



Review Paper

Recent Progresses in Preparation and Characterization of RO Membranes

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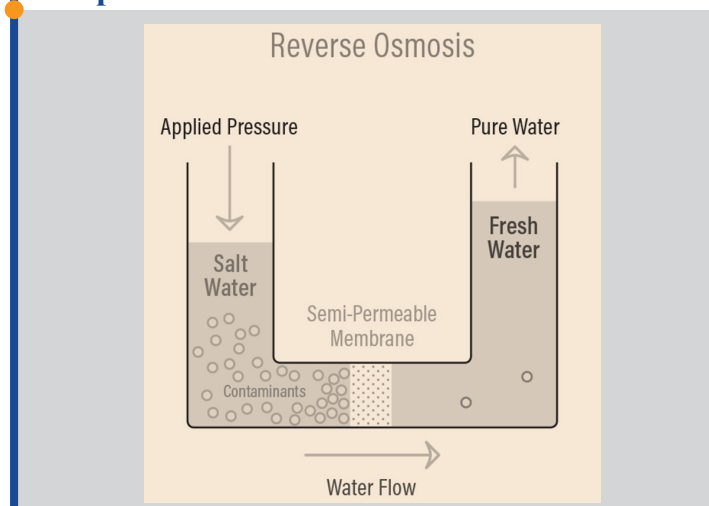
Keywords

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Highlights

- Recent progress in preparation of membranes from different materials is discussed.
- Different aspects of RO membranes and proposed characterization methods, as well as recent progresses have been reviewed.
- Inorganic membranes have potential in future.

Graphical abstract



Abstract

Reverse osmosis (RO) is a water purification technology that uses a semipermeable membrane to remove ions, molecules, and larger particles for the production of drinking water. The first RO membrane for seawater desalination, wastewater treatment and other applications were made of cellulose acetate. But, the polyamide thin-film composite membrane that can tolerate wide pH ranges, higher temperatures, and harsh chemical environments is the most popular, currently. To further improve the membranes' performances, the recent trend in polymer-based membrane research has been focused to investigate various types of nanocomposite membranes, in which nanosized fillers such as SMCNT, MWCNT, graphene, graphene oxide, silica, or zeolite are incorporated. However, there are many challenges to commercialize the application of these membranes. Nowadays, it is a norm to characterize membranes by the advanced characterization techniques such as Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscope (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy and others for studying the physical and chemical properties of membranes and to co-relate those properties to the performances of the membranes. In this work, different aspects of RO membranes and proposed characterization methods, as well as recent progresses have been reviewed, comprehensively.

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1. Introduction

Reverse osmosis (RO) is currently the most important desalination technology, experiencing significant growth. It is a separation process that uses hydrostatic pressure to drive a solution (usually a saline brine) passes through a membrane. In better words, RO membrane retains the solute on one side and allows the solvent to pass to the other side. RO is an efficient desalination technology for providing safe drinking water from saline resources, including brackish and sea water. The membranes used for RO have a thin dense barrier layer at the top of the membrane, where most separation occurs (i.e. selective layer). In most cases, the membrane is designed to allow only water to pass through this dense layer, while preventing the passage of solutes (such as salt ions). In RO, chemical potential difference of the solvent is the driving force for the solvent flow through the membrane, which is achieved by applying hydrostatic pressure on the feed to overcome the osmotic pressure difference between the feed and permeate. Recently, many review papers on RO have appeared demonstrating historical background, development and etc. In the proposed review papers, nano-structured membranes are often discussed, including zeolite membranes, thin film nano-composite membranes, carbon nano-tube membranes, and biomimetic membranes [1-4]. It is proposed that these novel materials represent the most likely opportunities for enhanced RO performance in the future, but a number of challenges remain with regard to their practical implementation.

Soltanieh and Gill [5] published a review on the RO technology and discussed in particular, the structure and properties of membranes and membrane transport theory after a short introduction to membrane processes. In a recent review, Rodríguez-Calvo et al. [6] discussed the limitation of solvents and polymeric materials used in RO membrane preparation. Then, authors discussed on inorganic membranes, mainly made of zeolites, which can offer higher tolerance to a variety of feed waters and harsh cleaning methods. They have further discussed on two carbon derived materials. Carbon nanotubes exhibit high permeability and high rejection rate, and graphene exhibits high breaking strength but is impermeable to molecules as small as standard gases. Finally, they discussed on a novel concept of membranes called Mixed Matrix Membrane (MMM) which combines organic and inorganic material and the benefits of both.

Today, RO systems can be found in a wide range of facilities: kitchens, hospitals, food industries, dairy industries, refineries, power plants, pulp and paper industries, crude palm oil milling, semiconductor manufacturing facilities, manned spacecraft, sailboats, and etc. For instance, RO membranes in desalination plants are represented by 60% of the total number of worldwide desalination plants [7].

2. Properties and morphology of reverse osmosis membrane

The performance of RO membrane is, most importantly, governed by the properties of the membrane used in the process. These properties depend on the chemical nature of the membrane material (almost always a polymer) as well as its physical structure. In general, RO membranes fall into two categories:

- i) Asymmetric membranes containing one polymer,
- ii) Thin-film, composite membranes consisting of two or more polymeric (or even mixed matrix with inorganic particles) layers.

Asymmetric RO membranes have a very thin, permselective skin layer supported on a more porous sublayer of the same polymer. The dense skin layer determines the fluxes and selectivities of these membranes, while the porous sublayer serves only as a mechanical support for the skin (selective) layer. In better words, the sublayer (support layer) has little effect on the membrane separation properties. Since the skin layer is very thin (from 0.1 to 1 μm), the membrane resistance to water transport (which is proportional to the dense skin thickness) is much lower. As a result, the water flux is much higher than symmetric membranes. In the thin-film composite (TFC) membrane, on the other hand, the permselective layer and the porous support layer are made of different materials. Hence, they can be chosen according to the desired properties. TFC membranes can tolerate wide pH ranges, higher temperatures, and harsh chemical environments. Water flux and solute separation characteristics have also been highly improved. These membranes are loaded in two types of RO modules:

- i) Spiral wound
- ii) Hollow fiber

Both are designed to increase the surface/volume ratio but the ratio is much higher for hollow fiber module. The main features of RO membrane are as follows [8]:

- i) It eliminates all pollutants such as heavy metals, virus, bacteria and organic chemicals through pores of sub nanometer size.
- ii) It separates electrolytes better than non-electrolytes. It can eliminate not only the substances of particulate nature, but also the substances of ionic nature, the size of which is very small.
- iii) It separates substances without changing their phase, and is applicable to various fields as it has good physical and chemical durability.

3. Preparation of membrane

3.1. Preparation by phase inversion method

Phase inversion is a process of controlled polymer transformation from a liquid phase to solid phase. There are four basic techniques used to create phase inversion membranes including precipitation from vapor phase, precipitation by controlled evaporation, thermally induced phase separation, and immersion precipitation. Out of the four, immersion precipitation is the most widely-used technique for preparing polymeric membranes.

i) Precipitation from the vapor phase

Once a solvent-polymer mixture is cast on the film, it is placed in a vapor atmosphere that contains a nonsolvent saturated with the solvent in the casting dope. Due to the high concentration of solvent in the vapor atmosphere, the solvent from the cast film stays instead of evaporating into the atmosphere. Membrane forms by diffusion of nonsolvent into the cast film. This process results in a porous membrane.

ii) Precipitation by controlled evaporation

The polymer in this case is dissolved in a solvent and nonsolvent mixture. The evaporation of the solvent due to high volatility occurs, causing the composition to have a higher nonsolvent and polymer content. The polymer eventually precipitates and forms a skinned membrane.

iii) Thermally induced phase separation

A mixed or single solvent/polymer solution is cooled down to achieve phase separation. This method is often used in preparing microfiltration (MF) membranes.

iv) Phase inversion via immersion precipitation

Phase inversion via immersion precipitation is the most widely-used membrane preparation method. A polymer plus solvent (polymer solution) is cast on a proper supporting layer and then submerged in a coagulation bath containing nonsolvent. Due to the solvent and nonsolvent exchange, polymer precipitation takes place. The combination of phase separation and mass transfer affects the membrane structure.

3.2. Preparation of thin film composite membrane

TFC membranes can be made via several methods, including interfacial *in-situ* polymerization, solution coating, plasma polymerization or surface treatment. However, the interfacial *in-situ* polymerization method is currently by far the most popular method. The method of TFC membrane fabrication is described in section 4.1.2 more in detail.

3.3. Preparation by layer by layer method (LBL)

The membranes prepared by LBL (layer by layer) method have the potential to be applied to various different aspects of water treatment like water softening, desalination and recovery of certain ions [9]. But, this method is currently not used in large scale membrane manufacturing. By this technique, a polycation and a polyanion are alternately deposited on a substrate and are adsorbed by electrostatic interaction. The advantages of this technique are as follow [10]:

- i) Film thickness can be controlled at the nanometer scale which is necessary for the high water flux.
- ii) Film properties can be optimized by varying the type of polyelectrolytes and deposition conditions.

- iii) The surface charge of the film can be made, either positive or negative, depending on whether the outer film is specified with a polycation or polyanion.
- iv) Rough morphology of the membrane can be smoothed by polyelectrolyte deposition.

4. Materials used for RO membranes

RO membrane material can be divided in two categories i.e. organic and inorganic.

4.1. Organic RO membranes

The majority of the commercially manufactured RO membranes are made from cellulose acetate and polyamide. Different polymeric materials were proposed with excellent performances during the early development period of RO membranes, but only the above two materials could survive in the market. Yet, the search for alternative polymeric materials is being continued.

For example, SRI's Materials Research Laboratory has recently announced an advanced hollow-fiber membrane for reverse osmosis that is based on a sulfonated-imidazole (SIM) polymer. It is currently being tested for shipboard desalination of seawater and brackish water [11]. Nowadays, the mainstream of RO membrane development is the fabrication of nano-structured RO membranes. Many scientists believe that nanotechnology could possibly bring revolutionary advancements to the desalination industry. In order to improve the membrane performances, the recent trend in polymer-based membrane research has been focused on various types of nanocomposite films as an active layer of RO membrane, so-called nanocomposite membranes, in which these films are fabricated using a nanosized filler such as MWCNT, graphene, graphene oxide, silica, or zeolite [12].

4.1.1. Cellulose acetate and cellulose based membranes

Cellulose acetate (CA) is the acetate ester of cellulose that is world's most abundant organic compound. Cellulose triacetate, also known simply as triacetate (CTA and TAC), is a chemical compound manufactured from cellulose and a source of acetate esters, typically acetic anhydride. CTA is then partially hydrolyzed to form cellulose acetate in which about 2.5 of the 3 hydroxyl groups of cellulose are acetylated. The hydrophilic nature of cellulose acetate comes from the hydroxyl group left unreacted, the presence of which is desirable in osmotically driven membrane processes. Membranes made of cellulose acetate have mainly been used for brackish water or seawater desalination and also for filtering methanol, ethanol, and urea in a reverse osmosis process.

Cellulose acetate (CA) membranes are the oldest form of commercial RO membranes. They are available in diacetate (actually it is 2.5 acetate as above mentioned) and triacetate grades as well as blends of the two. All commercial CA membranes are structurally classified as asymmetric membranes. The dense surface skin "membrane" and the thick supporting under layer have the same composition, but are structurally dissimilar. It is worth quoting that RO membranes were first developed from cellulose diacetate and cellulose triacetate (CTA). These CA based membranes have been in commercial use for many years. The hollow fiber CTA membrane is still being used for seawater desalination. This wide spread use demonstrates the superior properties of CTA for RO membranes that can be produced with a wide range of permeability, from low-flux to super high-flux performances [13].

Researchers at the Bureau of Reclamation have developed a new generation of CA membranes that demonstrate higher rejection of salts than that of current CA membranes leading to reduction of operational cost of RO treatment [14].

Duarte et al. [15] investigated the optimization of the composition of cellulose acetate for RO membrane preparation. It was concluded that the best membrane formulation had the following composition: 45.77 wt % dioxane, 17.61 wt % acetone, and 8.45 wt % acetic acid (solvents); 4.22 wt % cellulose triacetate and 9.86 wt % cellulose diacetate (polymers); 14.09 wt % methanol (non-solvent); and 0.5 wt % cellulose fibers (with respect to the total polymer content).

Silva et al. [16] developed a hybrid membrane based on CA with embedded silver and/or aluminum nanoparticles, for the remediation of contaminated aquatic environments with microorganism. The membranes can also be used for remediation of water contaminated with phosphate ion. The developed membranes showed good antimicrobial behavior preventing the growth of microorganisms. The results indicated that the synthesized CA/Ag-NPs/Al-NPs membranes could have potential to be used in the remediation of water resources.

Bódaló et al. [17] studied the behavior of cellulose acetate membranes (commercially available) in the RO treatment of aqueous solutions containing ammonium ion by using the simulation model for a semi-batch and unsteady-state system based on Slater's et al.'s [18] work. It was reported by the authors that SEPA SS1C membrane from Osmonics Inc. can be used for the removal of ammonium ions from aqueous solutions with a rejection factor higher than 98%.

Mosry et al. [19] modified a CA-RO membrane, prepared by phase inversion, by grafting 2-acrylamido-2-methylpropanesulfonic acid (AMPSPA) on the top surface of the membrane. Grafting improved the hydrophilicity, salt rejection and water flux performances. The effect of the grafting percentages of AMPSPA on the water flux and salt rejection was studied using a cross flow RO unit. The salt rejection and water flux of the grafted CA-RO membrane with 15 wt% were 99.03% and 6 L/m²h.

Ali and Abdallah [20] developed RO membranes by blending a matrix polymer of polyethersulfone (PES) and cellulose diacetate (CA) by phase inversion. The heat treatment of casted blend membrane at annealing temperature 120 °C improved mechanical properties of the blend membrane. The developed membranes' permeate flux measured at 21 kg/m²h and the salt rejection measured at 99%.

Perera et al. [21] developed a cellulose acetate thin film composite (CA TFC) membrane by direct casting of CA onto an UF membrane support. The flux through the CA TFC membrane was inversely proportional to the selective layer thickness. The membrane with the lowest thickness of the CA film (217 nm) initially had poor salt rejection (~55%), but relatively high permeability (~0.5 L/m²h bar). The membrane was modified by subsequent swelling in room temperature water baths, thermal annealing at 81 °C, and with room-temperature incorporation of silver nanoparticles onto CA TFC surfaces by chemical reduction. Without significant flux deterioration, modified membrane showed about 94% salt rejection. It was also observed that the swelling time generally improved the flux performance whilst the silver nanoparticle treatment reduced bacterial surface coverage by four orders of magnitude.

Hassanien et al. [22] synthesized and characterized a multilayer PVA/CA/PEG RO membrane and reported that the PVA/CA/PEG composite multilayer membrane is acceptable for practical uses in desalination of brackish, highly saline and sea (extremely saline water) water, where the salt rejection (%) was 70, 63 and 59, respectively. The water salinity of brackish (3333 mg/L), highly saline groundwater (13986 mg/L) and sea water (42847 mg/L) became 933, 5059 and 16722 mg/L after desalination time of 24 h.

Recently, cellulose acetate membranes have been replaced by the polyamide (PA) based TFC membrane for the following reasons.

- i) CA membranes are susceptible to hydrolysis by acids and alkalis, leading to poor rejection.
- ii) CA membranes are also susceptible to biodegradation, and chlorine feed treatment is often required.
- iii) CA membrane's salt rejection is lower than TFC membrane.
- iv) CA membranes are workable in a narrow pH range (4-8).
- v) CA membranes are workable in a relatively narrow temperature range (0-35°C).
- vi) CA membranes are subject to compaction at high operating pressures.
- vii) CA membrane's permeability is lower than TFC membranes, requiring higher pressures and operating costs.

Despite above mentioned drawbacks, CA membranes are still in use after four decades of their introduction. The reasons behind are CA membranes are less expensive, simple in manufacturing technique, have a longer life, require less cleaning, and are much more resistant to chlorine in comparison of PA-TFC membrane

4.1.2. Polyamide based membranes

Polyamide (PA) TFC membrane consists of a polyester material upon which a porous substrate (usually polysulfone) is cast for mechanical support. The active layer, which is deposited as a thin film on the porous layer consists of a crosslinked PA layer. In the nineteen seventies, Cadotte and co-workers [23-25] announced TFC membrane fabricated by the interfacial polymerization (IP) technique. Interfacial polymerization is a type of step-growth polymerization in which it occurs at an interface between an aqueous solution containing one monomer and an organic solution containing a second monomer. The most common polymer made by this method is polyamide, where diamine and diacid chloride react to form polyamide and hydrogen chloride [26]. In the last 40 years, a significant progress has been made in the development of composite membrane using IP technique for water and wastewater purification purposes. The performance of the top selective layer of TFC membrane can be basically determined by its physiochemical properties such as permeability, selectivity, surface roughness, charge

performance and hydrophilicity. TFC membranes have a thin and dense active layer that controls membrane performance (i.e. permeability and selectivity), and a much thicker porous substrate that provides mechanical support to the active layer. In order to achieve high values of permeability and selectivity, the active layer should be ultrathin and (super)-hydrophilic [27].

Khorshidi et al. [28] discussed to enhance water permeability of thin film composite (TFC) polyamide membranes by decreasing the thickness of the selective PA layer. The composite membranes were prepared by interfacial polymerization (IP) reaction between meta-phenylene diamine (MPD)-aqueous and trimesoyl chloride (TMC)-organic solvents at the surface of polyethersulfone (PES) microporous support. A number of PA TFC membranes were prepared at different temperatures of the organic solution, ranging from -20 °C to 50 °C. It was reported that the TFC membranes, synthesized at sub-zero temperatures of organic solution, had thinner and smoother PA layer with a greater degree of cross-linking and wettability compared to the PA films prepared at 50 °C. The most water permeable membrane was prepared at -20 °C and exhibited nine times higher water flux compared to the membrane synthesized at room temperature.

El-Aassar [27] fabricated a variety of PA-TFC membranes via IP technique. IP technique was carried out between aqueous solution of MPD and TMC in dodecane as organic solvent onto polysulfone (PSf) supporting membrane. RO performance, including permeate flux (L/m²h) and salt rejection (%), was evaluated as a function of the synthesis conditions to investigate the optimum conditions that give the best performance membrane. The optimum conditions of synthesized membranes were soaking in MPD solution (1.5 wt.%) for 5 min and soaking in TMC (0.05 wt.%) for 30 s. The best synthesized membrane exhibited high salt rejection (99.81%) with high permeates flux (36.15 L/m²h) (2000 ppm NaCl, pH range 7 ± 0.2 at 25 °C, flow rate 1 g/min, applied pressure 225 psi (15.5 bar)).

Joshi et al. [29] prepared a TFC RO membrane by using 1,3-phenylene diamine in the gelation bath, as well as in coating conditions. The membrane was prepared on an asymmetric polyethersulfone via IP reaction of 1,3-phenylene diamine and trimesoyl chloride at water-hexane interface. The salt rejection performance followed the order of Na₂SO₄>NaCl> MgSO₄> MgCl₂, as expected.

Tarboush et al. [30] suggested a new concept for the preparation of TFC RO membrane by IP technique on porous PSf support using novel additives. Hydrophilic surface modifying macromolecules (LSMM) were synthesized both *ex-situ* by conventional method (cLSMM), and *in-situ* within the organic solvent of the TFC system (iLSMM). It was reported by authors [30] that the RO performance results showed that the addition of the cLSMM significantly decreased the salt rejection of the membrane and slightly reduced the flux. But, in the case of the iLSMM, salt rejection was improved but the flux declined at different rates for different iLSMM concentrations.

Cath et al. [31] reported that the TFC polyamide membrane exhibited higher water and salt permeability than the asymmetric cellulose-based membrane. But, results with the high permeability TFC membrane were more scattered. While salt rejection results in RO mode were relatively similar, salt permeability coefficients for both membranes in FO mode were more varied. Results suggested that for high permeability ODMP (osmotically driven membrane processes), membranes should be tested at lower hydraulic pressure in RO mode and that RO testing should be conducted with the same membrane sample used for testing in FO mode.

The presence of nanoparticles (NPs) on the membrane surface augmented hydrophilicity. Dong et al. [32] fabricated thin film nanocomposite (TFN) membranes incorporated with NaY zeolite nanoparticles via interfacial polymerization (IP) of trimesoyl chloride and m-phenylenediamine on nanoporous polysulfone supports. Under the optimum conditions, the water flux increased from 0.95 to 1.78 m³/m²/day (23.3 to 43.7 gal/ft²/day (gfd)) with incorporating the zeolite nanoparticles, while provided a high salt rejection of 98.8% (2000 ppm NaCl solution, 225 psi (1.55 MPa), 25 °C). It was observed that a longer IP reaction time was necessary to form a denser zeolite-polyamide layer for higher salt rejection, and the optimum zeolite loading. When the TFN membranes were treated with aqueous solutions containing glycerol, camphorsulfonic acid-triethylamine salt, and sodium lauryl sulfate, water flux was further improved.

Zhao and Ho [33] studied the effect of hydrophilic additive on the performance of TFC RO membranes. They fabricated a TFC membrane by incorporating the hydrophilic additive, o-aminobenzoic acid-triethylamine (o-ABA-TEA) salt, into the aqueous m-phenylenediamine (MPD) solution to react with trimesoyl chloride (TMC) in the organic solution during the interfacial polymerization on a nanoporous polysulfone support. The membrane was used for seawater desalination. The synthesized membranes showed a very high flux of 1.81 m³/m²/day (44.4 gallons/ft²/day (gfd)) and a salt rejection of 99.41% (3.28 wt% NaCl solution under seawater desalination conditions at 800 psi (5.52 MPa) and 25 °C).

Kwak et al. [34] fabricated hybrid organic/inorganic RO membranes

composed of aromatic polyamide thin films underneath titanium dioxide (TiO₂) nanosized particles. The hybrid TFC aromatic polyamide membranes were prepared by self-assembly of the TiO₂ nanoparticles on the polymer chains with -COOH groups along the surface. It was observed that water flux was slightly increased. Moreover, the antibacterial fouling potential of the TiO₂ hybrid membrane was improved when compared with the membrane without TiO₂ particles.

Peyki et al. [35] modified the TFC polyamide RO membranes by silica (SiO₂) nanoparticles. FT-IR spectroscopy revealed that the polymerization reaction was completed. Moreover, SEM images of the prepared membranes indicated that the nanoparticles were successfully placed on the membrane surface. This means that all the membranes had composite structure with a spongy sublayer. The surface roughness and hydrophilicity increased with an increasing SiO₂ content in the aqueous amine solution. Moreover, the flux of the membranes increased gradually at lower levels of nanoparticles (0.005–0.1 wt.%), and then decreased at 0.5 wt.%. The NaCl rejection had also a maximum level at 0.005 wt.%. The modified membranes showed better antifouling properties.

Al-Hobaib et al. [36] embedded silver oxide nanoparticles into the polyamide membrane via IP technique, between MPD and TMC. Modified membranes were characterized by EDX (Energy Dispersive X-ray Spectroscopy), AFM (atomic force microscopy), TEM, and contact angle measurements. Hydrophilicity of the membranes was improved and the contact angle decreased to 41° at 0.009 wt% silver oxide. It was reported that the flux increased from 26 to 40 L/m² h and the salt rejection was 99%, with 0.003 wt% Ag₂O nanoparticles.

Ghanbari et al. [37] fabricated a new type of TFN RO membrane which was prepared by incorporating different amounts of halloysite nanotubes (HNTs) into the polyamide selective layer via *in-situ* IP reaction. It was concluded that incorporating an appropriate amount of HNTs into the PA selective layer could potentially improve the performance of TFC membrane during RO process.

Baroña et al. [38] developed a new method to fabricate TFN membranes composed of aluminosilicate single-walled nanotubes (SWNT) in a polyamide matrix for low pressure RO process using IP technique. With the incorporation of the aluminosilicate SWNT, higher permeate flux was achieved while sustaining high rejection of monovalent and divalent ions. As the aluminosilicate SWNT content in the polyamide layer increased, the water flux increased, too. The polyamide TFC membrane showed a water flux value of 10.5 L/m²h at 16 bar. This value increased almost 50% as the aluminosilicate nanotubes (TFN-1, 0.05% (w/v) of SWNT in TMC-hexane solution for loading) were incorporated to polyamide matrix. The pure water flux increased to as high as 24.6 L/m²h, a 1.5-fold magnitude increase, as 0.59 wt.% of aluminosilicate nanotubes in PA active layer (TFN-3, 0.2 % (w/v) of SWNT in TMC-hexane solution for loading) was incorporated.

In another work, Qui et al [39] fabricated a composite RO membrane with extra-thin separative layer by the IP reaction of metaphenylene diamine (MPD) with trimesoyl chloride (TMC) on the surface of polysulfone (PS) support membrane. The effects of the monomer concentration on membrane flux and salt rejection were investigated, comprehensively.

Kim et al. [40] fabricated nanocomposite RO membranes made from sulfonated poly(arylene ether sulfone) containing amino groups (aPES) and hyper-branched aromatic polyamide-grafted silica (HBP-g-silica). The performance of the RO membranes containing aPES and HBP-g-silica were comprehensively evaluated. The salt rejection and water flux were measured at 96% and 34 L/m²h, respectively. It was concluded that the functional amino groups of HBP-g-silica nanoparticle and additional amide bond of active layer from HBP-TMC effectively protect the membrane surface from chlorine attack in water and improve the membrane's hydrophilicity.

Several reports have acknowledged the benefits of adding carbon nanotubes to aromatic PA nanocomposite membranes. Recent research on the transport of water through hydrophobic double-walled carbon nanotubes is promising, demonstrating water fluxes that are over three orders of magnitude higher than those predicted from continuum hydrodynamic models.

Cruz-Silva et al. [41] prepared a high flux RO nanocomposite PA membrane by interfacial polymerization in presence of multiwalled carbon nanotubes (CNTs). It was reported that the addition of CNTs not only improved the membrane performance in terms of flow and antifouling features, but also inhibited the chlorine degradation of membranes.

Ratto et al. [42] made a patent in which they compared membranes fabricated with and without embedded CNTs, to demonstrate the enhanced flow generated by the CNT pathways. Based on the obtained results, it was concluded that with CNT's presence a slightly higher salt rejection was achieved (97.69% as compared with 96.19% (without CNTs)). Moreover, a near doubling water flux (44 L/m² day bar as compared with 26 L/m² day bar) was obtained.

Polyamide RO membranes with carbon nanotubes were prepared by Kim

et al. via interfacial polymerization of TMC in n-hexane and aqueous MPD solution using functionalized carbon nanotube as fillers. [43]. The RO membrane containing the nanotubes in this work also showed improved durability and chemical resistance against NaCl solution compared with the RO membrane without any nanotubes. These characteristics were due to the hydrophobic nanochannels of carbon nanotubes and well-dispersed states in the polyamide layers formed through the interactions between them and polyamide in the active layers.

Zhang et al. [44] synthesized acidified MWNTs (multi-walled nanotubes) from pristine MWNTs, and prepared MWNT-polyamide nanocomposite thin films via the interfacial polymerization technique. The modified TFC membrane's surface morphology was studied by SEM, FTIR, contact angle and TEM. It was revealed that modified MWNTs yielded some hydrophilic groups, such as -COOH and -OH, which make acidified MWNTs disperse more evenly in the aqueous solution. As a result, the MWNT-polyamide thin film nanocomposite membranes have more hydrophilic surface in comparison with bare polyamide membrane. Water flux of MWNT-polyamide membranes improved dramatically. The SEM and TEM results demonstrate that the functionalized MWNTs penetrate through the polyamide layer, and might play the role of water channel. For 2000 ppm NaCl solution, the water permeability increases from 26 L/m²h without MWNTs to 71 L/m²h at the acidified MWNTs loading of 0.1% (w/v), while NaCl rejection of MWNT-polyamide membranes decreases obviously compared to bare polyamide membrane. It was claimed in this work (see Ref. [44]) that this MWNT polyamide thin film nanocomposite RO membrane will have a potential application in separation of organic aqueous solution.

In another work, Inukai et al. [45] fabricated RO composite membrane using multi-walled carbon nanotubes (MWCNT) and aromatic polyamide (PA) via the interfacial polymerization technique. It was reported that a suitable amount of MWCNT in PA, 15.5 wt. %, not only improves the membrane performance in terms of flow and antifouling, but also inhibits the chlorine degradation of these membranes.

Araki et al. [46] studied the influence of single walled carbon nanotubes (SWCNTs) in the polyamide molecular structure as a model case of a carbon nanotubes/polyamide nanocomposite RO by using molecular dynamics to simulate membrane. It was reported that the addition of SWCNTs increases the Na⁺ and Cl⁻ ion rejection and decreases the pore size of the composite membrane. Analysis of the radial distribution function of water confined in the pores of the membranes shows that SWCNT+PA nanocomposite membranes also exhibit smaller clusters of water molecules within the membrane, so suggesting a dense membrane structure (i.e. SWCNT+PA composite membranes were 3.9% denser than bare PA).

Hegab and Zou [47] demonstrated that various membrane features including mechanical strength, antimicrobial and antifouling properties, selectivity, water flux and thermal properties are significantly improved after the incorporation of GO (graphene oxide). Polyamide RO membranes containing carbon nanotubes with acidic groups (CNTa), graphene oxide (GO), and both CNTa and GO (CNTa-GO) were prepared via interfacial polymerization reaction of trimesoyl chloride solutions in hexane and m-phenylenediamine aqueous solutions containing carbon nanomaterials by Kim et al. [48]. It was observed that performances (such as water flux, chlorine resistance, long-term durability, and mechanical properties) were considerably improved for all membranes containing fillers (i.e. CNTs and GO), when compared to the polyamide membrane without any filler. The largest improvement of membrane performances was observed in the polyamide membrane with CNTa-GO (the mixture of CNTa and GO).

Titanium oxide (TiO₂) is a well-known photocatalytic material, widely used for disinfection and decomposition of organic compounds [49] and these properties make it interesting as an anti-fouling coating. Madaeni and Ghaemi [50] reported the coating of membrane surface with TiO₂ particles and UV radiation resulted in a self-cleaning membrane. Membrane used for this study was TFC-SR composite membrane. This is a hydrophilic reverse osmosis membrane manufactured by the Fluid Systems Company. This composite membrane consisted of three layers. The top layer of the membrane is made of polyvinylalcohol and the support materials were polyarylsulfone-ether and polyester. Surface coating was carried out by self-assembly of TiO₂ particles through co-ordination bonds with -OH functional groups of polymer on the membrane surface. Coated membrane with TiO₂ particles treated with UV radiation. The coated membrane showed higher flux in comparison with flux obtained with uncoated membrane. The flux of the TiO₂-coated membrane after being radiated by UV light was increased, significantly, in comparison with an uncoated membrane. This indicates that the self-cleaning property have been created by TiO₂ particles on the surface of membrane [50].

The modification of PA TFC membrane by chitosan is also an important development. In this regard, Raval et al. [51] demonstrated a novel method to produce a high-flux membrane by surface modification of thin-film composite RO membrane. The TFC-RO membrane was modified by exposing the

membrane to a sodium hypochlorite solution of 1250 mg/L for 30 minutes and 60 minutes at pH 11.0, followed by 1000 mg/L chitosan solution for 60 minutes at pH 2.5. There was up to 2.5 times increment in flux with ca. 3% increase in solute rejection in the case of chitosan-treated membrane. In another work, Raval and Maiti [52] demonstrated that controlled oxidation of polyamide layer by sodium hypochlorite at high pH improved flow performance of the membrane. Moreover, the TFC RO membrane became more hydrophilic by proposed treatment.

4.1.3. Biomimetic aquaporin membranes

Recently, aquaporin based biomimetic membranes have caught attention due to their intrinsically high water permeability and salt rejection of aquaporin. Commercializations of aquaporin incorporated TFC membranes are now being attempted.

Tang et al. [53] published a review paper on the properties of aquaporin's, their preparation and characterization methods. Highly permeable membranes with high salt rejection performance can be obtained based on aquaporin protein function [54]. Kumar et al. [54], based on the measured water permeability of AqpZ containing proteoliposomes, postulated that AqpZ based biomimetic membranes can potentially achieve a membrane permeability as high as 167 $\mu\text{m}^2/\text{s bar}$ (i.e., 601 $\text{L}/\text{m}^2 \text{h bar}$). This is about two orders of magnitude more permeable compared to existing commercially available seawater RO membranes [55]. Zhao et al. [56] successfully fabricated an aquaporin-based biomimetic membrane via interfacial polymerization method. It was noticed that the resulting membrane AMB-wild, with area greater than 200 cm^2 , had good mechanical stability when tested up to 10 bar under RO conditions. High water permeability (4.0 $\text{L}/\text{m}^2 \text{h bar}$) and good NaCl rejection (~97%) were observed at an applied pressure of 5 bar. Rejection was further improved at higher pressure. The membrane had superior separation performance compared to investigated commercial RO membranes (BW30 and SW30HR), demonstrating the great potential of intracellularly polymerized ABM membranes.

Several design approaches have been pursued in facing the challenge of making the biomimetic membranes as stable, robust, scalable, and cost-effective as their polymeric counterparts in the form of existing technologies such as RO membranes [55]. However, aquaporin membranes are still in laboratory scale, but production of these membranes can easily be established on an industrial scale (full scale applications) in near future.

4.1.4. Graphene membrane

Graphene made of pure carbon atoms, is arranged in a honeycomb lattice structure at the atomic-level. The use of graphene membranes for RO purpose is still in the very early stage, but it may have a great future in brine desalination.

In 2011 the US National Resources Council reported that the costs of traditional sources of water are from \$0.90 to \$2.50 per 1000 gallons produced. The cost of desalination on the other hand ranges from \$1.50 to \$8.00 for the same amount of water. With the new graphene technology the cost of desalination will now be comparable to traditional water sources [57].

Some recent studies have explored the transport of ions through pores in graphene membranes [58,59]. Casey [60] from the *New Oak Ridge Graphene Research* announced that so far the graphene desalination membrane has passed its tests with flying colors, achieving almost 100% salt rejection while allowing water to flow through at a rapid pace.

"Graphene is hydrophobic -- it repels water -- but narrow capillaries made from graphene vigorously suck in water allowing its rapid permeation, if the water layer is only one atom thick -- that is, as thin as graphene itself. This bizarre property has attracted intense academic and industrial interest with intent to develop new water filtration and desalination technologies" [61].

Suk and Aluru [59] explored the water transport through a porous graphene membrane and compared the results with water transport through thin carbon nanotube (CNT) membranes (less than 10 nm in thickness/length). It was suggested that graphene membrane can be used as an ultra-efficient water transporter, compared to thin CNT membranes, whenever the diameter is larger than 0.8 nm.

While graphene isn't ready, a derivative of graphene may be closer to practical application. A research team at the *University of Manchester*, led by Dr. Rahul Nair and Professor Andre Geim, recently published a paper in the journal Science describing their experimentation with a water filter made of graphene oxide. Graphene oxide, as it turns out, has excellent water filtration properties similar to graphene but is cheaper and easier to produce [62].

4.2. Inorganic RO membranes

4.2.1. Preparation of inorganic membranes

There are different inorganic membranes for a wide range of applications,

but show a few RO membrane performance. Zeolite based membranes, however, exhibit some RO membrane characteristics. There are several methods for fabricating of zeolite membranes which are as follows [63].

1. Embedded method: Barrer and James [64] were the first team to fabricate zeolite membranes in which microcrystalline ion-exchanging zeolites are bonded by inert polymeric fillers in such a way that the electrochemical behavior is determined by the crystals and by crystal contacts. The embedded method is not a good choice due to existence of many defects, and the performance is not reliable, as well.
2. *In-situ* hydrothermal synthesis method: This method is commonly used for preparing the zeolite-based membranes. In this method a porous support is brought into direct contact with the synthesis solution or gel, to allow the growth of a zeolite film on the surface of the support under hydrothermal conditions. The formation of the zeolite membrane under hydrothermal conditions involves different steps including the formation of the supersaturation region adjacent to the substrate surface, nucleation, aggregation, crystallization and crystal growth.
3. Seeding technique (Secondary growth method): To enable better control of nucleation and crystal growth steps, seeding technique would be better than other techniques. In this method, first a colloidal zeolite suspension of sub- μm -sized seed crystals is prepared. These crystals will be coated as a seed layer on the surface of the substrate. Hydrothermal synthesis is followed to grow zeolite film on the seed layer. The preparation of zeolite sol as crystal seeds is the key step in the secondary method.
4. Microwave method: The microwave method for the preparation of zeolite membranes is similar to the conventional hydrothermal method except that the autoclave is placed in a microwave field. The synthesis time is then reduced greatly.
5. DGC (direct gel crystallization) method was first proposed by Xu et al. [65], which is a novel method to synthesize a zeolite-based membrane on porous supports. The zeolite ZSM-5 has been synthesized from amorphous aluminosilicate gels in a vapor of ethylenediamine, triethylamine and water. DGC has the benefit of better thickness control compared with liquid phase synthesis, since the amount of nutrient for growing zeolite is directly controlled by the amount of gel applied.

4.2.2. Properties of inorganic membranes

Inorganic RO membranes are resistant to chlorine and other disinfectants. So, they can withstand steam treatments making them less vulnerable to bio-fouling with a very long lifetime for water treatment applications.

Inorganic membranes can be composed of a wide range of materials (from alpha alumina to zirconia). The most common membranes are made of Al, Si, Ti or Zr oxides. Each oxide has a different surface charge in solution. Zeolites are capable of providing the required desalination properties while being potentially tolerant to feed waters which readily foul polymer membranes and/or can withstand more cost effective cleaning methods [66]. Ceramic membranes "deserve more attention" as they are "energy-efficient and have a much smaller footprint, with a life-cycle cost which is expected to be lower compared with existing membrane systems.

Lin and Murad [67] developed molecular simulation scheme for studying solutions undergoing osmosis, and reverse osmosis was used to study the separation of aqueous solutions using thin ZK-4 zeolite membranes. This method allows for the preservation of the atomic roughness of the membranes, while the molecules that constitute the membranes are also allowed to vibrate. In the proposed simulations, two thin membranes cut from a cubic cell of ZK-4 zeolite were used as the semi-permeable membranes to separate water from aqueous NaCl solutions. Both osmosis and reverse-osmosis phenomena were observed. The study showed (see Ref. [67]) that ZK-4 zeolite membranes show promise for use in membrane-based separation of aqueous electrolyte solutions, as well as other similar systems.

Liu and Chen [68], by using comprehensive molecular dynamics simulations, studied the possibility of employing a zeolite nano-membrane for seawater desalination. Two types of zeolite with different wetting properties, the hydrophilic FAU and hydrophobic MFI, were used as the reverse osmosis membrane. Both zeolite membranes showed 100% rejection of salt ions. The permeability was about 2×10^{-9} $\text{m}/\text{Pa}\cdot\text{s}$ when the membrane thickness was less than 3.5 nm. This data was two orders of magnitude higher than that of the commercial state-of-the-art RO membranes.

In another work, Heiranian et al. [69] reported that a nanopore in a single-layer molybdenum disulfide can effectively reject ions and allow transport of water at a high rate via molecular dynamics simulations. More than 88% of ions are rejected by membranes having pore areas ranging from 20 to 60 \AA . Pore chemistry is shown to play a significant role in modulating the water flux.

Though the improvement of zeolite membranes has been remarkable in the past 10 years, their performance and economics aren't still match for

polymeric membranes. The zeolite membrane thickness is still at least 3 times higher than the current state of the art polymeric RO membranes, causing higher resistance to water flux and due to this, inorganic membranes require at least 50 times higher membrane area than polymeric ones to achieve an equivalent production capacity [70].

4.2.3. Examples of inorganic membranes

Lia et al. [71] reported the use of inorganic RO membranes for brine desalination. They successfully separated ions from aqueous solutions by reverse osmosis process on an α -alumina-supported MFI-type zeolite membrane synthesized by *in-situ* crystallization.

Li et al. [72] used hydrothermal synthesis to develop 0.5–3 μm thick membranes consisting of hydrophobic MFI (mordenite framework inverted) type zeolites with an average pore diameter of 5.6 \AA on a porous α -alumina support. Under an applied pressure of 2.07 MPa (20.7 bar) and with 0.1 M NaCl feed water, the membranes rejected 76% of Na^+ ions while permitting a water flux of 0.112 $\text{kg/m}^2\text{h}$.

In another work, Xu et al. [73] developed a new type of microporous organosilica (sol-gel derived) RO membrane which was chlorine resistant and withstood higher temperatures. Organosilica membranes were prepared using the sol-gel technique via a polymeric route with $(\text{EtO})_3\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}(\text{OEt})_3$ (BTESE) as a single precursor. The membrane rejected isopropanol with rejection higher than 95% including superior molecular sieving ability for neutral solutes of low molecular weight.

Li et al. [74] synthesized MFI-type zeolite membranes with different Si/Al ratios by seeding and secondary growth. Ion separation of 0.10 M NaCl solution by zeolite membranes was investigated through a cross-flow RO system. On incorporating aluminum ions into the zeolite frame work, both water flux and ion rejection increased considerably (water flux increase from 0.112 to 1.129 $\text{kg/m}^2\text{h}$ and ion rejection improvement from 90.6% to 92.9%).

5. Characterization

Characterization of RO membranes is an important issue since this allows insight into the relationship between membrane chemistry, structure, and transport properties. The most widely used characterization method is the measurement of water flux and solute (usually NaCl) rejection. These can be easily measured and so give a quick indication of the suitability of the membrane for a particular application. However, fluxes provide only limited information about the characteristics and structure of the membrane and the role these play in water and solute transport. As a result, other characterization techniques are beginning to be employed in order to determine parameters such as pore size, barrier layer thickness, and membrane elemental composition.

There are many common methods such as bubble point method, liquid-liquid porosimetry, nitrogen adsorption/desorption, permoporometry, scanning electron microscopy, transmission electron microscopy and contact angle measurement to characterize the membranes. Recently, new techniques such as AFM, ATR-FTIR, X-ray Photoelectron Spectroscopy (XPS) are available to go deep to understand the structure, mechanism, morphology, and other features of the membrane, which can help to make desirable membranes. Following are new techniques to characterize the membranes. Ismail et al. [75] described these methods more in detail elsewhere. It should be noted that most of the characterization methods are routinely used nowadays. Therefore, only few typical examples are shown in the following sections.

5.1. Membrane morphology

5.1.1. Scanning electric microscope (SEM)

Scanning electron microscope is used to study the morphology of membrane by examining the top layers and cross-sections in detail. It is a very common tool for membranes' characterization.

SEM equipped with EDS detector (EDAX) was used to image the surface and cross-sections of freeze dried membranes and to identify the elemental compositions and distribution of inorganic particles present on the surface of cake layer formed during fouling process in RO membranes [76].

Perreault et al. [77] studied the strong antimicrobial properties of thin-film composite polyamide membranes by a simple graphene oxide surface functionalization. Surface binding of graphene oxide was demonstrated by SEM and Raman spectroscopy.

5.1.2. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. An image is formed from the interaction of the electrons transmitted through the specimen; the image is

magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD (charge-coupled device) camera. Inukai et al. [45] synthesized high-performance composite thin RO membrane using multi-walled carbon nanotubes (MWCNT) and aromatic polyamide (PA), by the interfacial polymerization. The microstructure of the MWCNT-PA nanocomposite membrane was studied by using high-resolution transmission electron microscopy (HRTEM). It was noticed that traces of PA attached to the surface of MWCNT. It suggested that there was a good interaction between the monomers and the MWCNT walls, forming an ordered region several nanometers thick, in agreement with the SEM observation. By conducting FFT (Fast Fourier Transformation) of TEM images it was revealed that order of the polymer network (pattern) along the nanotubes surfaces might represent a unique aromatic PA structure when compared to the bulk PA.

5.1.3. Atomic Force Microscopy (AFM)

Nowadays AFM is a very common tool to study the surface topography of membranes. AFM is used in RO membranes to find the roughness, nodule size and nodule aggregate, pore size and its distribution, phases on the surface of membranes, and etc. In some cases, roughness is directly proportional to flux. Surface property of RO membranes affecting membrane fouling includes both chemical and physical characteristics. It is believed that membranes with smoother surface are favorable for reducing membrane fouling caused by particulate and organic matters.

Fang and Duranceau [78] analyzed different RO membranes and CA-NF (cellulose acetate nanofiltration) membrane's productivity by AFM technique. Analysis of membrane surfaces by AFM revealed that the higher productivity decline rates associated with polyamide RO membranes as compared to that of a cellulose acetate NF membrane was due to the inherent ridge-and-valley morphology of the active layer. The unique polyamide active layer morphology was directly related to the surface roughness.

5.1.4. Positron annihilation lifetime spectroscopy (PALS)

PALS technique can provide an unprecedented level of insight to our understanding of the internal structure of the active skin layer of RO membranes. It is capable of determining the free-volume and holes' properties directly at the atomic and nano- scale. This capability arises from the fact that positronium (bound state of positron and electron; Ps) is preferentially localized in regions of low electron density sites, such as free volumes, holes, interfaces, and pores. Kim et al. [79], for the first time, showed that the thin films of cross-linked aromatic polyamide RO membranes are composed of two types of pores; i.e. pores with radii of about 2.1-2.4 \AA were detected from the τ_3 lifetime component and those with 3.5-4.5 \AA from τ_4 component. They have identified the former pores as the network pore and the latter aggregate pore. Moreover, this study was applied to explain the flux-enhancement mechanism in thin-film-composite membranes.

5.1.5. Neutron scattering (NS)

Neutron scattering, the scattering of free neutrons by matter, can refer to either the physical process or the experimental technique which uses this process for the investigation of materials. Since neutrons are electrically neutral, they penetrate matter more deeply than electrically charged particles of comparable kinetic energy. Therefore, they are valuable probes of bulk properties. Small-angle neutron scattering (SANS) is a powerful technique to understand the polymer chain nanostructure as well as the pore structure characteristics of the membrane in order to improve the membrane performance. Singh and Aswal [80] studied the typical polyamide RO PA membrane prepared by the interfacial reaction between an aqueous solution of m-phenylenediamine or piperazine and n-hexane solution of trimesoyl chloride using SANS. It was observed that membrane was comprised of nanoscale building blocks.

In another work, Dahdal et al. [81] used small-angle neutron (SANS) technique to understand the fouling mechanism of RO membranes, mainly biofouling and scaling by calcium phosphate.

5.1.6. Electron paramagnetic resonance spectroscopy (EPR)

EPR, also called electron spin resonance (ESR), is a technique used to study chemical species with unpaired electrons. EPR spectroscopy plays an important role in the understanding of organic and inorganic radicals, transition metal complexes, and some biomolecules including studying the structure and function of biological membranes. EPR was also applied to study synthetic membranes. Any substance that has unpaired electrons will give EPR. Polymers themselves contain paramagnetic free radicals.

A stable radical can also be introduced into polymeric material. The radical, so introduced, is often called a spin label or a spin probe. It is invariably a nitroxide radical, which exhibits a three-line hyperfine structure. The peak shape and splitting depend on the radical's environments. The

nitroxide label is a monitor of motion. The shape of the ESR signal depends also on the orientation of the magnetic field relative to the axis of the radical. Thus, the spin label method is useful to study the environment of radicals at a molecular level.

Khulbe et al. [82] studied the structure of the skin layer of asymmetric cellulose acetate RO membranes with TEMPO probe ((2,2,6,6-Tetramethylpiperidin-1-yl)oxy). It was observed that the mobility of TEMPO in the asymmetric membrane shrunk at 90 °C was the same as TEMPO in a dense homogeneous membrane prepared from the same casting solution. Authors reported the following conclusions:

- i) The pore sizes of the asymmetric membranes are larger when they were shrunk at lower temperatures.
- ii) The space in the polymer network (the origin of the network pore) in the dense film was smaller when no swelling agent is added to the casting solution.
- iii) The space in the polymer network in the dense film was smaller when the membrane was dry.

In another work, Khulbe et al. [83] reported the EPR study on the structure and transport of asymmetric aromatic polyamide membranes for RO. It was concluded that aromatic polyamide membranes contain water channels in the polymer matrix like cellulose acetate membranes. A comparison was then made with CA RO membrane. It was suggested that the EPR technique can be used to study the structure of RO membranes. The presence of water channels in the polymer matrix seems indispensable for the RO membrane.

5.1.7. Wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS)

Small-angle X-ray scattering (SAXS) is a small-angle scattering (SAS) technique where the elastic scattering of X-rays (wavelength 0.1-0.2 nm) by a sample which has inhomogeneities in the nm-range, is recorded at very low angles (typically 0.1-10°). Wide-angle X-ray scattering (WAXS) or wide-angle X-ray diffraction (WAXD) is an X-ray-diffraction technique that is often used to determine the crystalline structure of polymers. Wide-angle X-ray scattering is the same technique as small-angle X-ray scattering (SAXS) only the distance from sample to the detector is shorter and thus diffraction maxima at larger angles are observed. Depending on the measurement instrument used, it is possible to do WAXS and SAXS in a single run (small- and wide-angle scattering, SWAXS). Tamlin [84] successfully used Grazing incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS) to study polyamide on polysulfone reverse osmosis membrane's morphology (interfaces).

Cruz-Silva et al. [41] made a comprehensive study of the chemical and physical effects of carbon nanotubes on the fully cross-linked polyamide network. The microstructure of the nanocomposite membrane was studied by small and wide angle X-ray scattering, high resolution transmission electron microscopy, and molecular dynamics.

5.2. Membrane surface chemistry

Much attention has been given to the application of spectroscopic techniques to the characterization of RO membranes. For instance, Bartels [85] examined RO membranes using infrared (IR) spectroscopy. Author found that IR can provide valuable information on the functional groups (such as carboxylic acid or amide groups) present in the investigated composite membrane. The XPS, ATR-FTIR, TEM microscopy, and streaming potential analysis are valuable tools for characterizing RO membranes. When used together, this concluded that these characterization tools can provide strong evidence of the presence of a coating layer for some commercial RO membranes [86].

5.2.1. FTIR-ATR

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. Attenuated Total Reflectance (ATR) is a FTIR sampling tool. FTIR technique is able to probe *in-situ* single or multiple layers of adsorbed/deposited species at a solid/liquid interface.

Fourier transform infrared (FTIR) spectroscopy has been employed for analyzing microbial aggregates on membrane surfaces and can provide information about the chemical nature of the fouling layer. It allows one to distinguish the different kinds of fouling on the same membrane, but cannot provide information about biofilm thickness [87].

Poly(ethylene ether sulfone)/modified silica nanocomposite RO membrane, synthesized by Kim et al. [40] was characterized by FTIR spectra, SEM and TGA. The study showed that in HBP-g-silica, amine groups were grafted onto

the silica surface, and amide bonds were successfully conjugated between aPES and HBP-g-silica.

5.2.2. Auger electron spectroscopy (AES)

Auger Electron Spectroscopy (AES) provides quantitative elemental and chemical state information from surfaces of solid materials. The average depth of analysis for an AES measurement is approximately 5 nm. Hydrophobicity and hydrophilicity are controlled by the thin surface layer. Surface hydrogen and oxygen functionalities contribute to hydrophobic and hydrophilic properties, respectively. A wettability characteristics of RO membranes was studied by AES, which details can be found elsewhere [88, 89].

5.2.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand ranges. Moreover, empirical formula, chemical state and electronic state of the elements that exist within a material can also be determined by XPS. Sometimes called ESCA, it is used to study elemental compositions of composite RO membranes near the surface. This technique supplied verification of the polymer chemical structures expected from the interfacial polymerization reactions that formed the membranes.

Wagner et al. [90] modified polyamide reverse osmosis (XLE, polyamide thin film composite membranes manufactured by Dow Water & Process Solutions (Edina, MN) extra low energy) by grafting poly(ethylene glycol) (PEG) diglycidyl ether (PEGDE) to their top surfaces from aqueous solution to improve fouling resistance. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface elemental content of modified and unmodified membranes. XPS indicated the qualitative evidence of the presence of PEGDE on the membrane surface and the thickness of PEGDE layer. Further, XPS results were qualitatively consistent with the ATR-FTIR results.

5.2.4. Electron dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. EDS analysis can be used to determine the elemental composition of individual points or to map out the lateral distribution of elements from the imaged area. It can also be used to obtain compositional information on quasi-bulk specimens (low SEM magnification, high accelerating voltage) or on specific particles, morphologies, or isolated areas on filters or within deposits. Energy dispersive X-ray spectroscopy (EDS) has an analytical capability that can be coupled with several applications including scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). For instance, Beverly et al. [91] demonstrated that EDS, combined with XPS, FTIR and SEM, is a valuable diagnostic tool for failure analysis of polymeric RO membranes and provides valuable information to aid the manufacturers in designing better membranes for reverse osmosis.

5.2.5. Raman spectroscopy

Kim et al. [43] studied spatial distribution of CNTs in the polyamide membranes, which were used for RO process. Raman spectroscopic mapping has been utilized to visualize spatially the distribution of CNTs or other nanomaterials in other matrix. In another work, Cui et al. [92] showed that Surface-Enhanced Raman Spectroscopy (SERS) could be used as a new and versatile tool for examining the fouling of protein on polyvinylidene fluoride (PVDF) membranes. The fouled area can be visualized by a combination of Raman mapping and silver staining.

5.2.6. Scanning transmission X-ray microscopy (STXM)

This can be used for examining hydrated biofilms (in RO fouling) due to the ability of soft X-rays to penetrate water. Lawrence et al. [93] have employed STXM, CLSM (Confocal laser scanning microscopy) and TEM to map the distribution of macromolecular subcomponents (e.g., polysaccharides, proteins, lipids, and nucleic acids) in a biofilm and demonstrated that this combination of multi-microscopy analysis can be used to create a detailed correlative map of biofilm structure and composition. It can help to understand the chemistry of fouling.

5.3. Other characterization technique

5.3.1. Nuclear magnetic resonance (NMR)

Glaves and Smith [94] indicated that nuclear magnetic resonance (NMR) may also be suitable for determining membrane pore structures. In another

work, Schmid et al. [95] used NMR microscopy, for the first time, to study biofouling of industrial spiral wound RO modules [66]. NMR microscopy can provide a non-invasive quantitative measurement of RO membrane biofouling and its impact on hydrodynamics and mass transport in RO systems.

Graft von der Schulenburg et al. [96] demonstrated the application of NMR to a spiral wound RO membrane module to understand the key design and operational parameters influencing the biofilm fouling in the membrane module. From the NMR data they were able to quantify an effective membrane surface area. Moreover, using the NMR data they studied the extraction of (i) the spatial biofilm distribution in the membrane module, (ii) the velocity field and its evolution with biofouling and (iii) propagators, which are distributions of molecular displacement of a passive tracer (e.g. salts, organic molecules) in the membrane.

In a recent study, Fridjonsson et al. [97] demonstrated that the use of Earth's field (EF) NMR can provide early non-destructive detection of active biofouling of a commercial spiral wound RO membrane module.

5.3.2. Photoacoustic spectroscopy (PAS)

Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection. The absorbed energy from the light cause's local heating and through thermal expansion a pressure wave or sound. A photoacoustic spectrum of a sample can be recorded by measuring the sound at different wavelengths of the light. This spectrum can be used to identify the absorbing components of the sample. The photoacoustic effect can be used to study solids, liquids and gases [98]. The major advantage of photoacoustic spectroscopy is that it is suitable for highly absorbing samples.

For instance, Flemming [99] suggested that photoacoustic spectroscopy can be used for monitoring the biofilm formation on the membrane during RO process. Schmid et al. [95] then used photoacoustic spectroscopy (PAS) as a new biofilm monitoring technique. PAS combines features of optical spectroscopy and ultrasonic tomography and allows a depth-resolved analysis of optically and acoustically inhomogeneous media.

5.3.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA analysis helps to study the morphology/characterization of membranes.

Kim et al. [40] synthesized composite RO membranes from sulfonated poly(arylene ether sulfone) containing amino groups (aPES) and hyper-branched aromatic polyamide-grafted silica (HBP-g-silica) with the aim of enhancing chlorination resistance and improving membrane performance. With the help of TGA analysis of HBP-g-silica, it was observed that amine groups were grafted onto the silica surface, and amide bonds were successfully conjugated between aPES and HBP-g-silica.

In another study, Mohan and Kullová [100] characterized the high-performance thin-film composite polyamide membranes by TGA for inorganic solute separation which were prepared by the interfacial polymerization of trimesoyl chloride (TMC) with diethylenetriamine, 1,3-cyclohexanebis(methylamine), 2,3-diaminopyridine (DAP), m-phenylenediamine (MPD), piperazine (PIP) or a mixture of MPD and PIP/DAP, on the surface of a reinforced microporous polyethersulfone (PES) membrane support.

5.3.4. Contact angle measurement

Contact angle is the angle between a tangential to the liquid surface at the line of meeting three phases and the plane of the solid surface (either real or apparent) on which liquid resides or moves. Contact angle is the most commonly used parameter to indicate membrane's hydrophilicity or hydrophobicity, where the higher the contact angle is, the higher the hydrophobicity is. It is conducted to determine surface hydrophilicity of RO membrane with the intention of predicting membrane performance or fouling potential. It is necessary to consider effective factors for contact angle measurement such as measurement time, drop volume and membrane sample preparation. Due to these reasons, different contact angles were reported in literature for a same RO membrane [101]. Contact angle of membrane is basically decided by the building material of the membrane, but it can widely vary depending on chemical additives, solvents, manufacturing method, process condition, surface roughness, and etc. Following two methods are widely used for measuring the contact angle:

- i) Sessile drop.
- ii) Captive bubble methods,

5.3.5. Zeta potential measurement

Zeta potential is an important tool to measure the electrical charge of the membrane surface. The zeta potential of particles in the suspension is evaluated based on the electrophoretic mobility. On the other hand, zeta potential of the membrane surface is evaluated by measuring the streaming potential. The zeta potential of the membrane often changes from positive to negative as the pH of the solution is increased, affecting the deposition of charged particles on the membrane surface (fouling).

Wagner et al. [90] measured the zeta potential of a commercial RO membrane grafted with PEGDE by using an Anton Paar Sur PASS Electrokinetic Analyzer and associated software (Anton Paar USA, Ashland, VA). Two membrane samples separated by a spacer were loaded into the clamping cell, creating a channel for electrolyte flow. A 10 mM NaCl solution was used as the background electrolyte. Streaming potential was measured as a function of feed pH, and the Fairbrother–Mastin approximation was used in the calculation of zeta potential from streaming potential.

5.3.6. Graft density

RO membranes can be modified by grafting the active layer on the surface. For instance, Wagner et al. [90] measured the density of PEGDE on the membrane surface by using a Rubotherm Magnetic Suspension Balance (Rubotherm GmbH, Bochum, Germany). A diagram of the apparatus appears in Figure 1.

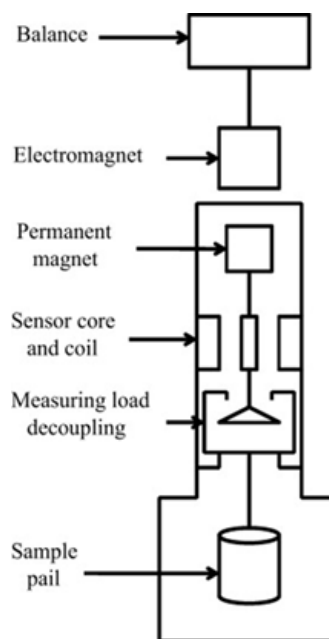


Fig. 1. Schematic of the magnetic suspension balance used to characterize PEGDE grafting density.

5.3.7. Tensile strength measurement

Tensile strength is defined as the ability of a material to resist a force that tends to pull it apart. It is usually expressed as the measure of the largest force that can be applied in this way before the material breaks apart. It is an important property of an RO membrane as they are usually operates at high pressure. ASTM D882 is commonly used for testing the tensile strength of polymer films. Ginga and Sitarman [102] discussed a new fracture testing technique that can be used to determine the tensile strength of low-strength thin films. This technique uses finite element analysis to extract the tensile strength from the experimental data.

6. Summary and future prospects

Table 1 shows the summary of recently developed RO membranes. As the Table 1 shows, that many attempts have been made to improve the performances of RO membranes, especially those of polyamide TFC membranes by incorporating nanosized fillers such as SWCNT, MWCNT, graphene, graphene oxide, silica, zeolite and etc. Fouling mitigation,

especially that induced by biofouling by grafting polymer chains to the membrane surface, coating highly hydrophilic layer, manipulation of surface charge, etc. have also been attempted with some successes. Inorganic membranes are more robust than polymeric membranes in an aggressive

environment but their commercial applications are hampered by their high production cost. Yet, they seem to have a potential in the future.

Table 1
Summary of recently developed RO membranes.

No.	Modification of membrane	Use/properties	Ref.
Cellulosic			
1	Embedded silver and/or aluminum nanoparticles.	Contaminated with phosphate ion. Good antimicrobial behavior and prevents the growth of microorganisms.	[16]
2	CA, simulation method.	Ammonium ions from aqueous solutions with a rejection factor higher than 98%.	[17]
3	Grafting by 2-acrylamido-2-methylpropanesulfonic acid (MPSA) on the top surface of the membrane.	Improved the hydrophilicity, salt rejection and water flux performances.	[19]
4	Blending PES and cellulose diacetate (CA). The heat treatment of casted blend membrane at annealing temperature 120°C.	Improved mechanical properties of blend membrane. Permeate flux was 21 kg/m ² . h and the salt rejection was 99%.	[20]
5	TFC coating CA onto an UF membrane support. Swelling in water baths, thermal annealing at 81 °C. Silver nanoparticles onto CA TFC surfaces.	94% salt rejection level without significant deterioration of flux. Reduced bacterial surface coverage by four orders of magnitude.	[21]
6	Multilayer PVA/CA/PEG RO membrane.	Acceptable for practical uses in desalination of brackish, highly saline and sea (extremely saline water), where the salt rejection (%) was 70, 63 and 59, respectively.	[22]
Polyamide TFC			
7	Decreasing the thickness of the selective layer.	Enhanced water permeability.	[28]
8	(PA-TFC) membrane was synthesized via IP technique. IP was carried out between aqueous solution of MPD and TMC in dodecane onto PSf supporting membrane.	High salt rejection (99.81%) with high permeate flux (36.15 L/m ² h).	[27]
9	TFC Polyamide.	TFC polyamide membrane exhibited higher water and salt permeability than the asymmetric cellulose-based membrane.	[31]
10	HNTs into the polyamide (PA) selective layer.	Potentially improve the performance of TFC membrane during RO application.	[37]
11	PA incorporated with NaY zeolite.	Water flux increased from 0.95 to 1.78 m ³ /m ² day (23.3 to 43.7 gal/ft ² day (gfd)) and high salt rejection of 98.8%.	[32]
12	PA thin films underneath titanium dioxide (TiO ₂) nanosized particles.	Water flux and the antibacterial fouling potential were improved.	[34]
13	PA-CNTs	Higher salt rejection achieved (97.69% as compared with 96.19% (without CNTs)) and a near doubling of water flux (44 L/m ² day bar as compared with 26 L/m ² day bar) was obtained.	[43]
14	PA-SiO ₂	Hydrophilicity of the membrane surface was increased. Flux increased gradually at lower levels of nanoparticles (0.005–0.1 wt.%) and then decreased at 0.5 wt.%. NaCl rejection increased at lower concentration of SiO ₂ (0.005 and 0.01 wt.%) and then decreased with an increasing content of SiO ₂ .	[35]
15	Hydrophilic additive, o-aminobenzoic acid–	Improve membrane desalination performance under seawater	[33]
	triethylamine (o-ABA-TEA) salt, into the aqueous m-phenylenediamine (MPD) solution to react with trimesoyl chloride (TMC) in the organic solution during the interfacial polymerization.	conditions.	
16	PA membrane containing CNTs.	Water flux found significantly increased. Also, the durability and chemical resistance against NaCl solutions of the membranes containing CNTs are found to be improved as compared with those of the membrane without CNTs.	[43]
17	Acidified MWNTs (multiwalled nanotubes)- PA.	Water flux found significantly improved. Membrane may have a potential application in separation of organic aqueous solution.	[44]
18	PA-aluminosilicate.	Higher permeate flux was achieved while sustaining high rejection of monovalent and divalent ions.	[38]
19	Multi-walled carbon nanotubes (MWCNT) and aromatic PA.	Improves the membrane performance in terms of flow and antifouling, inhibits the chlorine degradation on these membranes.	[45]
20	SWCNT+PA.	I Increase the Na and Cl ion rejection and decreases the pore size of the composite membrane.	[46]
21	PA- carbon nanotubes with acidic groups (CNTa), graphene oxide (GO), and both CNTa and GO (CNTa-GO)	Mechanical strength, antimicrobial and antifouling properties, selectivity, water flux and thermal properties are significantly improved after the incorporation of GO.	[47]
22	PA TFC membrane by chitosan	High flux and salt rejection.	[51]
Other RO membranes			
23	The top layer was of poly vinyl alcohol and the support materials were poly aryl sulfone ether and poly ester. Membrane coated with TiO ₂ particles and treated with UV radiation.	Higher flux in comparison with flux obtained with virgin (uncoated) membrane.	[50]
24	New type of microporous organosilica (sol-gel derived) RO membrane (Organosilica).	Rejected isopropanol with rejection higher than 95% including superior molecular sieving ability for neutral solutes of low molecular weight. Chlorine resistant and withstands higher temperatures.	[73]
25	The membrane was prepared on an asymmetric polyether sulfone via interfacial polymerization of 1,3-phenylene diamine and trimesoyl chloride at water-hexane interface.	The performances of the salt rejection follows the order Na ₂ SO ₄ >NaCl> MgSO ₄ > MgCl ₂ .	[29]
26	PA- CNTa-GO.	Water flux, chlorine resistance, long-term durability, and mechanical properties considerably improved.	[48]
27	Aquaporin membrane	High water permeability (4.0 L/m ² h bar) and good NaCl rejection (around 97%)	[56]
Inorganic Membranes (Zeolite)			
28	Hydrophobic MFI	With 0.1 M NaCl feed water, the membranes rejected 76% of Na ⁺ ions while permitting a water flux of 0.112 kg/ m ² h .	[72]

Table 1

Continued.

No.	Modification of membrane	Use/properties	Ref.
29	MFI-type zeolite	Both water flux and ion rejection increased considerably as aluminum ions were incorporated into the zeolite framework with a water flux increase from 0.112 to 1.129 kg/m ² h and ion rejection improvement from 90.6% to 92.9%.	[74]
30	ZK-4 zeolites.	100% of ion rejection from aqueous NaCl solutions (results were based on a molecular dynamic simulation).	[67]
31	Thin film of Zeolite Zk-4.	Use in membrane-based separation of aqueous electrolyte solutions, as well as other similar systems.	[67]
32	Zeolite nano-membrane (Hydrophilic FAU and hydrophobic MFI).	100% rejection of salt ions. The permeability was about 2×10^{-9} m/ Pa s when the membrane thickness was less than 3.5 nm.	[68]
33	Hydroxysodalite (HS) zeolite	Useful for treating various kinds of water and wastewater that cannot be handled effectively by polymeric membranes	[103]

For the future, the major area of membrane research will be surface hydrophilization by post-treatment to increase permeability and decrease fouling tendency. It is an enormous challenge to fabricate RO membranes with higher water flux, near complete rejection of dissolved species, low fouling propensity, and tolerance to oxidants used in pretreatment for biofouling control and long durability, but progresses are being made day by day in these directions by the efforts of many researchers involved worldwide.

Abbreviations

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
o-ABA-TEA	o-aminobenzoic acid-triethylamine
AMPSA	2-acrylamido-2-methylpropanesulfonic acid
CA	Cellulose acetate
CCD	Charge-coupled device
CNTs	Carbon Nano Tubes
CTA	Cellulose triacetate
DAP	2,3-diaminopyridine
EDX	Energy Dispersive X-ray Spectroscopy
EPR	Electron Paramagnetic Resonance
ESR	Electron Spin Resonance
FAU	Fauzite
FFT	Fast Fourier Transformation
FTIR	Fourier transform infrared
FO	Forward Osmosis
GO	Graphene oxide
HBP-g-silica	Hyper-branched aromatic polyamide-grafted silica
HNTs	Halloysite nanotubes
IP	Interfacial polymerization
LBL	Layer by Layer Method
LSMM	Hydrophilic surface modifying macromolecules
MFI	Mordenite Framework Inverted
MMMs	Mixed Matrix Membranes
MPD	meta-phenylene diamine
MWCNT	Multiwalled carbon nanotubes
NPs	Nanoparticles
NS	Newton Scattering
ODMP	Osmotically driven membrane processes
PALS	Positron Annihilation Lifetime Spectroscopy
PAS	Photoacoustic spectroscopy
PEG	Poly(ethyl glycol)

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