

Chapter 8

Fabrication of Advanced 2D Nanomaterials Membranes for Desalination and Wastewater Treatment



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Abstract Environmental concerns regarding water shortages due to industrialization and pollution have led to escalation in research towards efficiency in wastewater treatment and desalination. To date, nanotechnology is the most effective solution towards water shortages and is currently used for wastewater treatment and desalination. Among the emerging nanosheets, two-dimensional (2D) nanosheets have gained much attention since graphene was discovered in the fabrication of cost-effective and sustainable membranes for environmental remediation. Recently, 2D nanoengineered membrane technologies have revealed a new potential for removing hazardous compounds from our surroundings. The present chapter gives an overview of the concept of membrane technology, membrane fabrication techniques and the importance of 2D nanomaterials in the desalination and wastewater treatment membranes. Firstly, popular fabrication methods for membranes, such as electrospinning, drop-casting, spin-coating, solution casting and phase inversion, will be discussed. This will be followed by the application of 2D nanoengineered membranes incorporated with graphene, MXenes, molybdenum disulfide (MoS_2) and other nanosheets, in their 2D form, for excellent improvement in desalination and wastewater treatment. Notably, the chapter emphasizes the wide range of membrane applications as well as their potential and challenges for use in the development of nanotechnology-based environmental remediation.

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8.1 Introduction

For centuries, inadequate water supply (for industrial, domestic and agricultural water use) has been one of the greatest global challenges facing modern society [1]. Given The amount of wastewater produced industrially, most water supplies are currently heavily polluted with hazardous/toxic chemicals such as heavy metal ions, synthetic dyes, and radioactive substances. Therefore, wastewater treatment serves as a solution to alleviate these challenges. On the other hand, the divalent ions and the minute monovalent salt ions are removed by desalination of brackish and seawater. Additionally, desalination offers another alternative fresh water supply, owing to its abundance (with more than 97% of the overall water resources covering the land) and easily accessible seawater. Various contaminants in wastewater include artificial and natural components such as natural organic matter, microorganisms, heavy metals, and synthetic dyes [2–7]. Many wastewater treatment plants use various techniques for water purification of such contaminants. These techniques include flocculation/sedimentation filtration, chlorine disinfection, adsorption, ion-exchange adsorption, ion exchange, membrane filtration, adsorption, and precipitation [8–10]. Membrane-based separation technology rapidly dominates wastewater treatment and desalination, including microfiltration, ultrafiltration and nanofiltration. Membrane filtration technology has been employed in chemical, pharmaceutical and water industries, amongst others. It offers several advantages such as cost-effectiveness, energy saving, good selectivity, compactness, ease of fabrication, simple operation and environmental friendliness [11]. Selectivity and permeability are the two factors that contribute towards membrane performance in water purification. However, the compromise between membrane rejection properties and porosity has led to more interest in nanotechnology as a solution amongst the various wastewater treatment methods, such as nanomaterials for the fabrication of innovative membranes [12].

The discovery and isolation of mono-sheet graphene in 2004 unlocked more access to fresh opportunities for exploring advanced 2D nanomaterials due to their distinctive features, such as atomic thickness, large lateral sizes, and reactive sites [13–15]. Various 2D materials, namely graphene-based materials, MXenes, h-boron nitride, and others, have been widely used to fabricate advanced 2D membranes with improved filtration performance [16, 17]. The 2D nanomaterials are thus promising as potential candidates to ensure improvement in the quality and availability of water treatment while also ensuring growing global water supplies.

8.2 2D Materials: Their Exceptional Characteristics for Membrane Fabrication

Figure 8.1 shows the structure of various popular 2D materials. The 2D nanostructures have unique features, shapes and properties. They are considered ideal replacements for traditional desalination and water treatment membranes. Owing to their

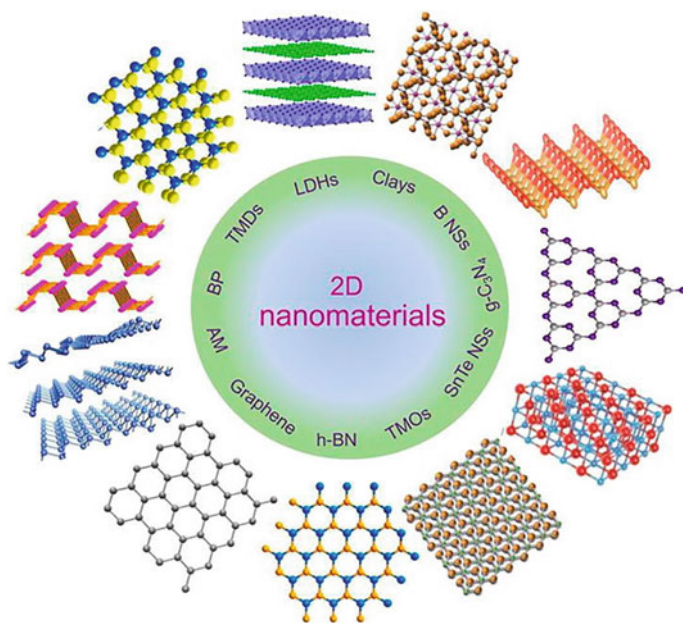


Fig. 8.1 Structure of various 2D nanomaterials. Reproduced with permission from ref. [16]. Copyright 2022, Frontiers

distinctive structural properties (atomic thickness and robustness) and precise molecular filtration capability, 2D nanomaterials are fascinating materials for outstanding nanofiltration operations such as organic solvent nanofiltration membranes [18, 19].

8.2.1 Graphene-Based Materials

Graphene, a very thin and light 2D material made of a single graphite atomic layer, is one of the strongest materials ever known due to the presence of sp^2 bonds. Due to the repulsive forces of dense and delocalized π -orbital cloud repulsive forces, graphene sheets are impermeable to even the smallest molecules, that is, monoatomic-sized particles such as helium and hydrogen, regardless of their thickness of one atom. The presence of defects in graphene sheets will impart permeability. Therefore, the introduction of controlled pores on the sheets gives them potential in membrane and separation processes (to allow water permeation while rejecting ions). The high mechanical strength, chemical resistance, and unique physiochemical properties make graphene-based nanomaterials [graphene, graphene oxide (GO) and reduced GO (rGO)] highly beneficial as a membrane material that is very suitable for water desalination. These properties include high surface area, hydrophilicity, reactivity, and chlorine resistance, in addition to the antibacterial property for biofouling

control [20, 21]. Graphene-based nanomaterials, mainly GO, are the most superior carbon-based nanomaterials for ease of fabrication and economic viability [22].

GO is essentially a single-layer-thick with a hexagonal pattern lattice that contains many oxygen-rich sites on its base and edges, which lead to good hydrophilic and antifouling properties [23, 24]. GO is synthesized by various methods; these include the Hummers and Brodie's methods, and their improved versions [25, 26]. GO is produced by the oxidation of graphite by strong oxidizing agents such as KMnO_4 and NaNO_3 along with a strong acid such as H_2SO_4 , using a well-known improved Hummers method. With the hydrophilic oxygen-rich surface, the edges possess carboxylic groups, while the basal plane contains hydroxyl and epoxy groups. GO sheet is composed of oxidized domains surrounding the isolated pristine graphene domains, which did not oxidize. It comprises of 82% oxidized, 16% pristine graphene and 2% holes [27, 28]. Reduction of GO (thermally or chemically) produces a structure similar to that of pristine graphene. Although in its reduced form (rGO), the carbon-to-oxygen ratio is reduced from 2:1 to 3:1 [14].

Graphene is an emerging 2D material not only with a large surface area, but also with good elasticity, exceptional electrical conductivity and highly active, thus good enough characteristics for desalination [29]. Owing to its high rejecting capabilities and good permeability, GO has opened new opportunities as a membrane material. The water flow through GO membranes is through the GO galleries, gaps between the edges, wrinkles and surface openings created by the functional groups. GO membranes are chemically and thermally stable for use in processes such as membrane pervaporation [30]. As GO sheets tend to form laminates, as microcrystallites, they form interconnected layers stacked above and adjacent to each other with interlayer spacing between them. The interlayer gap is due to the oxygen functional groups attached to the nanosheets. The GO interlayer gap may require adjustment to get the desired performance regarding the rejection of solutes and permeation (water flux) [31]. The 2D interlayer gap between the GO sheets acts as the nanochannels for water transport and solute rejection, which can further be modified or adjusted to achieve desired rejection based on the size of solute particles [32].

Unlike GO, rGO is less hydrophilic with tighter nanochannels and less swelling and, therefore, more stable in water environments as it contains less oxygen functional groups [14, 29]. However, water transport through the lamellar GO or rGO sheets may be limited owing to the strong capillary force of the tight nanochannels [33]. The rGO nanochannels can thus be adjusted to control the water transport behavior and to achieve size-selective molecular filtration [32]. This can be achieved by the intercalation of materials within the nanochannels, such as soft polymers and polyelectrolytes [34]. Intercalation of more rigid materials is to avoid unstable/instability or fluctuation in the interlayer spacing over time. This led to the use or inclusion of more rigid metal oxide and metal sulfide materials. These include metal oxides such as Zinc Oxide, Copper Oxide, Magnesium Oxide, etc., and metal sulfides such as Zinc Sulphide and MoS_2 nanoparticles. The rigid spacers also enable efficient filtration by size exclusion by expanding their lateral tortuous paths for water permeability, thereby solving the permeability-selectivity trade-off. The metal oxide nanoparticles

enlarge the interlayer gap of the rGO sheets, thereby, also expanding their lateral tortuous paths [29, 35].

8.2.2 Transition Metal Dichalcogenides (MoS_2)

MoS_2 , another category of 2D nanomaterials comparable to graphene, is available as single layer or a few layers through exfoliation of the bulk MoS_2 [36, 37]. Like graphene, MoS_2 can also be produced by a bottom-up synthesis approach using Molybdenum (Mo) and sulphur (S) salts [38, 39]. MoS_2 is a graphene-like 2D transition metal dichalcogenide with formula MX_2 , with “M” representing a transition metal element such as titanium, molybdenum, tungsten, while “ X_2 ” denotes chalcogen atoms such as selenium, sulphur, telluride (i.e., MoS_2 is a negatively charged layered analogue of graphene). Compared to graphene, MoS_2 single-layer is diatomic as it contains (Mo) and sulphur (S) (i.e., a monolayer contains three atomic layers, whereas graphene is a single layer). MoS_2 consists of monolayers with strong covalent bonds between Mo and S_2 atoms and weak Van der Waals forces amongst neighboring sheets. MoS_2 single-layer membrane is 1 nm thick, with hydrophilic Mo edge and hydrophobic S edge and mechanical strength of steel (~ 270 GPa) [40]. The Mo atom is packed between the two S atoms, giving an interlayer gap of 0.62 nm between two Mo atoms and a free gap of about 0.30 nm as the laminar channel space, smaller than the salt ions Na^+ (0.716 nm) and Cl^- (0.664 nm), and larger than water molecules (0.276 nm), thus making them excellent candidates for desalination [37, 41]. Due to their tremendous physiochemical, biological, antifouling, and mechanical properties, MoS_2 nanosheets have been used in catalysis, sensing and optoelectronics and have recently gained considerable attention in water separation and purification [42–44]. Like graphene, it is a promising material for membrane separation due to its exceptional mechanical, thermal, and antibacterial properties. Lack of π - π bonds in MoS_2 prevents membrane scaling and biofouling. This makes it a good candidate as adsorption filtration membrane for contaminants and disinfection. Single sheet membranes of 1–10 nm sized nanopores can be sculpted by a highly focused electron beam, large enough to allow water passage while restricting ions through the membrane [45].

The single-layer nanosheets function as nanoporous membranes that can effectively filter ions while permitting fast water passage without modification when compared to other nanoporous membranes of GO and carbon nanotubes (CNT). The separation or isolation of Mo and S_2 affects membrane performance; for example, having Mo only on the nanopore induces hydrophilicity, thus increasing water transport through the nanopore. These hydrophilic sites give more permeability to the membrane as they can attract water molecules through hydrogen bonding. Molecular simulations have shown that MoS_2 membranes have higher flux than GO-based membranes [46]. MoS_2 nanopores thus have a pore chemistry good enough to control the water flux 70% higher than that of graphene nanopores without needing any further surface chemical modification, unlike the graphene nanoporous membranes

that require further modification. The functionalization affects salt rejection (trade-off effect), and the rough surface caused by functional groups exposed on the carbon plane causes water flow resistance [45, 46].

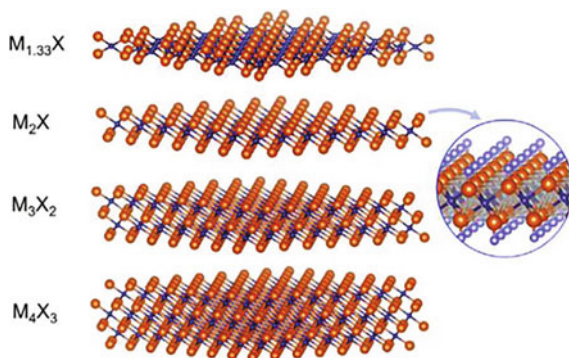
Moreover, the termination of Mo leads to the creation of charged edges of MoS₂ nanopore edges. Therefore, it creates positive charges on nanopores and repels Na⁺ ions, unlike graphene with neutral carbon atoms. At the same time, hydrophilic Mo at the tip of the nozzle-like nanopore draws water to the inside of the MoS₂. It was found that a nanopore area of 20–60 Å² can easily reject 88% of salt ions. Unlike GO, the smoothness is due to the lack of functional groups. Yet, pore chemistry can control the flux and salt rejection without needing further modification/pore functionalization. Therefore, it can be said that membranes with stacked MoS₂ sheets thus have higher water permeability than GO membranes. Chemically exfoliated MoS₂ is hydrophilic, negatively charged, and smooth as the original 2D structure is maintained. On the other hand, the hydrophilicity and negative charge of GO are due to chemical oxidation, which produces oxygenated hydrophilic functional groups protruding from the carbon plane, thus, a rough surface [45, 47].

MoS₂ multi-layer membranes have successfully been applied in gas separation and water treatment for heavy metal ions and organic/inorganic contaminants removal by adsorption (i.e., intercalating contaminants into the interlayer spacing or by the S atoms that can be exposed by the exfoliation process of MoS₂) and electrostatic interaction due to the negative surface charge [48–51]. The hydrophilicity and negative charge of MoS₂ make it highly useful in modifying the physiochemical properties of the thin film nanocomposite (TFNC) membrane surface. MoS₂ are also stacked as multi-layers whereby the exfoliated monolayers are restacked by vacuum filtration for modification of physiochemical properties of the TFNC reverse osmosis desalination membranes, which include hydrophilicity, surface charge and roughness. Advantages such as thinner selective skin layer and a decrease in membrane smoothness, enhanced surface hydrophilicity, negative surface charge and interlayer spacing) contribute towards the separation efficiency of the MoS₂ multi-layer TFNC membrane. MoS₂ is a good candidate for membrane-based separation as nanoporous membranes and multi-layer (laminar) membranes [37].

8.2.3 MXenes

Since the discovery of MXenes in 2011 by Drexel University, the production of multi-layer MXenes has become quite popular for preparing robust lamellar water purification membranes [11]. MXenes are a new addition to the existing 2D materials as a new collection of 2D transition metal carbides, nitrides and carbonitrides [52]. MXenes are one of the rapidly-expanding 2D nanomaterials. The three atomic structures are shown in Fig. 8.2, M₂X to M₃X₂ and M₄X₃ represent Ti₂C, Ti₃C₂ and Ti₄C₃, as the three types of MXene, respectively [53]. MXenes are commonly characterized by the formula, M_{n+1}X_nT_x; where M is an early transition metal such as Ti, Mo, Sc, W, V, Zr, with interleaving n + 1 layers; X symbolizes carbon or

Fig. 8.2 Structure of mono-MXenes. Reproduced with permission from ref. [53]. Copyright 2020, Elsevier Science Ltd.



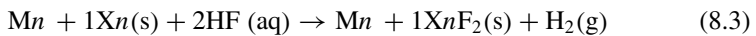
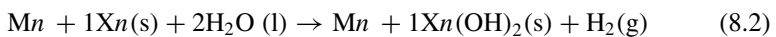
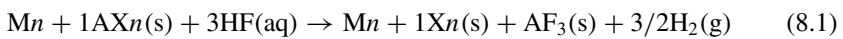
nitrogen with n layers; T signifies surface end groups such as $-\text{Cl}$, $-\text{F}$, $-\text{O}$, and $-\text{OH}$; the x denotes the number of surface functional groups, and n is from 1 to 4 [54]. MXenes materials have recently emerged as exceptional materials for application in various fields such as energy storage [52, 55], catalysis [56], electromagnetic interference shielding [57] and novel membranes for water desalination [58]. MXenes have exceptional properties such as hydrophilicity, large interlayer gap, high surface area and sufficient amount of very active surface sites (the surface chemistry is easily tunable (owing to the existence of the free electrons associated with transition metal atoms) and are negatively charged materials [53, 59]. The intriguing structural and chemical properties are highly influenced by their synthesis conditions: starting material for MXene, material used for etching, etching and intercalation techniques. The properties can further be tailored to suit the particular application MXene M and X arrangements and surface terminations ($-\text{F}$, $-\text{OH}$, and $-\text{O}$). This includes chemical stabilities, outstanding electrical conductivities, and environmentally benign nature. MXenes as their ability to host and Li^+ , Na^+ , Mg^{2+} , K^+ , intercalate cations, such as and NH_4^+ inside the Ti_3C_2 sheet in aqueous environments. With these properties, they are proficient in removing heavy metals, dyes, and radioactive nuclides through adsorption or adsorptive, electrostatic interactions and steric exclusion [53].

The remarkable structural properties of MXenes include simplicity of functionalization and activated metallic hydroxide sites, biocompatibility, and superior adsorption-reduction capability. In addition to their antifouling properties, their electrical conductivity, mechanical, thermal, chemically stable, and adsorbent and catalytic properties make them highly suited as desalination membranes and nanofiltration (NF) membranes for removal of pollutants such as dyes and ions (metal and salt ions), oil/water emulsion/mixtures from wastewater [60].

MXene membranes have proven great potential as water treatment and desalination membranes. MXenes are materials as barrier layers of high flux filtration membranes owing to their ultrathin 2D structure and ease of surface functionalization [61]. They have shown the ability to remove pollutants from the water as pristine and modified membranes. MXenes are synthesized economically at room temperature. Multi-layer MXenes are synthesized through an exfoliation process by

selective etching of group A elements from their MAX phases (Fig. 8.3). It is a wet-chemical etching process in hydrofluoric acid (HF) or HF-containing or HF-forming etching materials that will add $-O$, $-F$, or $-OH$ functionalities (represented by T_x in the MXene formula). MAX phases are transition metal layered ternary carbides, nitrides, and carbonitrides comprising of M, A and X layers, “M” is an early transition metal, the “A” groups are mostly groups 13 and 14 elements, and “X” is C and/or N. Some of the MAX phases, amongst the 60+ others that are known to exist, include: Ti_2AlC , Ta_4AlC_3 , $(Ti_{0.5}, Nb_{0.5})_2AlC$, $(V_{0.5}, Cr_{0.5})_3AlC_2$, and Ti_3AlCN . These powders are treated in HF acid at room temperature and then sonicated. Thus, the “A” group layer is eliminated from the MAX phases, forming the 2-D sheets and referred to as MXenes (the term highlights their similarities to graphene, as these have the same structure as the graphene, but with hydrophilic surfaces) [62]. Titanium carbides ($Ti_{n+1}C_n$, for example, $Ti_3C_2T_x$ (Titanium (III) carbide (II)); with T_x representing surface groups such as $-OH_x$ and $-F_x$) is the most investigated class of MXenes, synthesized using ammonium bifluoride salt (NH_4HF_2) as a HF-containing etchant that replaces HF [54, 63]. The toxicity of concentrated HF has led to a less hazardous synthesis route that uses milder etchants for exfoliation and delamination. For example, a combination of less hazardous hydrochloric acid (HCl) and lithium fluoride (LiF) salts can be used to etch Al from Ti_3AlC_2 [64]. This procedure is followed by intercalating water molecules and cations to form large interlayer spacing between the MXene layers. Another etchant example is ammonium bifluoride (NH_4HF_2), followed by intercalation of molecules such as ammonium species $-NH_3$ and $-NH_4^+$, for the delamination of sheets from each other to form single sheets. Other safer etchants include fluoride salts. These include potassium, sodium, calcium tetrabutyl ammonium and cesium fluorides. These are used with either HCl or sulphuric acid (H_2SO_4) [63].

The equations below represent the wet-etching synthesis using HF at room temperature [53]:



8.3 Fabrication of 2D-Enabled Membranes

The fabrication methods for 2D-based membranes make use of three commonly used routes: (i) 2D nanosheets are used as functional materials for the fabrication of lamellar membranes; (ii) 2D nanosheets as additives for mixed matrix membranes;

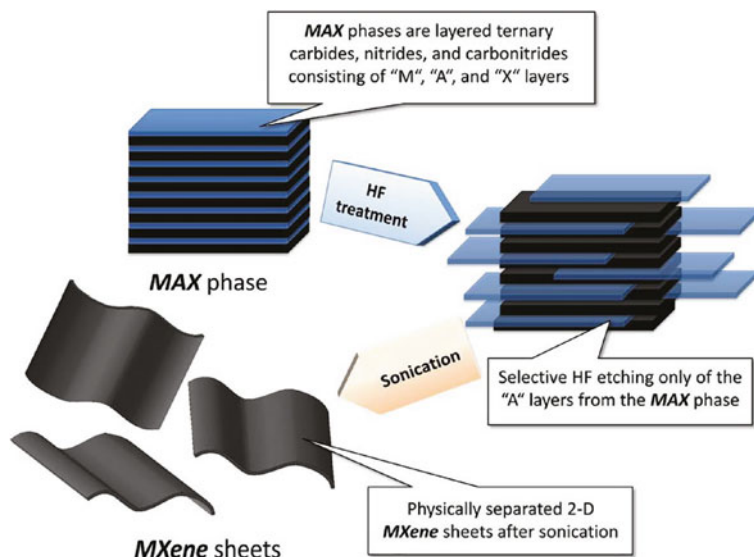


Fig. 8.3 Synthesis of MXenes using HF as the etchant. Reproduced with permission from ref. [62], Copyright 2012, American Chemical Society

and (iii) the 2D sheets used as coating layers to improve the membrane substrates [65].

8.3.1 Fabrication of Layered Membranes

Multi-layer 2D sheets of the lamellar structure can be used for layered membranes that are needed for the NF method. NF membrane filtration method can efficiently filter multi-valent salts and organic contaminants. NF membranes have nano-sized pore sizes ranging from 0.5 to 5 nm (nanoporous) with a nominal molecular weight cut-off of 200–1000 Da [29]. The filtration mechanism of NF membranes is based on size and charge exclusion, which is determined by the membrane structure and its interactions with the solute particles. On the other hand, desalination membranes have tighter pore sizes below 0.5 nm and usually use 2D single sheets as nonporous membranes that reject the monovalent ions [66].

8.3.1.1 Fabrication of Layered or Lamella Membranes by a Vacuum-Assisted Filtration

The vacuum-assisted assembly is a solution-processing membrane fabrication method, particularly for the preparation of ultrafine nanofiltration membranes

(Fig. 8.4b) [29]. In this method, the nanosheets are piled together and interlocked in a parallel fashion, leading to the construction of a robust 2D nanomaterial lamellar membrane. The narrow interlayer spaces formed are highly adaptable and facilitate water permeability while blocking particles larger than the interlayer spacing. Lamellar membranes can be prepared as free-standing films or supported onto porous support such as polyethersulfone, poly(vinylidene fluoride) (PVDF), polycarbonate or Nylon ultrafiltration membranes. The lamellar sheets of the 2D nanomaterials (GO, rGO, MXenes, MoS₂), as free-standing membranes, are highly promising for water treatment and desalination owing to their unique structures. These sub- μm thick membranes are robust yet flexible [31].

In the case of MXenes, following the synthesis (etching) step (e.g., Ti₃C₂T_x synthesized from Ti₃AlC₂ as the corresponding MAX precursor) [61], the exfoliation of the multi-layered MXene flakes into a single-layer or a few layers is due to the intercalation of guest particles. These enlarge the c-lattice factor and deteriorate the hydrogen and the electrostatic forces between the 2D MXene layers. The exfoliated MXene layers have a negative surface charge, possess a higher surface area than multi-layered MXene layers and have C atoms, -F and -OH groups exposed on their surface, which are responsible for capturing contaminants in the wastewater [68]. The exfoliated sheets are then dispersed in a suitable solvent, forming a homogenous

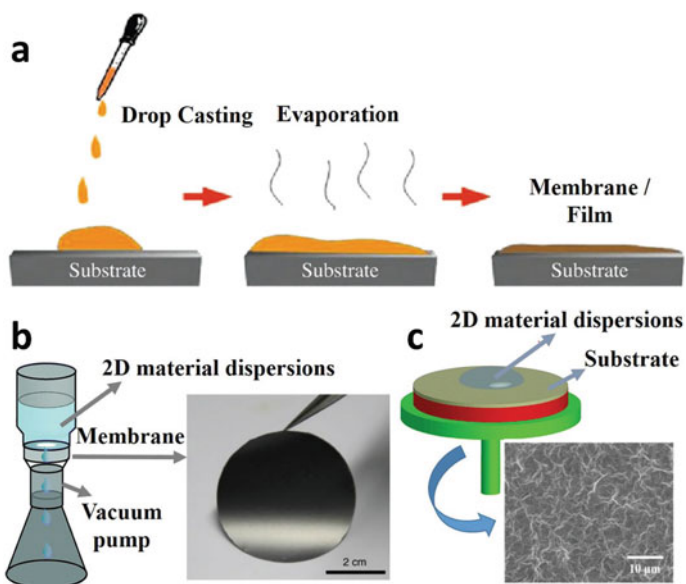


Fig. 8.4 Common membrane fabrication methods used for 2D nanomaterial-based lamellar membranes: **a** Evaporation-assisted self-assembly and drop casting methods. **b** Vacuum-assisted method and **c** spin-coating methods. Reproduced with permission from ref. [67]. Copyright 2022, Taylor & Francis

dispersion. The sheets disperse well in polar solvents, e.g., H₂O, ethanol, *N*-methyl-2-pyrrolidone, propylene carbonate, *N*, *N*'-dimethylformamide, and DMSO [69]. The dispersions are deposited onto a porous substrate using a pressure filtration device. Usually, the pressure of 1 bar is utilized as it is sufficient enough to tightly pack the nanosheets in an orderly manner [70]. The vacuum filtration deposition is accompanied by calcination or sintering at temperatures up to 500 °C. This yields a thin film MXene active layer deposited onto a porous support layer such as polymer materials of pore sizes of ± 200 nm. The interlayer spacing of MXene sheets is a result of moisture loss. The assembly of the resulting lamellar membrane thickness can be controlled by simply controlling the loading of MXene nanosheets. In addition to the vacuum-assisted filtration other methods for laminar MXene membranes include layer assembly, dip-coating, slot-die coating, and phase-inversion methods.

Lamellar membranes separate target molecules by sieving through the stacked layers with the aid of electrostatic interaction between the target species and the negatively charged layers. Unlike impermeable nanoporous GO, free-standing lamellar GO membranes permit water molecules to pass through the interlayer spaces without any hindrance. However, the water molecules can show low-friction contact with the hydrophobic area of the GO sheets, thus limiting the water passage through the nanochannels. Providentially, one advantage for the lamellar membranes is the ability to tune the interlayer spacing between the sheets, enhancing water permeability or selectivity towards the pollutants [71]. Evidently, a decrease in interlayer spacing enhances ion rejection, while an increase in interlayer spacing enhances membrane permeability.

8.3.1.2 Drop Casting Method

Drop casting (or 2D film fabrication method) is another technique to fabricate laminar membranes. In this method, the prepared nanosheet dispersion solutions are drop-cast onto a support layer (e.g., silica, polymer (e.g., polysulfone), or anodic aluminum oxide (AAO)) followed by solvent evaporation at ambient temperature. However, low vapor-pressure solvents such as H₂O may cause poor membrane uniformity due to insufficient evaporation [67, 72] (Fig. 8.4a).

8.3.1.3 Spin Coating Method

Spin Coating Method is a method whereby laminar membranes are prepared by spreading the prepared 2D nanomaterial solutions onto a substrate surface (Fig. 8.4c). The spin coating removes water deposited between the 2D nanosheets in the solution, causing strong, attractive capillary forces for additional deposition. The deposition of the nanosheets is due to the electrostatic and hydrophilic interaction with the substrate. The repulsive and attractive interactions between the sheets allow for homogeneous deposition of the assembled sheets [67].

8.3.1.4 Modification of 2D Nanosheets and Post-Treatment of Fabricated Lamellar Membranes

The fabricated $Ti_3C_2T_x$ MXene lamellar membranes can often have defects along the edges of the sheets, thereby allowing penetration of target species and resulting in poor membrane performance. The defects are usually due to the synthesis route of using harsh etchants such as HF. MXene is thus blended with other 2D materials, such as GO, to improve the rejection performance of the MXene lamellar membranes. GO combined with $Ti_3C_2T_x$ with a certain percentage loading of 10–30 wt%, followed by sonication in H_2O to form a homogenous dispersion and filtered as described earlier [71].

Thermal crosslinking is self-crosslinking by drying in an oven for $90\text{ }^\circ\text{C}$ to remove free water between the sheets to control the interlayer spacing. Thermal crosslinking often requires enhancement of the MXene negative surface charge by hydroxylation. The fabricated MXene membrane is then hydroxylated after the self-curing using a potassium hydroxide mixture to substitute $-F$ with $-OH$ groups (improving the negative charge and wettability) [61, 73].

8.3.2 Fabrication of Mixed Matrix (Hybrid) Membranes

8.3.2.1 Solution Casting

2D nanomaterials, such as MXenes, are blended with polymers to fabricate composite polymer membranes to improve the microstructural and physicochemical properties of the membranes, such as enhanced antifouling properties. For example, when mixing MXene with polymers, the MXene oxygen-containing functional groups form chemical bonds with the polymer, thus, considerably reducing polymer chain motion and creating well-formed galleries for transporting molecules. Figure 8.5 shows the synthesis procedure of polyethersulfone (PES) and nickel (Ni)/MXene composites. MXene is blended with the Nickel nanoparticles (Ni-NPs) and incorporated into the PES polymer matrix to produce composite membranes through a phase inversion process. Fabrication of mixed matrix membranes is an easy and economical process. However, with this procedure, most of the MXene nanosheets remain in the bulk of the polymer matrix rather than being exposed to the membrane surface. Therefore, the membrane antifouling, hydrophilicity and permeability functionalities are compromised. The use of Ni-coated MXene is an attempt used to overcome this shortcoming. The magnetic NPs can thus be brought onto the membrane's outer surface using a magnet during the solution-based membrane fabrication process [74].

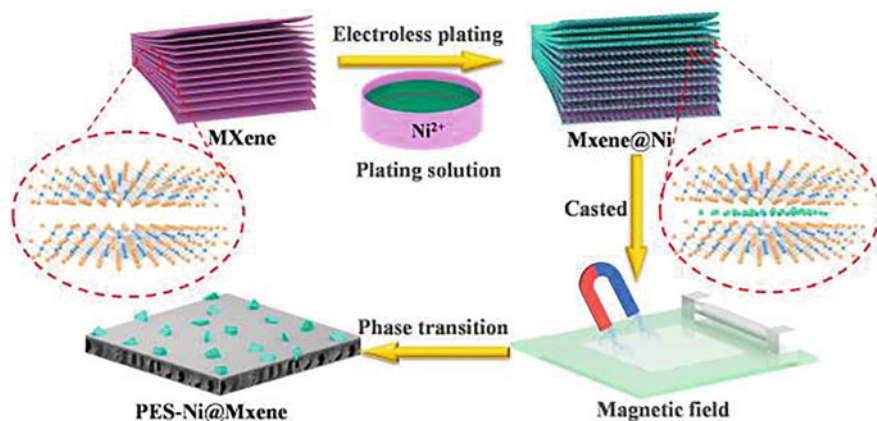


Fig. 8.5 Preparation process of PES-Ni@MXene composite membranes. Reproduced with permission from ref. [74]. Copyright 2021, Elsevier Science Ltd.

8.3.2.2 Electrospinning

Electrospinning, like the solution casting method, is a polymer solution-based membrane fabrication method used to load 2D nanosheets into the polymer matrix of the nanofibrous membranes. It is a more efficient and versatile method for fabricating mixed matrix membranes and is the preferred method over the solution casting process. It is a more suitable option for those nanosheets that tend to aggregate in solution-based processes. Electrospun membranes have recently gained attention in water treatment and are used as carrier substrates for loading MXene sheets. Although MXenes are hydrophilic, they tend to undergo oxidation in aqueous environments. MXenes are easily modified, owing to the inherent hydroxyl, fluorine and oxygen terminal groups, by using small particles, such as some organic compounds, polymers and NPs, as one of the strategies used to avoid aggregation. Therefore, electrospinning of polymer composites containing MXenes sheets in conjunction with palladium (Pd) as catalytic NPs, led to the successful fabrication of catalytic membranes for catalytic degradation of contaminants from the wastewater, e.g., PVA/PAA/MXene@PdNPs composites (Fig. 8.6) [75, 76].

8.3.2.3 The 2D Sheets as Coating Materials to Improve the Membrane Support Layer

GO sheets are coated onto existing polymer membrane surfaces by covalent bonding (e.g., TFNC desalination membranes) to enhance the membrane's antimicrobial ability, fouling resistance and hydrophilicity. In this process, the carboxylic groups of the GO nanosheets are linked with the other carboxylic groups on the surface of the polyamide (PA) film of the TFNC surface through amide coupling (Fig. 8.7) [77].

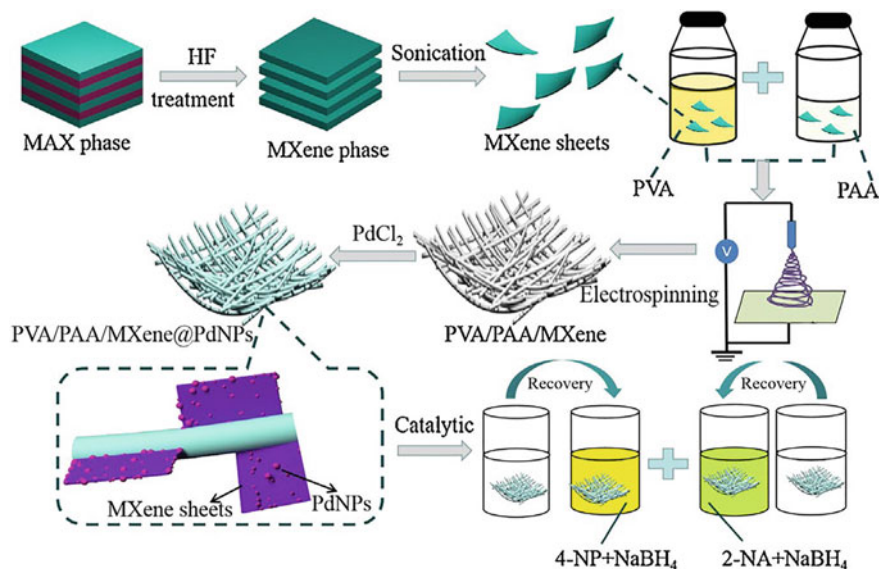


Fig. 8.6 Fabrication of mixed matrix 2D enabled membranes by electrospinning method. Reproduced with permission from ref [76]. Copyright 2019, Elsevier Science Ltd.

Graphene oxide functionalization → Antimicrobial properties

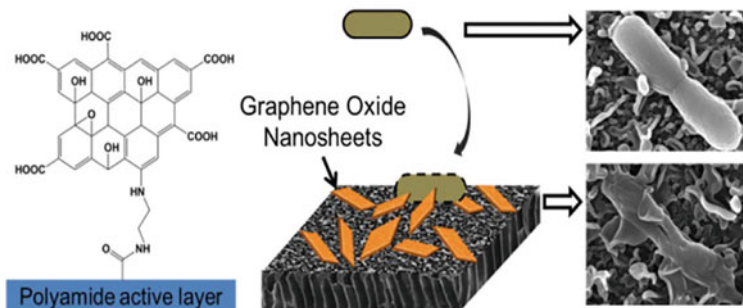


Fig. 8.7 GO surface coating onto PA-TFNC membrane. Reproduced with permission from ref. [77]. Copyright 2013, American Chemical Society

8.3.3 Layer-By-Layer Self-Assembly of 2D Nanomaterials onto Membrane Surfaces

Layer-by-layer self-assembly is the deposition of oppositely charged 2D nanomaterial sheets by the dip-coating method (Fig. 8.8). The coating is usually on membranes of negatively charged membrane surfaces such as the nanofiltration and RO desalination membranes. GO undergoes modification into positively charged sheets to form

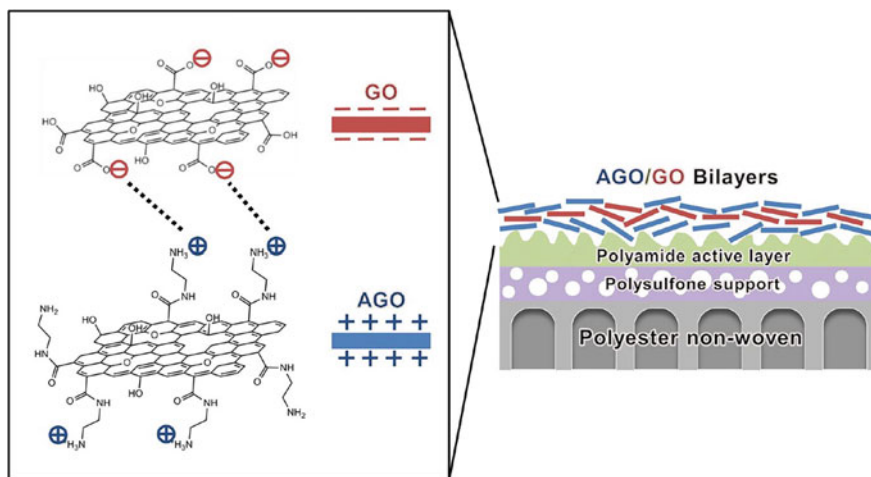


Fig. 8.8 Schematic illustration of a multi-layered graphene oxide (GO) coating on a polyamide thin-film composite membrane surface via layer-by-layer (LbL) deposition of oppositely charged GO and aminated-GO (aGO) nanosheets. Reproduced with permission from ref. [78]. Copyright 2013, American Chemical Society

aminated GO sheets (aGO) as follows: GO sheets are treated with ethylenediamine and EDC (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide). EDC methiodide is a carboxyl modifying reagent (crosslinking agent for amide bond-forming reactions), which acts as a linking agent that induces the amide group between the carboxylic acid group of GO and the amine terminal group of ethylenediamine. GO sheets are coated onto the membrane surfaces via a non-covalent bonding modification process whereby the negatively charged GO is coated onto the membrane surface, followed by a layer of positively charged aminated GO (aGO). The aGO functions as a bridging nanomaterial [78]. This is followed by the preparation of uniformly dispersed aqueous suspensions of the positive aGO and the negative GO sheets by sonication. The positively charged aGO sheets are then attached to a negatively charged membrane surface by dipping it into the positive aGO suspension, followed by dipping into a negative GO suspension. This forms a bilayer of GO/aGO onto the membrane surface, then dried in the oven. The process can be repeated to get the desired bilayer thickness.

8.4 Application of 2D-Enabled Membrane Materials in Environmental Applications

Modified and unmodified 2D-based membranes have been employed to remove different contaminants from water. The functionalization of the 2D nanomaterials, such as GO and MXenes, could also enhance the membrane rejection performance

and anti-fouling properties through adsorption, charges, and sieving [60]. However, the performance is highly dependent on membrane selectivity and permeability. As the stacked sheets of laminar membranes tend to have reduced permeability compared to the traditional polymer water purification membranes, the inclusion of NPs within the galleries of laminar membranes has a positive effect on membrane flux and pollutant rejection [65].

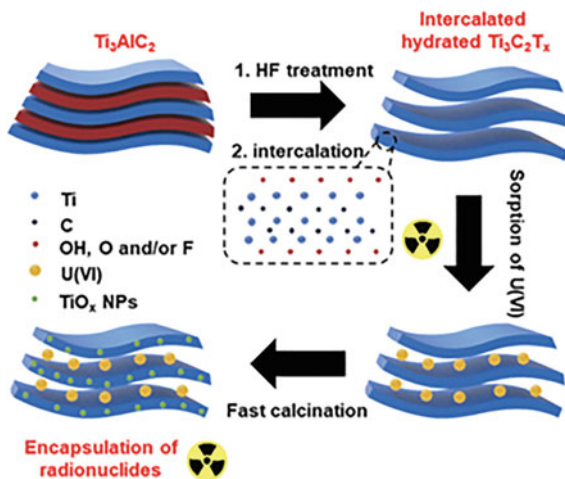
8.4.1 Radionuclide Removal

Radionuclide contamination originates from nuclear accidents during the mismanagement of radioactive liquid waste [10]. Barium isotopes (^{133}Ba and ^{140}Ba) and strontium (^{90}Sr) Ba^{2+} , Sr^{2+} , are the most toxic radionuclide substances. Radioactive barium isotopes adversely affect breathing, liver, heart, and kidneys and Sr^{2+} causes oxygen shortage in the lungs [10, 79]. Uranium (U) is the critical constituent of conventional nuclear fuel cycles, is a highly hazardous radionuclide with a long half-life and threatens the environment and ecological system. Hexavalent uranium U(VI) is exceptionally mobile, easily dissolves in water, forms the most stable uranyl ion (UO^{22+}) in solution, and has been mostly mitigated by adsorbents such as GO and activated carbon. In addition, MXenes have shown great potential as effective adsorbents for removing these pollutants [53].

8.4.2 Uranium Exclusion

Uranium is a naturally occurring radioactive substance found in soil, rocks, air and water. However, high concentration level in drinking water and groundwater used for agriculture is toxic to humans and causes kidney damage. With extensive exposure, uranium decays into other cancer-causing radioactive substances, such as radium. Uranium in the soil and human tissue may be sourced from phosphate fertilizers. Therefore, long-term usage of uranium-bearing fertilizers leads to an increase in the uranium concentrations in fertilized soil [80]. 2D materials such as MXenes are resilient to damage caused by radiation, have excellent chemical and mechanical properties, and can remove such contaminants from wastewater. They have shown the ability to function as desired adsorbents for radio-active nuclides from the environment, such as uranium (^{238}U), thorium (^{232}Th), cesium (^{137}Cs), and strontium (^{90}Sr) [53]. The mechanism/interaction pathways for MXenes for radionuclides removal include coordination, ion exchange, and reduction immobilization. Adsorption of Ba^{2+} , Sr^{2+} , Pd^{2+} , Cs^+ , Th^{4+} , Eu^{3+} , Re^{7+} , and U^{6+} ions on MXene materials has been investigated [53]. Wang et al. [81] developed a multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene membrane to capture U(VI) in aqueous solutions. They explored the adsorptive behavior of the pristine MXene and that of the hydrated MXene with DMSO. As the hydrated MXene was intercalated and had enlarged interlayer spacing, they

Fig. 8.9 Hydrated intercalation synthesis strategy of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene for efficient U(VI) uptake and imprisonment. Reproduced with permission from ref. [82]. Copyright 2022, Elsevier Science Ltd.



could capture the U^{6+} radionuclide within the MXene galleries. This was termed a “radionuclide imprisoning” approach (Fig. 8.9), which is a fast low-temperature post-adsorption calcination intercalation strategy of increasing the adsorption capacity of MXenes [81].

8.4.3 Dyes and Other Colorants Removal

Dyes are organic pollutants mainly from wastewater discharged by textile industries, thus posing a serious threat to the ecological environment. Removing dyes and other organic contaminants is dominated by adsorption and catalytic degradation [83]. MXenes have exceptional photocatalytic performance and thus can quickly and effectively eliminate dyes from the discharged wastewater. The 2D nanomaterials as sheets stacked into multi-layered laminar membranes function as NF membranes, and the dyes are removed mainly by means of size-exclusion separation of methyl blue [29]. However, the 2D laminar sheets such as MXenes and graphene-based laminar NF membranes produced by the vacuum filtration method result in a dense film with decreased porosity, thus reducing water permeability. The removal of the large dye molecules with different hydration radii, therefore, requires MXene sheets to be used in conjunction with other materials (intercalants) to enlarge/increase the interlayer spacing for enhanced permeability. Khang et al. [71] produced GO laminar membrane intercalated MXene sheets to enhance the membrane permeability (Fig. 8.10). The improvement was mostly because of the short transport pathway together with additional nanopores and interlayer gaps on the hydrophilic MXene nanosheet area [71, 84]. As the stability of GO-based membranes is weak owing to electrostatic repulsion between the nanosheet layers, MXene is incorporated to offer more stability due to reduced electrostatic repulsion and better π - π interaction.

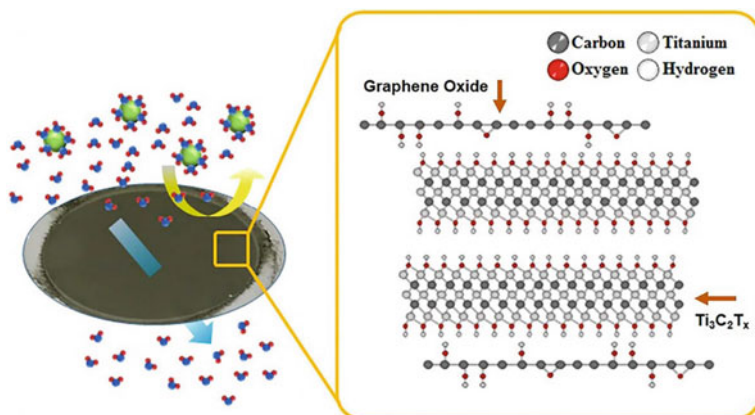


Fig. 8.10 MXene sheets incorporated/intercalated within the GO galleries ($\text{Ti}_3\text{C}_2\text{T}_x/\text{GO}$ composite membrane). Reproduced with permission from ref. [71]. Copyright 2017, American Chemical Society

8.4.4 Removal of Heavy Metal Salts

Heavy metals such as lead (Pb), Chromium (Cr), Copper (Cu) and Cadmium (Cd) are representative heavy metal ions extensively applied in numerous industries, such as oil refineries. Pb species mainly exist in Pb^{2+} , $\text{Pb}(\text{OH})^+$, and $\text{Pb}_2(\text{OH})^+$ in water solution. These pose a health threat when their concentrations exceed the maximum acceptable Pb(II) concentration in drinking water. Despite their lower surface area, 2D nanomaterials such as MXenes have proven to have higher removal capacities than other adsorbents like activated carbon. Therefore, MXene has recently been employed as a new, highly efficient material for the removal of Pb(II) from the water through electrostatic interaction and ion exchange mechanisms. In the high surface negative surface charge of MXenes, the heavy metal ions are mainly removed by ion exchange, electrostatic attraction, and inner-sphere complex formation mechanisms [85]. It was noticed that MXene-based laminar nanofiltration membranes perform well as composites. This was shown by using $\text{Fe}_3\text{O}_4@\text{MXene}$ membrane in a study by Yang et al. [30] that showed that the inclusion of NPs within the interlayer sheet spacing helps improve membrane permeability due to the construction of large permeation channels for water molecules. Fe_3O_4 contributed to MXene nanosheets adsorbing metal ions effectively.

8.4.5 2D Nanomaterial Membranes for Desalination

Nanoporous membranes are single-layer ultrathin 2D membranes with a sub-nanometer thickness (e.g., single-layer graphene with a thickness of $\sim 3.4 \text{ \AA}$). They

are impermeable to liquids and gases, including helium. Using focused ion beam and transmission electron microscopy, the nanoscale pores (nanoporous) are drilled or produced by eliminating atoms in the center of the membrane until the preferred pore size is attained. The nanoscale pores may range from 50 to 80 Å² [46, 66, 86]. Nanoporous membranes are usually employed for effective desalination and targeted to remove monovalent salt ions (Na⁺, Cl⁻). Nanoporous membrane performance is affected by factors such as the size, structure of 2D materials, pore chemistry, and geometry [66].

With simulations, water flux is calculated by determining the average rate of permeate molecules over time by fitting the gradient of the permeate molecules against the simulation time curve, often operated for desalination using the RO process (Fig. 8.11). For example, the selectivity against salt ions is calculated as the ratio of ions transported during the simulation time of 10 ns. Comparison can be made to compare the performance of the various 2D nanoporous membrane materials to determine their efficiencies. The pore area of 50 Å² for MXene nanoporous membranes gives a desired salt rejection of 99% and maximum water flux at a pressure of 100 MPa. The rejection rate decreases with an increase in pressure and an increase in pore volume. Ultimately, the performance comparison between the different MXenes (Ti₂C, Ti₃C₂, Ti₄C₃) shows that the membrane selectivity depends more on the pore than the membrane material [87].

Permeation coefficient is used to compute pressure invariant water permeability of

$$P = \frac{J_w}{-V_w \Delta C_s + \frac{V_w}{N_A k_B T} \Delta P}$$

where, J_w is the H₂O flux (#/ns), V_m is the H₂O molar volume (18.91 mL/mol), ΔC_s is the concentration gradient of the solute (2.28 M), N_A is Avogadro's number, k_B is the Boltzmann constant, T is the temperature (300 K), and ΔP is the applied hydrodynamic pressure (50 – 300 MPa) [66].

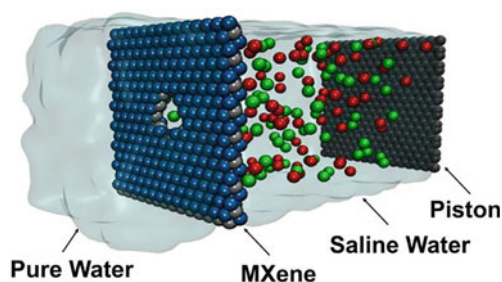


Fig. 8.11 A typical simulation box shows a graphene sheet piston, saline feed water with K⁺ and Cl⁻ ions, a MXene membrane with drilled pores, and a fresh/filtered water section. Reproduced with permission from ref. [66]. Copyright 2021, American Chemical Society

In addition to the single-sheet nanoporous membranes, MXene sheets could be used to produce salt rejection membranes for the precise filtration of ions from saline water and used as desalination membranes. Cations of various sizes, including the monovalent Na^+ , have shown the ability to intercalate between $\text{Ti}_3\text{C}_2\text{T}_x$ MXene layers, resulting in the expansion or contraction of the multi-layer laminar membrane produced by the vacuum filtration method [58].

8.5 Conclusion

This chapter covers the properties of 2D nanomaterial-based membranes in water treatment and desalination. It mainly focuses on the most commonly used emerging nanomaterials, namely graphene-based materials, MXenes and MoS_2 , and their membrane fabrication methods. These membranes have shown great potential in removing toxic organic and inorganic compounds in water treatment and desalination. Therefore, using nanomaterials in wastewater treatment is promising in efficiently removing toxic contaminants from wastewater streams. Considering the membrane fouling challenge faced by the currently used polymer membranes, the use of 2D nanomaterials in either improving or replacing the wastewater and desalination membrane properties is a promising solution. In addition, using 2D nanomaterials with their exceptional properties, desalination can become more sustainable and economical. Currently, desalination using the existing polymer membranes is facing challenges of membrane permeability. Thus, the low throughput of desalination plants makes them expensive. Therefore, using a membrane with improved permeability will make desalination possible to be used globally as an everyday water treatment technique. In this regard, a sustainable water supply can be secured using membrane technologies.

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