Review Paper

Progress and Perspective of Antifouling, Pressure Driven, Flat-Sheet Nanocomposite, Polymeric Membranes in Water Treatment

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Highlights
• Recent advances in membrane modification by nanomaterials is reviewed.
• Nanomaterials proven to be promising for augmenting the membrane properties.
• Nanocomposite membranes attenuate fouling against a wide range of pollutants.

Abstract
Membrane filtration, especially based on the size exclusion phenomenon, has long been established due to its abilities to addressing the growing demands of the clean water of the world’s population. However, widespread applications of the membranes face several challenges including chemical vulnerability, thermal deterioration, and biological degradation of the membranes that transpire while recovering the membrane flux after fouling. Therefore, developing antifouling membranes for water treatment purposes immensely increased in the past few years and inorganic nanoparticles played a significant role in this era. By considering the great potential of nanoparticles in the field of developing robust and small foot-print membranes, this study reviews the application of nanoparticles in pressure driven flat-sheet membranes and their impact on membrane characteristics and performance. It has been demonstrated that the application of nanoparticles has greatly improved the water permeability and antifouling potential of the membrane without compromising the selectivity of the membranes.

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1. Introduction

A continuously increasing demand of fresh water is one of the threatening issues to the world. The world’s water resources are distributed into conventional water resources (ground water, rivers, and lakes) providing clean water for direct utilization including drinking or industrial purposes and unconventional water resources (polluted water, wastewater, brackish water and sea water) that need treatment prior to use. The huge utilization of conventional water resources in everyday life by individuals (drinking, cleaning, flushing), agriculturalists and industrialists has promptly depleting the conventional water resources. According to an estimate, a huge amount of water is utilized by industrial and agricultural activities: 70% of the surface water and ground water, rest is served for domestic use [1]. The main challenges that are affecting the world into sever water crisis include but not limited to population growth, food security demand, and mining activities [2-5]. Due to extensive use of freshwater for agricultural and industrial activities nearly 750 million people lack access to the safe drinking water [6]. Many are forced to rely on contaminated water for potable use, which tends them prone to waterborne diseases like Typhoid, hepatitis A and hepatitis E, polio and cholera, birth defects, bladder cancer, and spontaneous abortion. Moreover, ~80% of the used water is directly discharged into the conventional water resources (lakes and rivers) that reduces the availability of fresh water for direct use [6]. In developing countries around half of the population is exposed to polluted water sources, which along with inadequate water supplies for personal hygiene and poor sanitation contribute to an estimated 4.3.3.5. Chemical grafting

Surface located nanocomposite

2. Membrane modifications for fouling mitigation

For several years, a huge devotion is employed for altering the membrane properties to reduce membrane fouling [9, 14-16]. Different researchers use different methods to alter membrane properties, which can produce fouling resistant membranes with longer life spans. Based on the particular requirement, various modifications are performed by adding new additives, including hydrophilic polymers (polydopamine, poly(ethylene glycol), etc.) [17, 18], amphiphilic copolymers (PVD-g-P(PEGMA), poly(vinylidene fluoride)-graft-poly(N,N-dimethylamino-2-ethylmethacrylate) (PVD-g-PDMAEMA), etc.) [19, 20], inorganic nanoparticles (SiO₂, ZnO, TiO₂, graphene oxide, etc.) [16, 17, 21-23] or some other charged molecules. The modification techniques can be broadly categorized into pre-modification and post-modification. In pre-modification, membrane properties are altered before fabrication of the membrane i.e. alteration of polymer backbone to use for membrane fabrication or modifiers are applied to membrane solution before membrane fabrication. In post-modification, membrane properties are altered after the fabrication of the membrane. A detailed summary is given in Table 1 about the types of modifications, polymer, and modifier used in
different researches.

### 3. Nanomaterials as membrane modifiers

The technical innovation introduces new methods for incorporation of NPs into the membrane to fabricate membranes with desirable properties. The location of NPs in membrane categorizes the prepared membrane as well as the preparation procedure. The incorporation of NPs not only improves the intrinsic properties of the membrane (e.g. hydrophilicity, surface charge, and surface roughness), but also introduces some additional properties to the membrane. Such properties include mechanical strength, thermal stability, change in pore size and porosity, and specific properties of respective NPs i.e. photocatalysis, antibacterial property, adsorption etc. The prepared membrane could be a nanocomposite or hybrid membrane in which NPs are dispersed throughout the membrane matrix; thin-film nanocomposite membrane in which NPs are incorporated at the surface of the membrane but dispersed in a thin-film of polymer; surface located nanocomposite membrane in which NPs are located at the surface. Each type of membrane modification, method to prepare such membranes, and advantages of these modification will be discussed in details in the following sections.

#### 3.1. Nanocomposite or hybrid membranes

It is the simplest method used to incorporate NPs into the membrane to improve membrane fouling characteristics: NPs are dispersed throughout the membrane matrix and improve antifouling properties of the membranes. In order to prepare such membranes, NPs are blended in polymer solution, and polymer-NPs blend is used to prepare the membrane. Thus, the process is largely known as physical blending process. The membrane preparation could be through phase inversion process (PIP) or by electrospinning process. In both cases, the NPs are incorporated into the membrane matrix. A schematic of physical blending followed by phase inversion method is given in Figure 1. 

Oli et al. [24] prepared flat-sheet PVDV UF membranes by dispersing TiO$_2$ NPs into casting solution. A shift of membrane surface property was found from hydrophobic to hydrophilic: the contact angle was decreased from 80$^\circ$ to 60$^\circ$. They further found that the addition of NPs decreased the average pore size (~0.24 to 0.12 µm) and surface roughness. The membrane fouling index was determined using casein solution that showed reduced fouling of modified membrane, which was attributed to the increase in hydrophilicity, decrease in pore size and surface roughness of the membrane.

Yan et al. [25] prepared Alumina (Al$_2$O$_3$) PVDV nanocomposite UF membrane by PIP. The prepared membranes were used for the rejection of oil from an oil field. More than 90% and 98% retention of chemical oxygen demand and total organic carbon (TOC) and less than 1 g L$^{-1}$ oil content was found in the permeate. Moreover, 100% of flux recovery ratio (FRR) of Al$_2$O$_3$-PVDV nanocomposite membranes was reported after cleaning with 1 wt.% OP-10 surfactant treatment at pH 10.

Cui et al. [26] prepared PVDF/SiO$_2$/dibutyl phthalate UF membrane using thermally induced phase separation (TIPS) and found that the presence of SiO$_2$ largely affected the membrane internal morphology. In more details, they reported that the porosity continuously decreased by increasing the concentration of SiO$_2$. The membrane flux increased by increasing the SiO$_2$ concentration and reached at maximum point i.e. 120 L m$^{-2}$ h$^{-1}$ at 0.1 MPa corresponding to 5 wt.% SiO$_2$, but a further increase in SiO$_2$ reduced the flux. Tensile strength also showed the similar trend as of flux, but the optimized concentration of SiO$_2$ was reported as 3 wt.% for tensile strength.

Shuai et al. [23] prepared PVDF nanocomposite membrane with a wide concentration range of Nano-ZnO (6.7% to 26.7 wt.%) as membrane modifier to fabricate anti-irreversible fouling membranes. They found almost 100% FRR for all the modified membranes whereas pristine PVDF membrane achieved only 78% FRR. Finally, the optimized dosage of nano-ZnO was determined as 6.7%, which increased the flux of the membrane almost double than that of pristine PVDF.

Another very interesting study was reported by Nang et al. [27]: PVDF-TiO$_2$ mixed matrix membrane was prepared and the modified membrane dramatically improved PWF i.e., 392.81±10.93 m$^{-2}$ h$^{-1}$ bar$^{-1}$ compared to that of the neat membrane (76.99±4.87 L m$^{-2}$ h$^{-1}$ bar$^{-1}$). The rejection coefficient was reported as 99% for methylene blue (MB) dye with modified membranes. Moreover, they induced the self-cleaning potential of the membrane under UV light, which showed 100% FRR.

The nanocomposite membranes showed an improvement in the basic characteristics of the membranes (hydrophilicity, pore size, porosity), which are considered crucial for the filtration purposes. The detailed properties of the nanocomposite membranes are discussed hereafter.

#### 3.1.1. Impact of physical blending on nanocomposite membranes

There are several advantages of nanocomposite membranes, some are specific to the applied NPs (antibacterial activity, oxidative behavior etc.) and some are irrespective of the NPs (hydrophilicity, surface roughness, tensile strength etc.). Some of the important modifications encountered after incorporation of NPs are mentioned below:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Modifier</th>
<th>Modification technique</th>
<th>Application/foulant</th>
<th>Membrane properties and performance evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>TiO$_2$</td>
<td>Pre-modification (blending)</td>
<td>UF/HA</td>
<td>hydrophilicity↑, PWF↑, fouling↓, S value↑, rejection coefficient↑, irreversible fouling↑ [28]</td>
</tr>
<tr>
<td>PSf</td>
<td>GO-TiO$_2$</td>
<td>Pre-modification (blending)</td>
<td>UF/HA</td>
<td>hydrophilicity↑, PWF↑, fouling↓, surface charge: more negative, fouling resistance↑, rejection coefficient↑, surface roughness↑ [29]</td>
</tr>
<tr>
<td>PVDF</td>
<td>CA</td>
<td>Pre-modification (blending)</td>
<td>UF/BSA and sewage waste water</td>
<td>hydrophilicity↑, PWF↑, porosity↑, fouling↑, fouling resistance↑, flux recovery ratio↑, tensile strength↑, pore size↑, rejection coefficient↑ [30]</td>
</tr>
<tr>
<td>PSf</td>
<td>Isocyanated-GO</td>
<td>Pre-modification (blending)</td>
<td>UF/BSA</td>
<td>hydrophilicity↑, PWF↑, surface charge: more negative, surface roughness↑, pore size↑, fouling resistance↑, flux recovery↑ [31]</td>
</tr>
<tr>
<td>PVDF</td>
<td>PVC-g-(P(PEGMA))*</td>
<td>Pre-modification (blending)</td>
<td>UF/BSA</td>
<td>hydrophilicity↑, PWF↑, pore size↑, porosity↑, fouling resistance↑, but higher absolute flux was recorded, rejection coefficient↑ [19]</td>
</tr>
<tr>
<td>PVDF</td>
<td>PVP-carboxylated TiO$_2$</td>
<td>Post-modification (TFN)</td>
<td>NF/BSA</td>
<td>hydrophilicity↑, PWF↑, fouling↑, rejection coefficient↑, flux recovery↑, surface roughness↑ [32]</td>
</tr>
<tr>
<td>PVDF</td>
<td>ZnO</td>
<td>Post-Modification (Atomic layer deposition)</td>
<td>MF/SA</td>
<td>hydrophilicity↑, PWF↑, fouling↑, pore size↑, surface charge: more negative, total surface energy↑, fouling resistance↑, rejection coefficient↑ [33]</td>
</tr>
<tr>
<td>PVDF</td>
<td>Acrylic and amino monomer</td>
<td>Post-modification (dip coating)</td>
<td>UF/Non-skim milk</td>
<td>hydrophilicity↑, PWF↑, fouling↑, fouling resistance↑, rejection coefficient↑, flux recovery↑ [34]</td>
</tr>
<tr>
<td>SMA/PVDF</td>
<td>TiO$_2$</td>
<td>Post-modification (self-assembly)</td>
<td>UF/BSA</td>
<td>hydrophilicity↑, PWF↑, fouling↑, rejection coefficient↑, flux recovery↑, MWCNT↑ [35]</td>
</tr>
<tr>
<td>PCTE**</td>
<td>Al$_2$O$_3$</td>
<td>Post-modification (Atomic layer deposition)</td>
<td>UF/BSA</td>
<td>hydrophilicity↑, PWF↑, fouling↑, pore size↑, rejection coefficient↑ [36]</td>
</tr>
</tbody>
</table>

*PVC-g-(P(PEGMA)): Poly(vinyl chloride)-grafted-poly(ethylene glycol) methylether methacrylate
**PCTE: track-etched poly carbonate membranes
HA: humic acid
BSA: bovine serum albumin
PWF: pure water permeance
S value: structural parameter value
3.1.2. Effect on membrane porous structure

Incorporation of NPs into polymer membrane alters the morphology of the membrane. Most of the studies found that porosity and pore size are largely affected by the incorporation of NPs into the membrane [37, 38]. Besides pore size and porosity, the type of interconnected porous network of the membrane is also influenced by NPs [28].

Zhang et al. [39] found that addition of TiO$_2$ NPs into PVDF membrane tailored the membrane porous structure and a shift was observed from fingerlike voids to spongy voids with an increase in NPs concentration. However, they found that a transformation of inherent porous network is dependent on optimized concentration of NPs.

Dong et al. [40] found that addition of Al$_2$O$_3$ NPs or Linda type L (LTL) zeolite NPs changed the pore size of the PSf membrane. Alpatova et al. [41] reported an insignificant change in the pore size of the PVDF membranes by incorporation of Fe$_2$O$_3$ NPs, but porosity of membrane was highly affected and linearly related to the concentration of Fe$_2$O$_3$ NPs. The addition of ZnO NPs also tailored the porosity and pore size of the membrane [23], but optimized concentration of NPs to be applied serves an important factor. The role of ZnO NPs for changing the porosity and pore size is shown in Figures 2a,b. Likewise, MgOH NPs also increased the porosity of the membrane that is directly correlated to the concentration of MgCl$_2$ in casting solution (Figure 2c), which reacted with NaOH in coagulation bath and produced MgOH NPs in membrane. In another study, CuO NPs were also found responsible for increase in membrane pore size, but after certain concentration of CuO, the pore size started to decrease. Similar trend was observed with porosity change caused by the addition of CuO NPs (Figure 2d). It was described that the hydrophilicity of NPs increased the water penetration during solvent-nonsolvent exchange period and more water rapidly entered the membrane, which increased the pore size and porosity. Conversely, by increasing the concentration of NPs from specific range, the dope solution became more viscous and reduced the penetration of water into membrane during phase transformation. As a result, smaller pore size and less porosity was recorded with high concentration of NPs [42].

![Fig. 1. Physical blending of NPs into membrane casting solution followed by PIP for membrane fabrication.](image)

![Fig. 2. Effect of NPs on the pore size and porosity of the membrane. (a) SEM images of the surface of membranes with different concentration of ZnO [23]; (b) average pore size of the membranes of ZnO containing membranes [23]; (c) effect of MgOH NPs concentration on the porosity of the membranes [43]; (d) effect of different concentrations of CuO NPs on the pore size and porosity of the membrane [42].](image)
3.1.3. Effect on hydrophilicity

Hydrophilicity is another major attribute of membrane affected by incorporation of NPs. The membrane imbedded NPs attract more water molecules because of their high surface energy by producing hydrogen bonds with water molecules resulting in the formation of tight hydration layer on the membrane. Therefore, NPs fail to express their actual impact. This become clear by a study where membranes were prepared by adding different concentrations of TiO$_2$ NPs, and the CA did not show remarkable changes [48]. It was found that 2% TiO$_2$ NPs in PES membrane decreased the CA from 72° to 60° but a further increase in TiO$_2$ NPs concentration: 4% and 6%, failed to significantly reduce CA from that of 2% TiO$_2$ NPs (Figure 3c).

3.1.4. Effect on surface charge

Surface charge density of the membranes could also be affected by the incorporation of NPs. Sometimes, NPs are functionalized with charged groups to induce charge on the membrane, which helps in reducing the fouling propensity of the membrane. Zhang et al. [31] prepared the PSF membranes with different concentration of isocyanate-treated GO (iGO) NPs. First, they analyzed the zeta potential of GO and iGO at different pH and found that zeta potential of both, GO and iGO, decreased continuously as pH increased from 2 to 11, but increased after pH 11. After incorporation of iGO into PSF membrane, the surface charge of the membrane was dramatically decreased and showed a linear relationship with iGO content in the membrane demonstrating more exposure of iGO to the surface by increasing the concentration of iGO in the dope solution.

3.1.5. Effect on mechanical strength

Mechanical strength influences the life-span of the membranes. A membrane with higher mechanical strength can resist the harsh conditions produced by the feed solution i.e. increase in transmembrane pressure. The mechanical strength of the membrane largely depends on the membrane morphology e.g. macroporous membrane has less mechanical strength and microporous membrane has higher mechanical strength. A good compatibility is usually found between NPs and polymer that increases the interaction (physical or chemical) among NPs and polymer molecules. As a result, membrane morphology is transformed from macroporous to microporous structure and membrane become mechanically strong [49]. Liang et al. [23] reported a linear relationship between the concentration of ZnO NPs present in membrane and mechanical strength of the membrane (Figure 4a).

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![Figure 3](image-url)  
Fig. 3. The impact of NPs on the hydrophilicity of the membranes, (a) change in contact angle of PVDF membrane by addition of SiO$_2$ NPs, SNTs, and PSNTs [45]; (b) correlation between contact angle and water permeability by addition of TiO$_2$ NPs to the PES membrane [44]; (c) effect of different concentrations of TiO$_2$ NPs (modified and unmodified) on the contact angle of the membrane [48]; (d) a decrease in contact angle of PVDF membrane by adding GO/OMWNTs to the membrane, and temporal behavior of contact angle by varied concentration of said modifiers [22].
The increase in mechanical strength was attributed to the shrinking of fingerlike voids beneath skin layer of the PVDF membrane by addition of ZnO NPs. Wang et al. [50] prepared nano Al₂O₃/EPDM composite and reported an increase in tensile strength and elongation at break with increase in nano Al₂O₃ concentration in membrane matrix. In another study, PVDF-LiClO₄-TiO₂ membrane was prepared by adding TiO₂ NPs into PVDF-LiClO₄ membrane [51]. It was found that the addition of LiClO₄ decreased the mechanical strength but the addition of TiO₂ NPs increased the mechanical strength of the membrane, which was exclusively attributed to strongly interconnected voids as an effect of TiO₂ NPs (Figures 4c,d). The thorough study on the stress and strain of the membranes with and without NPs strongly supports that addition of NPs in membrane adds mechanical strength to the membrane system, which could enhance the membrane resistance against harsh conditions i.e. high pressure, strong flow rate, mechanical cleaning. Sometimes inclusion of NPs reduces the mechanical strength, which is associated with high concentration of NPs (Figure 4b). High concentration of NPs favors the formation of macrovoids in membrane matrix resulting in decreased mechanical strength [39]. Therefore, it can be concluded that an appropriate concentration of NPs should be used that do not produce agglomerates in dope solution and macrovoids in membrane matrix, and results in strengthening of the membrane.

3.1.6. Effect on surface roughness

The relationship of surface roughness to membrane fouling has been described earlier but the impact of NPs incorporation into polymer membrane is contradictory. Some reports found that the surface roughness of the membrane decreased by incorporation of NPs while some stated that the surface roughness increased by introducing NPs into the membrane matrix. In both cases, either surface roughness decreases or increases after incorporation of NPs, the antifouling potential of the membrane was increased. Consequently, it remains challenging to relate the surface roughness with membrane fouling and impact of NPs on surface roughness. As observed by Zhang et al. [39] that incorporation of TiO₂ NPs constantly increased surface roughness of the membrane.Irrespective of increase in surface roughness, all the membranes showed improved fouling resistance (Figures 5a,b). On contrary, Razzmijou et al. [48] found that addition of TiO₂ NPs decreased the surface roughness of the membrane, thus the membrane fouling is reduced. They recorded a minute difference between surface roughness of PES membrane and PES-TiO₂ NPs nanocomposite membrane: from 50.76 nm to 39.77 nm, (Figure 5c). Likewise, Song et al. [17] also reported the impact of TiO₂ NPs towards reduced surface roughness of PVDF membrane, but the degree of difference was so minute (4 nm) to be considered effective in mitigating membrane fouling (Figure 5d).

3.2. Thin film nanocomposite membrane

With the development of thin film composite membrane over the past decade, the integration of nanoparticles in various fields have also drawn the attention of the researchers to modify the TFC membranes into thin film nanocomposite membranes. TFC membranes are majorly RO and NF membranes with the potential to remove salts through desalination of sea water and brackish water, emerging organic pollutant including pharmaceuticals and pesticides, and heavy metals. TFC membranes have several advantages over the conventional asymmetric membranes for high solute separation with high fluxes that is managed by optimized support layer of the membranes.

The preparation of TFN membranes is based on the same procedures as of TFC membrane with the difference of incorporation of NPs in the surfaces and support layer. During the fabrication step of the TFN membranes, NPs of various particle sizes are introduced in surface and sublayer that make the membrane more hydrophilic and/or alter the surface charge density of the membrane without compromising the membrane selectivity. TFN membranes can also be used for RO, FO, and NF for the removal of said foulants and also including organic solvents. The most commonly used procedures for the preparation of TFN membranes include in situ interfacial polymerization of polyamide and dip coating. Table 2 summarizes various types of TFN membranes, NPs modifications, and the obtained properties after modification.

Fig. 4. Role of NPs in improving mechanical strength of polymer membranes, (a) effect of ZnO NPs on the mechanical strength of PVDF membrane [23]; (b) effect of TiO₂ NPs concentration on the mechanical strength and elongation at break of PVDF membrane [19]; (c) stress vs. strain curves for the PVdF/LiClO₄/TiO₂ membranes, variation of Young’s modulus with the TiO₂ content for PVdF/LiClO₄/TiO₂ membranes, respectively [51].
Fig. 5. Effect of NPs addition to the membrane surface roughness, and its relation to the fouling of the membrane. (a, b) surface roughness parameters of TiO$_2$-PVDF nanocomposite membrane, and its relationship to the fouling of the membrane, the concentration of TiO$_2$ NPs increased from T1 to T5 [39]; (c) surface roughness (detected using AFM) of the PES membranes by addition of TiO$_2$ NPs and modified TiO$_2$ NPs [48]; (d) surface roughness parameters (measured by AFM) of (a) PVDF-PEG membrane and (b) PVDF-PEG-TiO$_2$ NPs composite membrane [17].

Table 2
Types of nanomaterial used to fabricate TFN membrane and changes in membrane properties acquired after modification.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Modifier</th>
<th>Modification Technique</th>
<th>Application/foulant</th>
<th>Membrane properties and performance evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf</td>
<td>GO</td>
<td>IP of PA</td>
<td>RO/ 2000 ppm NaCl</td>
<td>High flux, antibacterial activity, chlorine resistance [52]</td>
</tr>
<tr>
<td>PSf</td>
<td>GO nanosheets</td>
<td>IP of PA</td>
<td>RO/ 2000 ppm NaCl</td>
<td>High flux, antibacterial activity [53]</td>
</tr>
<tr>
<td>PSf</td>
<td>Al$_2$O$_3$</td>
<td>IP</td>
<td>NF</td>
<td>Excellent molecular separation properties [54]</td>
</tr>
<tr>
<td>Arylene sulfide sulfone O-PASS</td>
<td>SiO$_2$ and ZIF8</td>
<td>Filtration of OPASS solution</td>
<td>UF</td>
<td>Dye rejection [55]</td>
</tr>
<tr>
<td>PSf</td>
<td>Ag NPs</td>
<td>IP of PA</td>
<td>UF</td>
<td>Increased salt rejection of NaCl and MgSO$_4$, antimicrobial properties [56]</td>
</tr>
<tr>
<td>polyhedral oligomeric silsesquioxane (POSS)</td>
<td>TiO$_2$:SiO$_2$</td>
<td>IP of PA</td>
<td>RO</td>
<td>Seawater desalination [57]</td>
</tr>
<tr>
<td>PES</td>
<td>CNT</td>
<td>IP of PA</td>
<td>UF</td>
<td>Improved separation efficiency [58]</td>
</tr>
<tr>
<td></td>
<td>SAO-66</td>
<td>IP of PA</td>
<td>RO</td>
<td>boron rejection by ∼11% [59]</td>
</tr>
<tr>
<td>PA(TFC)</td>
<td>ZnO</td>
<td>IP of PA</td>
<td>RO</td>
<td>Improved water flux and salt rejection [60]</td>
</tr>
<tr>
<td>PA-TFN</td>
<td>graphene quantum dots (GQDs)</td>
<td>IP of PA</td>
<td>RO</td>
<td>Improved surface hydrophilicity, antimicrobial activity [61]</td>
</tr>
<tr>
<td>TFC</td>
<td>(ZIF-8)/chitosan layer</td>
<td>IP of PA</td>
<td>UF</td>
<td>NaCl rejection of &gt;99.5 [62]</td>
</tr>
<tr>
<td>PSS-TFN</td>
<td>ZIF-8</td>
<td>IP of PA</td>
<td>UF</td>
<td>Better swelling resistance [63]</td>
</tr>
<tr>
<td>PES</td>
<td>SAPO-34</td>
<td>IP of PA</td>
<td>UF</td>
<td>Dye removal methyl violet 6B, reactive blue 4 and acid blue 193) from water [64]</td>
</tr>
<tr>
<td>PSf</td>
<td>Functionalized MWCNTs</td>
<td>IP of PA</td>
<td>FO</td>
<td>High water permeability and acceptable salt rejection [65]</td>
</tr>
<tr>
<td>PSf</td>
<td>Modified SiO$_2$</td>
<td>Piperazine-TMC</td>
<td>NF</td>
<td>Anti-fouling ability, long-term stability [66]</td>
</tr>
</tbody>
</table>
3.2.1. Interfacial polymerization

The most common TFN membrane is polyamide (PA) membrane, where PA layer is formed on the surface of the porous support membrane. The process of IP initiated by depositing the reactive diamine monomer on the surface of the porous support membrane. Mostly, the membrane is dipped in the monomer solution of m-phenylenediamine (MDP), followed by immersion into organic solution of second reactive monomer, usually di/tri-acid chloride (trimesoyl chloride (TMC)). The highly reactive monomers start polymerization as soon as they come into contact and form a highly cross-linked thin layer of PA on the surface of the porous support membrane, which remains attached on the membrane. The polymerization process also prevents further diffusion of TMC into DMP that terminates the polymerization leaving a thin layer (up to 500 nm) of PA on the membrane. The chemical properties of the monomers play an important role in determining the thickness of the film, roughness, hydrophilicity and surface charge. Based on the chemical properties of the monomer, the membrane can be optimized for solute rejection for example zwitter-ion-based polymers possess strong anti-fouling and anti-biofouling potential for TFC membranes due to their high hydrophilicity, durability, and environmental stability [67]. The zwitterionic polymers contains both anionic and cationic groups within the same monomer unit, that strongly interact with surrounding water molecules via the electrostatic forces and form a tighter hydro-layer over the membrane [67-69]. It is also found that the zwitterionic polymer brushes extend the surface carboxylic groups that provide significant anti-fouling and anti-biofouling potential during water purification e.g., FO. [67, 68].

As mentioned previously that TiO₂ NPs have gained much attention in various water treatment processes due to its numerous characteristics, TiO₂ NPs have also been applied for the preparation of TFN membranes. Lee et al. [70] introduced a new method where aqueous solution of MDP and organic solution of TMC containing substantial amount (about 5%) of TiO₂ were in situ polymerized and the resulting PA layer was enriched in TiO₂ NPs. The resultant NF membrane rejected more than 95% of MgSO₄ salt with stable performance due to the presence of TiO₂. Emadzadeh et al. [71] prepared modified porous substrate by dispersing TiO₂ NPs in PSf and the PA thin film layer was established on the surface of PSf-TiO₂ membrane by first pouring 1,3-phenylenediamine (MDP) onto the substrate for 2 min, removed the excess MDP, and then pouring 1,3,5-benzencarbonyl trichloride on the MDP anchored substrate. The resultant TFN membrane showed 120% higher flux while 10 mM NaCl feed solution was used for FO process. Moreover, the internal concentration polarization (ICP) was also reduced several folds due to the modified porous substrate used to prepare TFN membrane.

SiO₂ NPs also showed the improve membrane morphology and performance of TFN membranes due to their strong surface energy, small size, thermal resistant and the most important is environmentally inert behavior that makes them applicable in a wide range of industries. Niksefat et al. [74] dispersed the SiO₂ NPs in the aqueous solution of MDP. The prepared porous substrate was immersed in MDP crosslinked by chemical polymerization. TiO₂ NPs dispersed in the MDP for some time and later the amine functionalized substrate membrane was soaked into organic solution of TMC for IP process. The resultant TFN membrane showed flux of 36 ± 2 LMH that was nearly twice the flux of TFC membrane. Moreover, the salt rejection was also more than 90% with 10 mM NaCl as feed solution and 2 mM NaCl as draw solution. Yin et al. [75] used porous MCM-41 (~100 nm) and non-porous spherical silica NPs (~100 nm) to fabricate the TFN membrane at concentrations ranging from 0 to 0.1 wt%, and reported that the MCM-41 NPs dispersed well in PA thin-film layer and suggested that the internal pores of MCM-41 NPs contributed significantly to the increase of water permeability. Where the permeate water flux increased from 28.5±1.0 to 46.6±1.1 L/m²h without compromising the salt rejection with the incorporation of MCM-41 NPs.

Recently, GO and carbon nanotubes (CNT) have been used for the preparation of TFN membranes including RO, FO, and NF membranes: GO is used due to its numerous hydrophilic functional groups [52], CNTs due to the similarity between their fluid transport properties and those of water transport channels in membranes [76-78]. The application of both GO and CNTs has been reported to improve various properties of the membrane s including modulus and tensile strength, water flux and permeability, and rejection. Chae et al. [52] reported that a TFN membrane with GO and PAA layer exhibited high water permeability and anti-biofouling property, and chlorine resistance without loss of salt rejection. The water permeability and anti-biofouling property of the GO-TFC membrane were enhanced by approximately 80% and 98%, respectively, as compared to TFC membrane only. Amini et al. [65] prepared TFN FO membranes by applying amine functionalized multi walled CNTs (MWCNTs) into PA thin film prepared by IP process. The performance of the prepared FO membrane was evaluated by using NaCl as feed (10 mM) and draw (2 mM) solutions. The TFN membranes exhibited 95.7 L/m²h flux with 0.1 wt% functionalized MWCNTs that was nearly 160% higher than TFC membrane. The high water flux with higher MWCNTs loading was attributed to the increase in hydrophilicity of the membrane that was evaluated with decrease in the CA.

3.3. Surface located nanocomposite

It has been previously seen that incorporation of NPs into membrane matrix improve the membrane intrinsic properties e.g. membrane porosity, membrane morphology, membrane internal resistance, membrane pore size, membrane mechanical strength, and membrane charge. In both types of the membranes stated above (nanocomposite and thin-film nanocomposite), NPs remain partially covered by the polymer. It is widely reported that blending of NPs with the polymer solution allows polymer to encase large amount of NPs, which prohibits the NPs to reveal their actual properties [28, 38, 79]. Therefore, huge efforts are allocated to develop membranes with maximum exposure of NPs and different procedures have been developed and adopted to attain NPs exposure and their stability on membrane surface. The major characteristics possessed by surface located NPs membranes are: decreased fouling tendency of the membranes, maximum hydrophilicity depending on the type of NPs, and reduced intrinsic resistance of membrane. Below, some of the commonly practiced techniques to incorporate NPs on the surface of the membrane are discussed.

3.3.1. Self-assembly

Self-assembly is a technique where NPs get assembled on the membrane surface without an external aid. This process is widely used to immobilize different NPs on the membrane. In self-assembly, the NPs are functionalized with different groups that are capable to produce hydrogen bonding with NPs. Some of the functional groups include –COOH, –SO₃H, and sulfone groups. If the membranes do not have any functional group, the membrane is pretreated to induce active functional group that can develop hydrogen bonding with the NPs. The TiO₂ NPs can be self-assembled on PSF based membrane (with PA thin-layer) by dipping the membrane in colloidal solution of TiO₂, which allows self-attachment of TiO₂ with –COOH group of polymer [80]. The possible assembly schemes of TiO₂ on membranes are given in Figure 6a, and schematic of self-assembled TiO₂ on membrane is shown in Figure 6e. Similar kind of interaction is also shown in the Figure 6b: between TiO₂ and PES film, and TiO₂ and DEA modified surface of PSf [81]. Bae and Tak [82, 83] successfully immobilized TiO₂ NPs on a commercially available PES MF membrane, where the membrane was immersed into 20% H₂SO₄ for different time durations (soaking for more time generated more sulfonic acid groups at the membrane surface) followed by immersion of membranes in laboratory made transparent TiO₂ colloidal suspension. It was seen that the membrane soaked for more time in H₂SO₄ contained more TiO₂ NPs on its surface (Figure 6d), which was ascribed to the formation of more sulfonic groups on the membrane as a factor of dipping time. The membranes with TiO₂ NPs exhibited low fouling tendency and photocatalytic degradation of organics; only partial membrane surface possesses such properties that is covered by NPs, rest of the membrane surface shows fouling and inability of self-cleaning [35, 84, 85].

3.3.2. Coating/deposition

Coating/deposition is the simplest technique used to immobilize NPs on the membrane surface. Either a membrane is dipped into NPs solution and pulled back with a constant slow rate [dip coating (Figure 7a)] or NPs solution is filtered through the membrane so as to force NPs to stay on the membrane: deposition [86, 87] (Figure 7b). Fan et al. [88] prepared hydrophilic PSf membrane by filtering polyaniline nanofiber aqueous dispersion and found a sharp increase in water flux and huge decline in contact angle i.e. 64° and 27° for simple PSf membrane and PANI nanofiber deposited membrane, respectively. Guo et al. [89] deposited NPs on cellulose acetate (CA) membrane by filtering 200 mg GO-TiO₂, P25 TiO₂, and TiO₂ microsphere NPs solution through CA membrane followed by 30 sec N₂ gas treatment. A deposition procedure usually results in a sharp decline of membrane water flux due to pore blocking and pore plugging by NPs. As shown in Figure 7c, the membrane with P25 TiO₂ NPs deposition showed the least flux that was attributed to the very small size of P25 plugging the pores. Irrespective of the low flux, membranes with different kinds of NPs deposited on the surface demonstrated TOC degradation in feed solution under UV light (Figure 7d), which was maximum with GO-TiO₂ deposited membrane that was in accordance to the high photocatalytic oxidation potential of GO-TiO₂ NPs as compared to other NPs.

Although membrane performance improves initially by depositing NPs on the membrane, NPs leach as a factor of time and membrane efficiency
This simple method seemed to be largely scalable but non-affirmative behavior of NPs on the membrane prohibited coating/deposition of NPs to be largely practiced.

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**Fig. 6.** Self-assembly mechanism of different NPs on different polymer based membranes: (a) mechanism of self-assembly of TiO$_2$ nanoparticles [35, 80]; (b) mechanism of self-assembly of TiO$_2$ nanoparticles: (a) on PES surface (b) on DEA-modified surface of PI [84]; (c) chemical bond structure model of the PES/TiO$_2$ composites [81]; (d) SEM photographs of the surface of neat and composite membranes (×20,000), (a) Neat membrane, (b) composite-1, (c) composite-2 and (d) composite-3 (composite 1-3 refers to the time for which membrane was soaked in sulfonic acid 0, 1, 2, 4 h) [82]; (e) schematic drawing of hybrid membrane self-assembled by TiO$_2$ NPs [80].

**Fig. 7.** (a) A schematic of dip-coating procedure and antimicrobial property of membranes [86]; (b) filtration deposition of different NPs on the membrane: [(a) schematic diagram of P25 membrane (left side) and FESEM image of P25 membrane surface (right side), (b) schematic diagram of TiO$_2$ microsphere membrane (left side) and FESEM image of TiO$_2$ microsphere membrane surface (right side (inset: digital photo of TiO$_2$ microsphere membrane)), (c) schematic diagram of GO–TiO$_2$ membrane (left side) and FESEM image of GO–TiO$_2$ membrane surface (right side (inset: digital photo of GO–TiO$_2$ membrane)) [89]; (c) changes in permeate flux of control (CA membrane), P25, TiO$_2$ microsphere and GO–TiO$_2$ membrane with different TMP, respectively; (d) Residual TOC rate in permeate water filtrated through different membranes [89].
3.3.3. Electrostatic attraction

Electrostatic attraction is the process in which two differently charged molecules are bound through physical attraction: electrostatic bonding. To attain electrostatic bonding, molecules must possess opposite charges. Usually, it is seen that most of the polymers are negatively charged. Therefore, NPs are tailored with a positively charged group that can interact with the polymer to successfully bind to the membrane through electrostatic attraction. Ben-Sasoon et al. [90] used PEI to charge Cu NPs (amine groups of PEI attracted with cupric ion to bind strongly with Cu NPs), as a result amine group of PEI produced electrostatic attraction with COO\(^{-}\) group of membrane. The membranes prepared with electrostatic interactions performed well as antibacterial membranes (due to presence of antibacterial Cu NPs) but leaching of active antibacterial species (Cu\(^{2+}\) or Cu NPs) suggested insignificant use of such membranes for long time and wide range applications. A high amount (30%) of Cu\(^{2+}\) and Cu NPs were detached from the membrane in first two days. Therefore, to sustain antibacterial activity of such membranes, Cu NPs or Ag NPs are required to be continuously recharged on the membrane surface [90].

3.3.4. Layer-by-layer assembly

In layer-by-layer assembly, several layers of materials are coated on the membrane by any or multiple procedures described earlier. During this procedure, several layers of NPs are deposited on the membrane. Park et al. [91] prepared the membrane with LBL deposition of MWCNTs. Initially, a PSf membrane was negatively charged under treatment of 0.5M H\(_2\)SO\(_4\), the negatively charged PSf membrane was alternatively dipped into cationic poly(allylamine hydrochloride) and anionic MWCNTs/poly(acrylic acid) solutions. Finally, a thermal annealing was done at 180 °C to induce crosslinking of MWCNTs and PE (Figure 8a). The resultant membranes exhibited high flux and high ion rejection. Wang et al. [92] prepared a PAN UF membrane with LBL deposition of modified GO NPs. At first, they hydrolyzed the PAN UF membrane by immersing in 2M NaOH solution at 65 °C for 30 min. Meanwhile, 0.25 wt.% PEI and 0.05 wt.% PAA solutions were prepared. In PEI solution, required amount of GO was dispersed to prepare modified GO i.e. PEI/GO. The hydrolyzed membrane was rinsed with pure water. The PEI-GO solution was filtered through hydrolyzed membrane followed by PAA solution filtration, and the filtration process with both solutions was repeated according to required deposition layer thickness. The membrane was rinsed gently, and dried at 50 °C for 2 h. Then the membrane was immersed in PVA solution at 75 °C for 30 min. Finally, the membrane was cross-linked with 3% glutaraldehyde solution (Figure 8b). The resultant membrane showed high level of selectivity for dye and monovalent ions and produced very high flux.

![Fig. 8. Layer-by-layer assembly of NPs on the membrane surface: (a) schematic illustration of the fabrication of nanocomposite (MWCNT-PAA/PAH\(_n\) multilayers via layer-by-layer assembly on PSf substrate [91]; (b) schematic illustration of the preparation of GO and polyelectrolyte complex nanohybrid membranes [92].](image-url)
3.3.5. Chemical grafting

The main challenge with the surface immobilized NPs is the leaching of NPs over a long duration of use. The leaching of the NPs could cause potential threat to the biological system of the water that should be avoided. Suitably, chemical grafting forms strong association of NPs with the membrane surface and resolves the leaching issue of NPs to a greater extent. However, the leaching of ionic species from NPs remains inevitable: leaching of usually Ag and Cu ions. The chemical grafting method is partly related to the self-assembly or electrostatic attraction method. But in chemical grafting, both membrane and NPs are chemically modified with strongly opposite charged groups, which produces a strong chemical bond at contact. Ling et al. [21] recently introduced a series of steps to immobilize SiO$_2$ NPs on PVDF membrane. First, a PVDF membrane was plasma treated to obtain -OOH groups on the membrane surface. Then, methacrylic acid (MAA) was chemically associated with -OOH group, and finally, amine group modified SiO$_2$ NPs solution was prepared. The MAA modified membrane was dip coated into NH$_2$-SiO$_2$ NPs solution (Figure 9a). The final membrane was anti fouling with high flux recovery by hydraulic flushing, and had a low attraction between organic foulant and membrane surface. Likewise, PEI modified Ag NPs were coated on the surface of PSf UF membrane that improved membrane selectivity and membrane flux with antibacterial properties [93]. In detail, oxygen plasma activates the PSf membrane skin layer with the addition of active and/or charged functional groups. The activated membrane is subsequently incubated with charged or functionalized NPs that generates electrostatic and covalent bonds to form a persistent coating of reactive NPs on the membrane (Figure 9b).

4. Challenges and future perspectives

An overall comparison among different membrane modification methods is presented in Table 3, which is our interpretation of the reported studies in the above-mentioned literature. Please note that it is not always straightforward to interpret and compare results, because many parameters may be influenced simultaneously by one modification method; here we only attempt to give a general impression. All the modification techniques improve the membrane performance; sometimes more fouling is reported but the absolute flux value increase by modification and occasionally less fouling is reported without any significant effect on the water permeation level. Mostly, nanocomposite membranes show completely different behavior than membranes with surface located NPs. At times, surface located membranes show more advantages than nanocomposite membranes and sometimes it shows more disadvantages. It is important to note that the advantages and limitations mentioned in Table 3 regarding surface located NPs are described based on the limited number of techniques which are widely practiced out of many different reported techniques. Overall, two most important factors considered for modification include stability of NPs in membrane system and exposure of NPs to the feed/foulant solution. In a larger picture, nanocomposite membranes provide excellent stability of NPs in the membrane system because NPs are completely embedded in the polymer but less exposure of the NPs is experienced, and surface located NPs membranes express complete exposure of the NPs but less stability of NPs in the membrane system. It is expected that membrane properties can be tuned for specific applications through the discussed methods, although they still need to be developed further in such a way that they allow even better and more environmentally friendly control over modification.

The nanocomposite membranes have been targeted as a dominant future technology for the purification of water using filtration techniques. However, to meet the future demands of safe potable water and to meet the stringent potential regulations, the fabrication of robust, durable and economically viable nanocomposite membranes with high water permeability and high selectivity deemed necessary for various kinds of water treatment. The permeability and selectivity of the membrane is highly dependent on membrane structure that is controlled by the polymer and NPs to be used along with the fabrication process. Thus, optimized polymer concentration and NPs loading plays a vital role in improving the membrane performance, which can be attained by understanding the deep phenomenon and to optimize the fabrication methods.

It is also important to assess the leaching of nanomaterials from the nanocomposite membranes and their toxicity to the environment during water purification. At first, health issues regarding the production of nanomaterials should be considered with great concerns that include from the exposure of labor in the industry at large scale nanomaterials production and the fate and impact of leached nanomaterials from the nanocomposite membrane. Moreover, nanomaterials itself are very expensive that possess major contribution in the cost of nanocomposite membrane. Thus, the leaching of the nanomaterials from the nanocomposite membranes would directly increase the cost of nanocomposite membrane and the potentially attained benefits from the nanomaterials would be outweighed due to the high cost of the nanocomposite membrane [94]. Also, the cost of environment by the leaching of the nanomaterials should be completely determined by keeping in view several previous cases such as Dichlorodiphenyltrichloroethane (DDT), that showed promising results against the insects and largely used in the agriculture but later it became the Achille’s heel. It has been reported about several kinds of NPs that they were leached out of the nanocomposite membrane during different steps of the filtration and lack the durability inside membrane matrix. Under normal conditions, the NPs show stability but under high pressure, high temperature, and chemical cleaning process the NPs are washed out of the membranes. Therefore, there is an urgent need for in-depth studies and advancement in the fabrication methods for the durable nanocomposite membranes that allow the long-term operational cycles of the membrane including filtration and cleaning without leaching of NPs. For durability of nanomaterials in nanocomposite membranes, the compatibility of polymer and nanocomposite could play an important role. The tightly bound nanomaterials with polymer could prevent the leaching of nanomaterials from the nanocomposite membrane and reduces the environmental foot-prints.

Fig. 9. Chemical grafting of NPs to the polymeric membrane surface: (a) schematic protocol of PVDF membrane functionalization, illustrating Argon plasma treatment, graft copolymerization, and NPs binding [21]; (b) post-synthesis grafting process for the fabrication of reactive membranes [93].
Table 3
Comparison of different modification techniques after application of NPs.

<table>
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<tr>
<th>Modification method</th>
<th>Advantages</th>
<th>Limitations</th>
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<tr>
<td>Nanocomposite/mixed matrix</td>
<td>• A simple technique</td>
<td>• Agglomeration of NPs is largely experienced.</td>
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<td></td>
<td>• Large amount of NPs can be loaded in the membrane.</td>
<td>• Huge number of NPs is masked by the polymer.</td>
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<td></td>
<td>• Different kind of polymers can be used for membrane preparation.</td>
<td>• Alteration in pore size, porosity, and void structure is inevitable and uncontrollable.</td>
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<tr>
<td></td>
<td>• Different kind of NPs can be applied to the membrane.</td>
<td>• Uneven distribution of NPs in the membrane matrix.</td>
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<tr>
<td></td>
<td>• NPs remain highly stable in the membrane.</td>
<td>• Instability in reproducibility because the level of agglomeration of NPs remains largely uncontrollable.</td>
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<td></td>
<td>• Environmentally safe technique because NPs do not leak out of the membrane.</td>
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<td></td>
<td>• Cost-effective.</td>
<td></td>
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<tr>
<td>Thin film nanocomposite</td>
<td>• The voids structure of the membranes is not affected.</td>
<td>• Active sites of NPs may interact with polymer and not exposed.</td>
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<tr>
<td></td>
<td>• Agglomeration of nanomaterials could be reduced by well dispersion</td>
<td>• Nanomaterials are masked by the IP of PA.</td>
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<td>in aqueous MDP.</td>
<td>• Loading of nanomaterials is limited due to interruption in IP process.</td>
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<td></td>
<td>• The resultant membrane exhibits increased tensile strength.</td>
<td></td>
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<tr>
<td>Surface located NPs</td>
<td>• NPs remain unmasked by any of the membrane material.</td>
<td>• The stability of NPs on the membrane is weak.</td>
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<td>• The loading of NPs is controllable.</td>
<td>• In some techniques (coating/deposition) pores are plugged and blocked by NPs (coating/deposition, LBL assembly).</td>
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<td>• Pore size and porosity can be altered based on the treatment adopted</td>
<td>• Most of the techniques possess potential hazards for environment (coating/deposition) because of NPs leaching.</td>
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<td></td>
<td>(plasma treatment, radiation treatment).</td>
<td>• Most of the techniques are economically ineffective because of number of chemicals used and the requirement of special equipment.</td>
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<tr>
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<td>• Some techniques are environmentally secure as NPs are not leached easily</td>
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<td>(chemical grafting).</td>
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<td></td>
<td>• Active sites of NPs are completely exposed.</td>
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<tr>
<td></td>
<td>• Highly reproducible (e.g. chemical grafting, LBL assembly, deposition).</td>
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The energy consumption is an important factor for nanocomposite membranes during separation process especially with high pressure filtration processes. For example, RO and NF both require large amount of energy that increase the operational cost for the application of the membranes. Therefore, developing new methods for fabrication of high permeability nanocomposite membranes in addition to energy harvesting devices and low-carbon foot prints processes is also the need of the time. With high permeability, less pressure is required to exert on the membrane for water to pass through across the membrane that consumes less energy. Moreover, under low pressure less foulants accumulate on the membrane and fouling is reduced that enhances the life time of the membrane and reduces the usage of chemicals for the cleaning of the membrane. Thus, by deep consideration of only one factor, permeability, overall energy consumption and running cost of the system decrease, which could help in the widespread application of the RO and NF membranes. Therefore, the optimal design of the installation system and selection of polymer materials and nano-materials for nanocomposite membrane by consideration the specific properties that influence the permeability and strength (pore size and porosity, thickness, tensile strength etc.) could help to achieve the low energy consuming membranes.

The influential factors in the fabrication of nanocomposite membrane includes type of nanomaterials used with specific physicochemical properties namely surface charge, surface area, size, compatibility with polymer and type of polymer itself. The nanocomposite membranes have proven to be promising membranes with showing significant performances regarding high water permeation and high solute rejections in various water treatments such as desalination, removal of organic pollutants, and removal of bacteria with high flux recovery potential. Nevertheless, still there is a need to conduct deep research and to develop high throughput nanocomposite membranes in wide range of applications including heavy metal removal, dye removal, and persistent and emerging organic contaminants removal from water and wastewater.

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