. Results of viral inactivation by the CNT-coated filter are conclusive, yet vary with CNT layer thickness indicating a lower limit of contact time required for inactivation. Full virus removal (5–7 log removal) is observed with a 6 μm skin layer; 3.2-log removal is seen with a thin 2 μm layer. Such uses of CNTs offer an exciting opportunity for use in disinfection and water filtration.

In theory, aligned cylinders formed through nanostructuring of block copolymers could enable a fully polymeric analog to aquaporin or aligned CNT membranes, providing an opportunity to take advantage of nanopore performance, while maintaining ease and economy of large-scale polymeric membrane fabrication. Membranes with aligned nanopores formed by self-assembly of block copolymers during phase inversion offer a significant promise as fully polymeric

analogs to aquaporin and aligned CNT membranes. In principle, these structures could be fine-tuned for water filtration applications, but may also serve as more ideal support substrates for high-flux, high-selectivity forward, and RO membranes for desalination and osmotic power production [52].

5. Materials and Methods

The work, following this review will involve studies on the desalination process of saline water. It will further entail water quality, in order to examine the water quality before the proposed desalination systems and water quality of the desalinated samples in different conditions. Therefore, the focus point will be the energy-efficient, greener approaches to synthesis and modification of a variety of nanomaterials to meet the present and future challenges. It will help the material scientist to have a comprehensive overview of the current situation and will provide decision-makers a guide for future planning in the treatment of saline water in closed and open systems on larger scales. During the research will do modification in the original CNT and zeolite membrane to make it more effective for saline water treatment. The aforementioned membrane nanotechnologies based on two categories:

- Performance enhancement included; (a) permeability, (b) selectivity, and (c) robustness over the current state-of-the-art. Robustness encompasses chemical, mechanical, and thermal stability as well as fouling resistance and enhanced cleanability.
- State of commercial readiness included; (a) anticipated material costs, (b) manufacturing scalability, and (c) apparent time to commercialization.

Those membrane nanotechnologies that promise significant performance improvements over current industry standard membranes were ranked positive, those that offer lower performance were ranked negative, and those that did not change the performance (or if no information was available) were given a neutral score. Membrane nanotechnologies close to commercial reality, cheaper than the state-of-the-art, and capable of being produced using existing membrane manufacturing infrastructure were ranked positive, those judged oppositely were ranked negative, and those not promising change in the specific metric (or if no information was available) were given a neutral score. The scores adapted only for Zeolite and CNT membranes nanotechnology reviewed above are shown in Table 4.

6. Discussion

Zeolite coated ceramic membranes promise improved performance with marginal changes in current inorganic membrane fabrication methods (i.e., low-cost impact). However, these innovations are not out of the laboratory yet and will most likely be limited by the same factors that have always limited ceramic membranes—high capital cost and low membrane area density relative to polymeric membrane equivalents. Zeolite membranes have been proven effective in laboratory studies, but more research needs to be done to produce commercially viable systems. Zeolitic coatings promise the ability to tune the molecular selectivity of ceramic membranes. Thanks to the extreme stability of inorganic materials, these membranes may have a future in desalination and purification of challenging wastewaters (needs currently met primarily by polymeric membranes); however, the synthesis of zeolite films must be improved to obtain thinner layers and achieve competitive water permeability without sacrificing selectivity. In terms of potential performance enhancements, zeolitic coatings are given a –1 rating for productivity because currently, these achieve lower flux than commercially available materials. These were rated neutral in terms of selectivity since rejections comparable to current membranes have been shown. These materials were given a +1 rating for robustness, however, because they pose a more chemically and thermally stable alternative to current membranes typically applied for high pressure and complex water separations. Zeolitic coatings are given neutral scores for commercial viability, with the exception of cost-effectiveness. The materials to produce fully zeolitic coatings made presumably cost more than typical polymer membrane materials and ceramic materials and so a –1 rating is assigned.

Zeolite TFNs show no significant change to membrane selectivity; however, nanoparticle TFNs do show some decrease in selectivity due to defect formation and so these are given a –1 rating for selectivity. All inorganic-organic materials also show an enhancement in robustness, through either compaction resistance or hydrophilic, antifouling surfaces due to the presence of filler materials, earning them a

Table 4
Comparison of nanotechnology-enabled technologies

Nanotechnology-enabled membrane concept	Potential performance enhancement			Potential commercial viability		
	Productivity	Selectivity	Robustness	Cost-effectiveness	Scalability	Time to commercialization
Nanostructured ceramic membrane: "zeolitic coating"	–	0	+	–	0	0
Inorganic- organic membrane: "zeolite TFNs"	+	0	+	0	+	+
Biologically-inspired membrane: "aligned nanotubes CNTs"	++	++	0	–	–	0

+1 rating for robustness. TFNs containing zeolites, however, have been shown to improve on all aspects of performance using only small amounts of relatively inexpensive filler materials and so were rated neutral for cost-effectiveness given a +1 rating for scalability since it can be produced through current polymeric membrane processes by simply adding nanoparticles to the casting or coating solutions, early stages of TFN membranes are now commercially available, earning them a +1 score. Biologically-inspired membranes all promise extremely high-performance enhancements but are currently far from commercial reality.

Aligned nanotubes CNTs membranes have also been predicted and shown to reach extreme flux enhancements, earning them a +2 rating for productivity. All biologically-inspired membranes promise to alter the bounds of membrane selectivity with extremely narrow pore distributions. The regular morphology of these membrane materials earns them a +2 for selectivity. Both aquaporin and nanotube-based membranes show no significant changes in membrane robustness if cast within or atop polymeric matrices; however, at this stage pure block copolymer membranes tested are less mechanically stable than current polymeric membranes available. Nanotubes are expensive to purify and have not yet been formed in large membrane areas and so receive a –1 rating for cost-effectiveness and scalability. Aligned CNT films have been produced uniformly, but only over small surfaces. At this point, both materials are in the laboratory production phase and so earn neutral scores for time to commercialization. If the polymerization conditions can be mastered so that fabrication of Aligned nanotube structures can occur reliably and at large scales with minor changes to infrastructure, they will pose a promising, low cost, the fully polymeric counterpart to high-performance aquaporin, and CNT membranes. Biologically-inspired membranes promise the greatest separation performance enhancements; however, their cost and robustness are unproven and they appear most challenging to produce for large commercial applications.

The ideal technology offers both revolutionary performance enhancements and is already commercially available. The zeolite TFN membranes offer moderate performance enhancement and appear nearest to commercial viability. None of the membrane nanotechnologies fell in the optimal, but this could change over time.

7. Final remarks

Nanofiltration membranes have had successful in water and wastewater treatment, desalination, pharmaceutical, biotechnology, and food applications. Desalinating the saline water can represent an important alternative resource for water utilities. High-pressure membranes that use RO and nanofiltration are recognized as viable desalination technologies. Although several membranes are available on the market, there is no universal and systematic protocol for evaluating their performance. Developing such a protocol will allow utilities to standardize membrane-screening procedures, which ultimately benefits the manufacturers as well as the utilities. Indeed, one may conclude that nanofiltration is one of the most powerful water treatment processes when the membranes and operating conditions are carefully chosen.

This filtration process exhibits critical attractive features such as ease of operation, reliability, comparatively low energy consumption level, and high efficiency of pollutant removal.

New developed nano functionalized membranes like as CNT membranes and other chemicals substrate using in various fields of research and industries. The manufacturing process and microscopic structure of nanoporous ceramic membranes, mainly focusing on zeolite materials, as well as the energy-saving effect of membrane separation expected in various chemical synthesis processes. It is expected that more and more separation membrane technologies that can fulfill the needs of various chemical synthesis processes are developed, and a significant reduction in environmental load in the chemical synthesis industry is also achieved.

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