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Recent advances in heavy metal removal by thin film nanocomposite membrane

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ABSTRACT

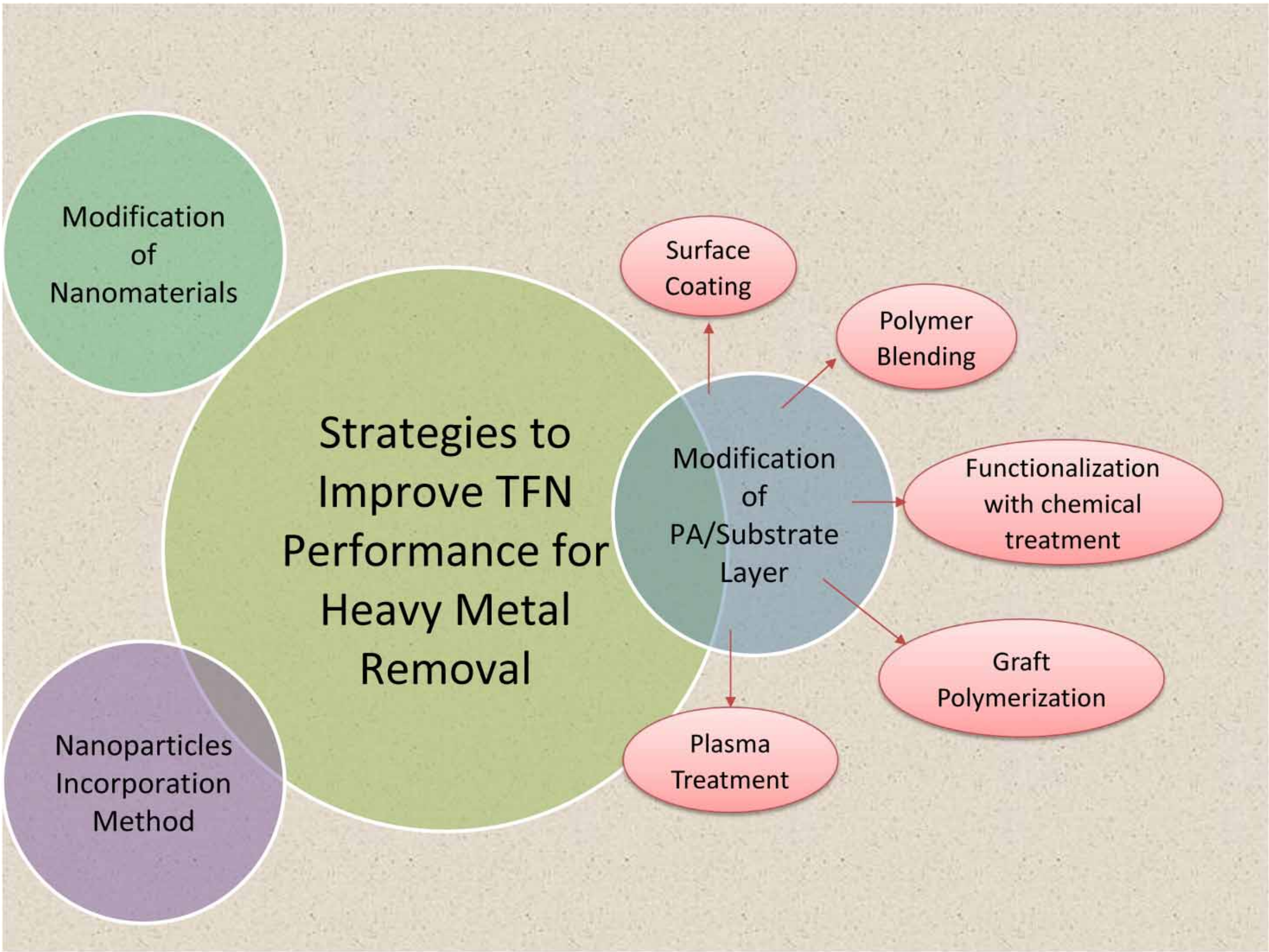
Rapid industrialization has become one of the root causes of environmental problems, particularly heavy metal pollution. Numerous methods, including chemical precipitation and ion exchange, have been used to remove heavy metal ions from aqueous solutions, but all of them have drawbacks, such as low metal removal effectiveness, significant reagent loss, excessive energy use, and the need for further development of the current techniques. Membrane-based technologies such as reverse osmosis (RO) and nanofiltration (NF) are gaining popularity in the removal of heavy metals due to their high rejection and low formation of secondary pollutants. Among the methods under consideration, the membrane-based approach holds the most promise for wastewater treatment with a focus on heavy metal ion removal due to its ease of manufacture, superior qualities, and increased separation effectiveness. Since membrane performance is typically hampered by fouling, low permeability, and significant contaminant permeation when compared to strict selectivity criteria, the development of novel membrane materials has emerged as an important area of research for academia, industry, and national laboratories. We have therefore reviewed previous initiatives and technological developments in order to achieve more effective heavy metal removal and recovery from industrial wastewater.

Key words: heavy metal, membrane technology, thin film nanocomposite

HIGHLIGHTS

- Wastewater treatment technologies and existing methods in heavy metal removal are reviewed.
- Five types of membranes are discussed on their strengths and weakness.
- Table of summary from previous research that used TFN membrane in heavy metal removal is included.
- Crucial challenges associated with TFN membrane production are discussed.
- Strategies to overcome the limitation of TFN are discussed in detail.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Water is essential to all human activities. Given that by 2025, it is expected that half of the world's population will actually live in water-stressed areas, water demand has been highlighted as one of the most significant challenges of the new century (Mekonnen & Hoekstra 2016). The amount of wastewater produced in the home, industrial, and agricultural sectors grow in tandem with the global population. Freshwater supplies are not renewed to meet the demands of an ever-increasing population, which causes fierce competition and an uneven distribution of the limited freshwater resources among many different sectors (Obotey Ezugbe & Rathilal 2020). Poor water quality and water-related diseases also will lead to a serious impact on human health. Due to rapid industrialization and development, the number of contaminants entering freshwater sources is increasing (Hebbar *et al.* 2016). As a result, many people worldwide, particularly in developing countries, lack access to clean drinking water, and the international community is currently looking into all practical solutions to reduce the overuse of limited freshwater resources (Obotey Ezugbe & Rathilal 2020).

Heavy or toxic metals are trace metals that are detrimental to human health and have a density at least five times of water. Heavy metals normally are absorbed into the body through inhalation, uptake, and absorption by the skin after being released into the environment either via air, drinking water, food, or a variety of chemicals and man-made products. Heavy metals basically accumulate in organisms because they cannot be biodegraded, and most heavy metal ions are considered toxic. The World Health Organization (WHO) has set standards for the maximum acceptable limit of certain harmful heavy metals in drinking water and industrial wastewater, as well as the health effects of exceeding those limits (Shrestha *et al.* 2021).

A large number of studies have been focused on the removal of heavy metals, which are a major pollutant in water supplies. Copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), and cobalt (Co) are heavy metals that play essential roles in biochemical processes in the human body. Heavy metals, in particular, arsenic (As), lead (Pb), and cadmium (Cd), have the ability to inflict ionic immobility and damage to numerous organs in organism, making them extremely dangerous to the environment, especially aquatic life (Hosseini *et al.* 2020). Pb^{2+} and Cu^{2+} have been reported to be the most frequently reported harmful metals in industrial effluent (Hoang *et al.* 2020) and excessive exposure to these metal ions can be detrimental. Under normal conditions, the human body can handle trace levels of metals without causing serious health concerns. However, long-term exposure to heavy metals can result in a large accumulation of toxins in the body, eventually leading to system failure and death (Sardar *et al.* 2013).

Heavy metals had been eliminated from industrial wastes for decades by using various techniques like chemical precipitation, ion exchange, and biological treatment to address this issue. Toxic sludge production, insufficient heavy metal removal, and high energy needs are just a few of the significant drawbacks and shortcomings of these low-cost advantage-oriented methods (He *et al.* 2019), followed by low metal removal efficiency, considerable reagent loss, uneconomical energy use, and post-treatment operations imposed by secondary waste production, requiring further improvement of the current methods (You *et al.* 2017). Membrane-based technologies such as reverse osmosis (RO), nanofiltration (NF), and electrodialysis (ED) have sparked growing interest in heavy metal removal due to high rejection and low secondary pollutant formation (You *et al.* 2017) also due to their benefits provided in water and wastewater treatment. This technology is frequently implemented in wastewater treatment processes due to their ease of manufacture, better properties, and enhanced separation efficiency (Kim *et al.* 2018).

Numerous advantages for improving wastewater treatment are provided by membrane technology, including decreased energy and equipment needs (Quist-Jensen *et al.* 2015). There are also some additional benefits including energy savings without phase change, high separation efficiency, ease of upgrade, and environmentally friendly. Despite the benefits and prospects for these actual applications, some inherent limitations linger, such as short membrane lifespan, low productivity, restricted selectivity, and economic impracticality membrane fouling and high energy costs continue to be stumbling challenges (Zhang *et al.* 2016; Roy & Ragunath 2018). Additionally, membrane-based technology has demonstrated a tremendous potential to close the gap between economics and sustainability owing to its minimal or non-existent chemical usage, environmental friendliness, and accessibility to a wide range of people. To put it another way, in recent years, membrane technology has emerged as a more favourable choice for the processes used to treat wastewater (Singh & Hankins 2016).

Thin film composite (TFC) and thin film nanocomposite (TFN) membranes are new generation membranes with numerous advantages over traditional membranes. TFC and TFN membranes have recently gained popularity in the treatment of heavy metal removals (see Figure 1). Despite the fact that the number of published articles related to ‘thin film composite membrane’ and ‘heavy metal removal’ is not large in the early 2000, the number of citations is enormous and growing until the current year 2023. This reflects the worldwide interest in TFC and TFN membranes for heavy metal removal. To the best of our knowledge, a limited reviews paper has been published on TFC/TFN membrane for heavy metal removals, and it is necessary to periodically update and summarize current research. Thus, the objective of this review is to give an overview and outlook of the prospects and issues encountered in the field of TFC/TFN membrane for the removal of heavy metals. Besides, the strategies for improving the performance of TFN membranes were thoroughly discussed in order to guide researchers in producing high-performance TFN membranes.

2. MEMBRANE TECHNOLOGIES

Over the years, several initiatives have been made to introduce different wastewater treatment technologies, and existing methods have also been modified to meet the most recent emission or reuse regulations (Obotey Ezugbe & Rathilal 2020). Among the methods under consideration, the membrane-based approach holds the most promise for wastewater treatment and heavy metal ion removal. Membrane-based materials are widely used in wastewater treatment because of their ease of preparation, superior properties, and improved separation efficiency (Kim *et al.* 2018). Since it has made significant advancements in recent years and is well known for the beneficial results it produces in the treatment of both water and wastewater, membrane technology has become one of the wastewater treatment technologies that has experienced tremendous advancement in recent years. Due to significant reductions in equipment size, energy requirements, and capital costs,

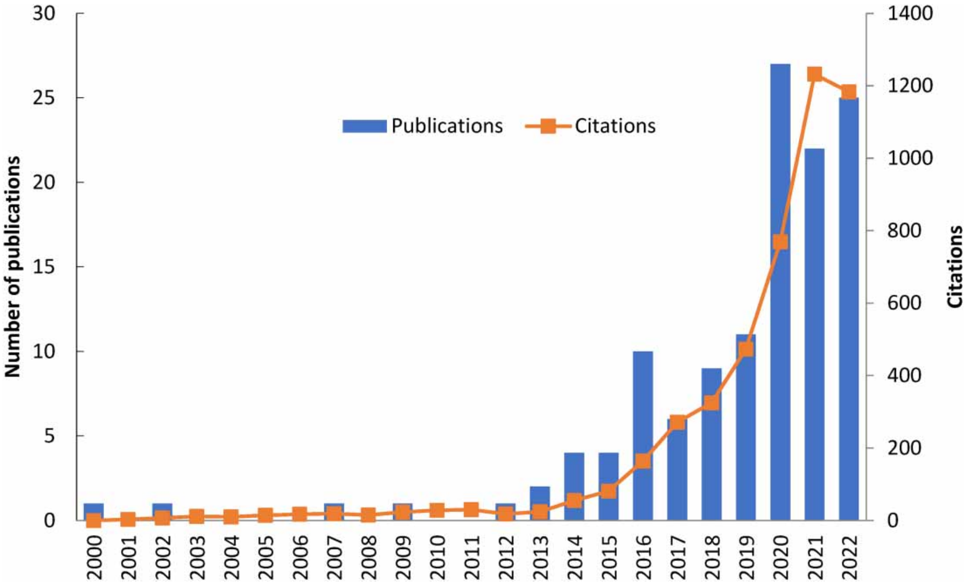


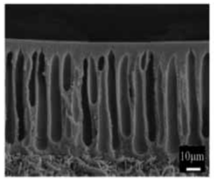
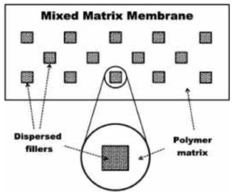
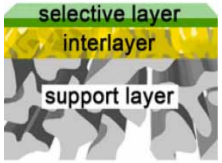
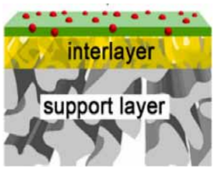
Figure 1 | The publications and citations of TFC and TFN membranes for heavy metal removal over the last 22 years. The information was retrieved from the Web of Science with the topics of 'thin film composite membrane' and 'heavy metal removal' on 10 January 2023.

membrane technology provides a broad range of opportunities in wastewater treatment (Quist-Jensen *et al.* 2015). Additionally, the minimization of membrane impurities, which is a significant challenge for the membrane process, is constantly being improved through the modification of membrane modules and membrane elements (Obotey Ezugbe & Rathilal 2020).

Membrane is basically a two-phase barrier that selectively separates and limits the transport of many chemicals and is classified into four types based on their structure: homogeneous, heterogeneous, symmetric, and asymmetric. Membranes can separate solids and liquids, and they can be positive or negative in charge, neutral, or bipolar and this membrane serves a dual purpose in separation, and the separation is simple where it started with first the membrane acts as a semi-permeable layer between two phases, and second, it transports between two phases (Yalcinkaya *et al.* 2020). Membranes are classified according to their material composition and structure (see Table 1). Organic membranes, also known as polymeric membranes, are made of synthetic organic polymers such as polyethylene (PE), polytetrafluorethylene (PTFE), polypropylene, and cellulose acetate. The majority of membranes used in pressure-driven separation processes (microfiltration (MF), ultrafiltration (UF), NF, and RO) are synthetic organic polymers (Obotey Ezugbe & Rathilal 2020). Meanwhile inorganic membranes are made of chemically and thermally stable materials such as ceramics, metals, zeolites, or silica and are widely used in industrial applications such as hydrogen separation, UF, and MF. Membranes with mixed matrix structures are produced by combining an inorganic or inorganic–organic hybrid material in the form of micro- or nanoparticles with a polymer matrix. TFC membrane, a new generation of membrane structure that overcomes the permeability-selectivity trade-off in conventional membrane, combines an ultrathin selective layer with an extremely porous substrate. Lastly, TFN membranes are a newer type of composite membrane created by the interfacial polymerization (IP) process, in which nanoparticles are incorporated within the selective layer of the TFC membrane in order to enhance the interfacial polymerized layer's characteristics.

In wastewater treatment, there are many different types of membrane filtration systems that had been applied and they basically rely on pore size to separate contaminants from the feed stream. There are equilibrium-based membrane processes, non-equilibrium-based membrane processes, pressure-driven, and non-pressure-driven processes (Obotey Ezugbe & Rathilal 2020). From pre-treatment to post-treatment, pressure-driven membrane processes appear to be the ones that are most frequently employed in the treatment of wastewater. These methods use the application of hydraulic pressure to achieve separation (Obotey Ezugbe & Rathilal 2020). The most often used methods for treating wastewater, from pre-treatment until post-treatment, are pressure-driven ones where separation is achieved by applying hydraulic pressure. The four different mechanisms are RO, MF, UF, and NF (Obotey Ezugbe & Rathilal 2020). The processes require more energy as the pores get smaller. The technologies are thus commonly divided into low pressure (MF, UF) and high pressure (NF, RO) categories

Table 1 | Strengths and weaknesses of membranes

Types of membrane	Polymeric membrane	Ceramic membrane	Mixed matrix membrane	Thin film composite (TFC) membrane	Thin film nanocomposite (TFN) membrane
	 Alqaheem & Alomair (2020)	 Asif & Zhang (2021)	 Maghami & Abdelrasoul (2018)	 Ji *et al.* (2021)	 Ji *et al.* (2021)
Strengths	High temperature stability, fouling resistance, low lifecycle costs, simple pore-forming mechanism, and high flexibility (Warsinger *et al.* 2018; Kamali *et al.* 2019)	Stronger mechanical, thermal, and chemical stability, higher fouling resistance and more extended membrane longevity, high removal efficiency (Abdullayev *et al.* 2019; Kamali *et al.* 2019; Asif & Zhang 2021)	Possibility of combining synergistically the easy processability of polymers, ability to overcome the trade-off between selectivity and permeability which is characteristic for pure polymer membranes, both polymer and filler qualities affect separation performance (Dechnik *et al.* 2017; Qadir *et al.* 2017; Cheng *et al.* 2018)	Able to achieve the optimal combination of flux and salt rejection, inexpensive, have good chemical and mechanical stability and can be formed into membranes using a simple phase inversion technique (Ji *et al.* 2021; Khoo *et al.* 2021; Peng *et al.* 2022)	While maintaining the TFC membrane's separation effectiveness, the interfacial polymerized layer's characteristics can be improved to increase hydrophilicity and/or surface charge density (Yang *et al.* 2020; Zhao *et al.* 2020; Liao *et al.* 2021)
Weaknesses	High selectivity for low solutes and species, membrane fouling, and low mechanical strength in polymeric membranes (Warsinger *et al.* 2018; Kamali *et al.* 2019)	Requires a large membrane area and energy, high production costs, uneconomical for most water treatment applications (Abdullayev *et al.* 2019; Kamali *et al.* 2019; Asif & Zhang 2021)	Poor filler – polymer compatibilities and filler segregation or blocking of its porosity by the polymer, selection of inorganic filler in order to fabricate MMM is quite challenging owing to their textural characteristics as well as their interaction with polymers (Dechnik *et al.* 2017; Qadir *et al.* 2017; Cheng *et al.* 2018)	Agglomeration of NP due to high surface energy, in the PA layer, which reduces the surface area of nanoparticles as well as creates defects in the active layer, lack of chemical interaction between the PA layer and NP (Ji *et al.* 2021; Khoo *et al.* 2021; Peng *et al.* 2022)	Aggregation or agglomeration of nanoparticles in the PA layer, since nanomaterials and PA matrix do not interact chemically, they are likely to easily leach out during the filtration and/or IP processes (Yang *et al.* 2020; Zhao *et al.* 2020; Liao *et al.* 2021)

(Tchobanoglous 2014). Both MF and UF operate under low pressure (2 bar). Separation by MF is primarily achieved through sieving and is limited to the removal of due to the relatively large pore size, separation by MF is primarily accomplished through sieving and is restricted to the removal of suspended solids or particles, bacteria, and, to a lesser extent, organic colloids (approximately 0.1–1.0 m) (Warsinger *et al.* 2018). UF membranes work similarly to MF membranes, but have a wider separation range and are able to remove particles, bacteria, viruses, and colloids depending on the pore size (usually between 0.01 and 0.1 m) (Warsinger *et al.* 2018). Both NF and RO are very similar processes that are designed to remove dissolved chemical constituents such as salts, where both require high hydraulic pressures and use similar membrane materials (Warsinger *et al.* 2018). NF removes many of the same solutes as RO, but to a lesser extent. The UF and MF processes are suggested over the NF and RO processes, which would additionally lower operating costs, in order to maintain a low transmembrane pressure and achieve a higher flux (Goswami *et al.* 2019).

2.1. Ceramic membrane

The International Union of Pure and Applied Chemistry classifies porous materials into three grades based on the diameter of their pores (D), microporous ($D < 2$ nm), mesoporous ($2\text{ nm} \geq D < 50$ nm), and macroporous ($D > 50$ nm). Ceramic membranes are classified as industrial porous materials (Ali *et al.* 2017). In water and wastewater treatment, ceramic membranes provide various advantages over polymer-based filtration systems, including high temperature stability, fouling resistance, and low maintenance requirements, all of which lead to lower lifecycle costs (Abdullayev *et al.* 2019).

When the pore size is small, such as in RO, UF, and NF, the fluid permeability is also influenced by the solute and solvent's affinity with the porous materials (Ohji & Fukushima 2012). Although it offers a high removal efficiency, using membrane separation techniques to treat contaminated water uses a lot of energy and membrane area. Therefore, it is crucial to create new membranes based on inexpensive components like clay and apatite that will be an effective treatment, especially when they are burned to create ceramic membranes that are regarded as industrial porous materials (Masmoudi *et al.* 2005; Khemakhem *et al.* 2007). However, the high production costs of most commercially available ceramic membranes, owing to raw material and processing costs, make such systems uneconomical for most water treatment applications (Abdullayev *et al.* 2019).

2.2. Polymeric membrane

Polymers are probably the most widely used membrane material in wastewater treatment because of their advantages such as a simple pore-forming mechanism, low cost, and high flexibility. This includes ED, UF, NF, and RO membrane-based technologies (Ng *et al.* 2013). Experimental evidence has shown that polymeric membranes are effective at removing a wide range of contaminants, including suspended pollutants, organic matter, and organic and inorganic compounds (such as heavy metal ions) (Wieszczycka & Staszak 2017). When polymeric membranes (typically made from naturally occurring or chemically synthesized polymers) are used to separate two adjacent phases (feed and permeate), they create a selective interface barrier that regulates the movement of species between the two phases (Castro-Muñoz *et al.* 2021).

The hydrophobic polymer polyvinylidene fluoride (PVDF), which is frequently used in a range of water treatment applications, with high chemical tolerance, as well as favourable mechanical and thermal properties, are just a few of its many benefits (Xia & Ni 2015). The performance of membrane separation is typically influenced by the characteristics of the transported species (such as molecule size, shape, and chemical nature) as well as the physicochemical characteristics (hydrophilicity/hydrophobicity, surface charge, roughness), particularly its porous structure, of the polymer membrane. Unfortunately, polymeric membranes still do not have all of the desired characteristics for membrane separation processes, such as high selectivity towards low solutes and species. Additionally, the main obstacle to their application is membrane fouling and polymeric membranes' weak mechanical strength (Castro-Muñoz *et al.* 2021).

2.3. Mixed matrix membrane

The development of membrane technology currently focuses on the addition of inorganic particulates to create mixed matrix membranes (MMMs), which are filled hybrid polymer composite membranes (Muthukumaraswamy Rangaraj *et al.* 2020). By combining an inorganic or inorganic–organic hybrid material in the form of micro- or nanoparticles (the discrete or dispersed phase; additive or filler) with a polymer matrix, composite membranes known as MMMs are developed (Dechnik *et al.* 2017). Specifically, the complicated process of incorporating various nanomaterials into membrane matrices can give the membrane's structure unique properties and affect the behaviour of gas transport. MMMs are a viable alternative to traditional polymeric membranes because they have the potential to eliminate the 'trade-off' effect found in commercial membranes and one of the most important parameters for designing efficient MMMs is the choice of filler material (Muthukumaraswamy Rangaraj *et al.* 2020).

Several approaches have been suggested over the last few decades to improve the performance of polymeric membranes where MMMs have been created by modifying various polymers with inorganic fillers such as zeolites, mesoporous silicas, activated carbons, carbon nanotubes (CNTs), and even non-porous solids (Zornoza *et al.* 2013). MMM is an intimate and homogeneous dispersion of filler particles in a polymeric matrix, where the properties of both the polymer and the filler influence MMM morphology and separation performance (Zornoza *et al.* 2013). The MMM has a bright future in gas separation because of its outstanding physical and chemical properties when compared to organic and inorganic membranes, but on the other hand, it encounters some challenges because of interfacial defects or adhesion between the organic and inorganic phases, possibly requiring countless modifications to address these problems (Nasir *et al.* 2013).

2.4. Thin film composite (TFC)

One of the most crucial elements in determining separation properties and transport mechanisms across the membrane is membrane structure. Since their production typically only requires one step of flat sheet casting or hollow fibre spinning, integrally asymmetric polymeric membranes have been utilized in numerous membrane processes for decades (Nguyen *et al.* 2015). Nevertheless, this new kind of membrane has drawn a lot of interest in the research and industrial sectors ever since the first polyamide TFC membrane was introduced because it can achieve the ideal balance between flux as well as salt rejection (Zhou *et al.* 2014; Kim *et al.* 2016). TFC membranes are broadly used in NF, RO, and FO, mostly for seawater and brackish water desalination. The versatility in selecting and optimizing the materials used to form a microporous substrate layer and a selective thin film layer is another appealing quality of TFC membrane (Xu *et al.* 2017a, 2017b).

As seen in Figure 2, the typical TFC membrane structure is made up of three layers: a thin selective layer, an intermediate polymeric porous support, and an optional non-woven polyester fabric (Chan *et al.* 2013). Semi-hydrophobic polymers, such as poly sulphone (PSF) and polyether sulphone (PES), are frequently used to make polymeric support layers because they are cost-effective, have excellent chemical and mechanical stability, and, most importantly, can be easily transformed into membranes using a phase inversion technique (Ahmad *et al.* 2018). The dope formulation and fabrication conditions, which are equivalent to those of integral asymmetric membranes, play a major role in determining how well the polymeric substrate layer performs in TFC membranes.

2.5. Thin film nanocomposite (TFN)

In MF and UF processes, polymers with outstanding permeability, selectivity, and chemical, mechanical, and thermal stability are frequently used as membrane materials. Examples of these polymers include PSF, PES, polyacrylonitrile (PAN), polypropylene (PP), and polytetrafluoroethylene (PTFE) (Ursino *et al.* 2018). For UF membranes, PSF and PES membranes have seemed to be among the most frequently used materials. These standard base polymers are also used in the creation of NF and RO composite membranes, whereas PP and PVDF are more frequently used for MF membranes (Pendergast & Hoek 2011). However, these polymeric membranes' separation performance must be optimized and improved (Alzahrani & Mohammad 2014), along with their stability, hydrophilicity profile, and fouling resistance (Abu Bakar & Tan 2016).

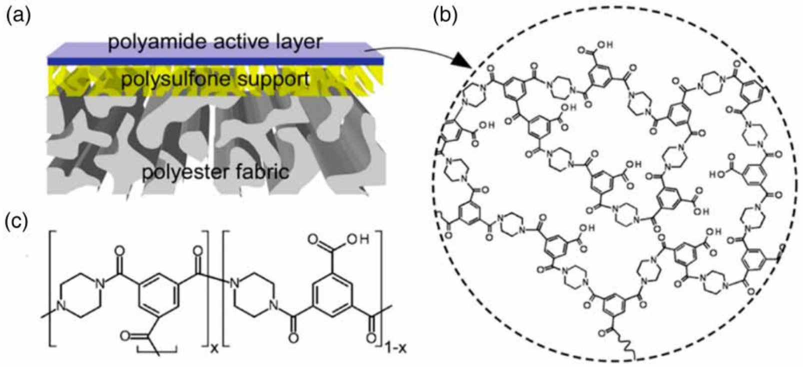


Figure 2 | Structure of typical TFC membrane (Chan *et al.* 2013).

A more recent type of composite membrane produced by the IP procedure are TFN membranes. In order to improve the properties of the interfacial polymerized layer, such as continuing to increase the hydrophilicity and/or surface charge density, nanoparticles are added to the thin polyamide (PA) dense layer of the TFC membrane without reducing the separation efficiency of the TFC membrane (Lau *et al.* 2015). Before membrane casting, nanoparticles can be either coated onto the membrane surface or dispersed in the polymer solution (Al Aani *et al.* 2017). The most typical way for membrane preparation is to blend nanoparticles into the polymeric matrix, however membrane surface coating with nanoparticles is becoming commonly employed to adjust membrane functionality (Lau *et al.* 2012). Incorporating NPs into the TFC membrane during the IP process has the potential to be one of a promising method. Researchers in the field of membrane science have used a variety of inorganic nanofillers with various properties, such as titanium dioxide (TiO_2), graphene oxide (GO), CNTs, titania nanotubes (TNTs), zinc oxide (ZnO), and silicon dioxide (SiO_2), to enhance the performance of TFN membranes for both pressure-driven and osmotically driven filtration processes (Ji *et al.* 2017; Lee *et al.* 2019).

Nanoparticles can be divided into many categories based on their size, shape, physical, and chemical properties. Another way to categorize nanoparticles is based on their morphology, size, and chemical characteristics. There are basically two types of nanoparticles: organic and inorganic. The first category includes micelles, dendrimers, liposomes, hybrid, and compact polymeric nanoparticles. The second category includes fullerenes, quantum dots, silica, and metal nanoparticles. Numerous studies have used various nanoparticles, such as carbon-based nanoparticles – carbon quantum dots (CQDs) and GO, ceramic-based nanoparticles – silica/silicon dioxide (SiO_2) and titania/titanium dioxide (TiO_2), metal oxide nanoparticles – copper oxide (CuO), semiconductor nanoparticles – zinc oxide (ZnO), polymeric nanoparticles – cellulose and polylactic acid (PLA), and lipid-based nanoparticles. Table 2 summarizes some examples from previous works that had used nanoparticles in TFN membrane for heavy metal removal.

From previous research, Saeedi-Jurkuyeh *et al.* (2020) discovered that at neutral pH, the rejection rate of a single heavy metal was way greater in the TFN 0.008 membrane than the TFC membrane. According to Table 2, water flux increased as GO concentration in membranes continued to increase. For instance, the water flux in the TFN 0.008 membrane (34.3 LMH) is essentially higher than in the conventional TFC membrane (12.5 LMH), which can be accounted for by the following factors: The presence of functional groups on the surface of GO improved the roughness and reduced the resistance to water diffusion through the active layer of TFN membranes. TFN 0.008 FO membranes rejected 99.9% of Pb, 99.7% of Cd, and 98.3% of Cr, respectively. In terms of membrane structure, FO performances, and separation properties, those modified FO membranes showed excellent improvement.

According to Karki & Ingole (2022), the TFN membrane with 0.02 wt% of TiO_2 has the highest in pure water flux of all, with 26.75 $L\,m^{-2}\,h^{-1}$. Table 2 clearly shows that all TFN membranes have greater permeability than TFC membranes. The data showing that TFC has the lowest permeability of any membrane are supported by the combination of a higher contact angle value and a lower surface roughness (Ra). The membranes permeated pure water at a rate of 13–27 LMH. The TFN-2 membrane had the highest permeability of all, with 26.75 LMH of pure water. The permeability of the membranes increases as the concentration of nanomaterial increases. However, as shown in Table 2, regardless of having higher nanomaterial concentrations than TFN-2, the TFN-3 and TFN-4 membranes failed to show higher permeability than the TFN-2 membrane. As previously reported, this is because the functionalized TiO_2 nanoparticles self-aggregated in the solution during IP. In comparison to the TFN-3 and TFN-4 membranes, the TFC, TFN-1, and TFN-2 membranes demonstrated excellent rejection of Cu, Hg, and Pb ions from their respective feed solutions during NF performance. The membranes displayed the % rejection 70–87% for Cu ion, 45–70% for Hg ion, and 60–85% for Pb ion. TFN-1 membrane had the maximum Cu ion rejection (86.89%), whereas TFN-2 membrane seemed to have the maximum rejection of the remaining ions (Hg – 77.01% and Pb – 83.42%).

All TFN/UiO-66-NH_2 membranes have higher water fluxes than the TFC membrane for both NF and FO membranes, as shown in Table 2 (Abdullah *et al.* 2021). According to the table, the flux obtained by the FO process has a lower value for TFN/UiO-66-NH_2 0.01 compared to the flux acquired by the NF process, which is 18.51 and 60.41 LMH, respectively. Flux steadily increased at low loading of TFN/UiO-66-NH_2 from 0.01 to 0.025 wt% and significantly decreased at 0.05 and 0.1 wt% loading. The hydrophilic properties of UiO-66-NH_2 and the additional water transport pathways provided by the UiO-66-NH_2 particles are responsible for the increased water flux. Table 2 shows the removal of Pb (II) at various starting values ranging from 50 to 500 mg/L. In each concentration, the removal trend is comparable, with TFN rejecting more than TFC at loadings of 0.005 and 0.01 wt% before declining at loadings of 0.025, 0.05, and 0.1 wt% for TFN. TFC and TFN/UiO-66-NH_2 rejection rates were 90 and 93%, respectively, at 50 ppm, 87.5 and 90.2% at 250 ppm, and 84.59 and 88.93% at 500 ppm, respectively. As can be seen, increasing the beginning concentrations resulted in a modest drop in Pb (II) rejections.

Table 2 | TFN membrane for heavy metal removal

Substrate layer	Nanoparticle	Nanoparticle loading	Contact angle	Pure water flux $Lm^{-2}h^{-1}$	Removal %	Reference
PSF	GO	0.000 wt%	64 ± 0.50	12.5	Pb (79.3), Cd (81.8), Cr (81.3)	Saeedi-Jurkuyeh *et al.* (2020)
		0.004 wt%	54 ± 0.37	16.4	Pb (97.6), Cd (97.4), Cr (97.2)	
		0.008 wt%	49 ± 0.40	34.3	Pb (99.9), Cd (99.7), Cr (98.3)	
		0.012 wt%	53 ± 0.70	19.4	Pb (98.7), Cd (98.3), Cr (97.9)	
PSF	TiO_2	0.00 wt%	61.4	13–15	Cu 80–85 Hg 70–80 Pb 80–85	Karki & Ingole (2022)
		0.01 wt%	49.4	13–15	Cu 86.89 (Highest) Hg 70–75 Pb 80–85	
		0.02 wt%	39.3	26.75 (Highest)	Cu 80–85 Hg 77.01 (Highest) Pb 83.42 (Highest)	
		0.05 wt%	50.3	15–18	Cu 70–75 Hg 50–55 Pb 60–65	
		1.00 wt%	54.0	15–18	Cu 70–75 Hg 45–50 Pb 60–65	
PSF	UiO-66-NH_2	0.00 wt%	36.63	31.15 (NF) 9.4527 (FO)	Pb (II) 50 ppm (90) Pb (II) 250 ppm (87.5) Pb (II) 500 ppm (84.95)	Abdullah *et al.* (2021)
		0.005 wt%	38.18	41.51 (NF) 12.94 (FO)	Pb (II) 50 ppm (90–93) Pb (II) 250 ppm (90–93) Pb (II) 500 ppm (80–90)	
		0.01 wt% (Optimum)	27.79	60.41 (NF) 18.51 (FO)	Pb (II) 50 ppm (93) Pb (II) 250 ppm (90.2) Pb (II) 500 ppm (88.93)	
		0.025 wt%	37.09	47.60 (NF) 12.43 (FO)	Pb (II) 50 ppm (70–80) Pb (II) 250 ppm (80–90) Pb (II) 500 ppm (80–90)	
		0.05 wt%	23.03	47.95 (NF) 10.29 (FO)	Pb (II) 50 ppm (60–70) Pb (II) 250 ppm (70–80) Pb (II) 500 ppm (70–80)	
		0.1 wt%	20.92	71.47 (NF) 12.63 (FO)	Pb (II) 50 ppm (50–60) Pb (II) 250 ppm (70–80) Pb (II) 500 ppm (60–70)	
PES	CQDs	0.00 wt%	54.6 ± 2.2	5.25–6.0	SeO_3 82.40 $HAsO_4$ 91.30	He *et al.* (2018)
		0.02 wt%	34.9 ± 2.0	8.25–9.0	SeO_3 97.20 $HAsO_4$ 98.10	
		0.05 wt%	29.1 ± 1.8	9.75–10.0	SeO_3 97.60 $HAsO_4$ 98.30	
		0.08 wt%	26.5 ± 1.9	7.5–8.25	SeO_3 98.00 $HAsO_4$ 98.95	
		0.12 wt%	23.5 ± 1.4	6.0–6.75	SeO_3 98.60 $HAsO_4$ 99.50	

The results showed that when the concentration is less than 100 ppm, the metal ion rejection is near to that predicted by the Donnan exclusion. As a result, at lower concentrations, Donnan exclusion is the primary influencing factor, whereas the solvation energy barrier effect plays a secondary role in ion rejection.

Water flux is reportedly decreased when more Na-CQDs are added to the PA layer, according to another study by He *et al.* (2018). This might be a result of a thicker PA layer, as hydrophilic Na-CQDs increase phosphatidylinositol phosphate (PIP) diffusivity and hasten its transit to the interface. Additionally, the PA layer's pores could become clogged as a result of higher nanoparticle loading. When using single ion solutions as feeds, the Na-CQD loading has an impact on how the membrane separates to Se and As ions. The optimal loading of Na-CQDs is 0.12 wt% (TFN-0.12). Rejection to SeO_3 rises from 82.4 to 98.6% when compared to the TFC membrane, while rejection to $HAsO_4$ rises from 91.3 to 99.5%. As shown in Table 2, Na-CQDs create a selective layer with small pore sizes and a narrow pore size distribution, which is largely responsible for these advantages. However, the pure water permeance (PWP) of the TFN-0.12 membrane is not the highest.

Recently, several new varieties of nanocomposite membranes have entered the market for use in various filtration applications. The characteristics of nanocomposite membranes that were used for industrial water treatment will be based on the production of tailored membranes with high selectivity, competitive flux, and self-cleaning properties while also meeting sustainability criteria such as environmental impact, flexibility, adaptability, and simplicity of use (Le & Nunes 2016). The hydrophilicity of polymeric membranes is generally increased by adding different classes of NPs, which reduces fouling in water treatment and enhances some of the polymers' other properties (mechanical, thermal, and chemical) (Ursino *et al.* 2018).

3. CHALLENGES AND STRATEGIES IN TFN

Although many researchers have demonstrated the potential of PA TFN membrane for water treatment processes in particular over the last few years, there are still several crucial challenges associated with TFN membrane production (Lau *et al.* 2015). One of the most frequent problems experienced during the development of TFN membranes is the aggregation or agglomeration of nanoparticles in the PA layer (see Figure 3). The adherence of particles to one another by weak forces results in the formation of (sub) micron-sized entities, which results in the aggregation or adhesion of nanoparticles. Defects (holes) appearing in the active layer as a result of nanoparticle aggregation in the thin PA layer limits the potential improvement of mechanical properties and performance in the membrane.

Another issue in TFN membranes is the incompatibility of nanomaterials with the PA matrix. Nanomaterials are likely to easily leak out during the IP and/or filtration process due to the lack of chemical interaction between them and the PA matrix, which reduces the effectiveness of the prepared TFN membrane and the effectiveness of using nanoparticles in production (Lau *et al.* 2015). The initiative for reducing NP release during the membrane process is to control the effective adhesion on the polymeric matrix and evaluate the stability over time and as a result, producing straightforward, inexpensive techniques to immobilize NPs on membranes without compromising their performance is one of the challenges (Qu *et al.* 2013). Numerous research studies are concentrated on the release of NPs, which presents a notable technical challenge for risk assessment, as well as the detection techniques, which are actually limited in number, typically sophisticated, expensive, and fraught with numerous limitations (Ursino *et al*. 2018). Few incompatibilities between inorganic nanomaterials and organic PA layers have been found in prior studies, but reports state that no thorough research has been done to assess nanoparticle leaching during prolonged filtration (Lau *et al.* 2015).

Membrane fouling, the most important limiting factor in industrial membrane applications, is yet another key problem with TFN membrane. When different solutes gather on the membrane surface or internal structure, membrane fouling occurs,

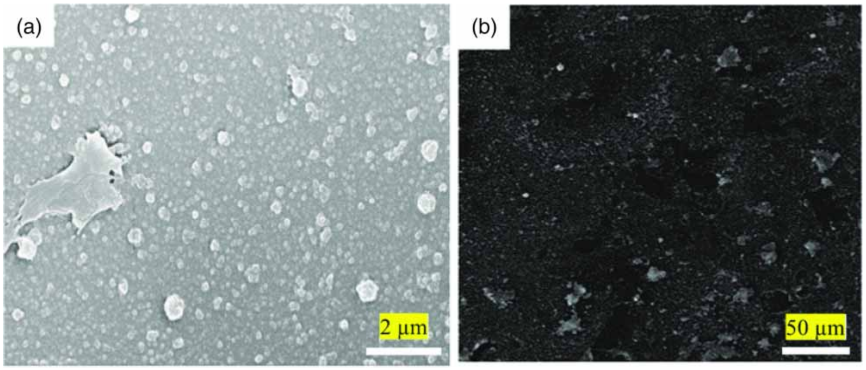


Figure 3 | (a) Agglomeration showing on SEM images of modified graphene oxide (Shao *et al.* 2019) and (b) multi-walled carbon nanotubes (MWCNTs) (Wu *et al.* 2010) in PA layer of membrane.

generating an extra barrier at the membrane surface or clogging the internal pores (Al Aani *et al.* 2017). This prevents the solvent from passing through the membrane, lowering the permeability and increasing the transmembrane pressure necessary to sustain productivity and as a result, the membrane's lifespan is reduced. Additionally, clogged membranes would require a lot of cleaning agents, which could harm the membrane surface and, in extreme cases, necessitate replacing the membrane. As a result of all of these issues, the cost of operating and maintaining the water treatment unit would increase (Contreras 2011). Fouling phenomena could be somewhat reduced by selecting the right membrane materials, operating designs, pretreatment techniques, and environmental conditions, but membrane sustainability at the industrial scale still poses a challenge because of its complexity and variety (Al Aani *et al.* 2017). In an effort to lessen their effects, membrane fouling phenomena have received extensive attention for a long period of time from a variety of angles, such as acknowledging fouling mechanisms, incidence, types, and factors influencing fouling growth.

Membrane hydrophilicity can be changed to minimize the fouling from constituents of the process fluids as part of a strategy to address this problem that has been employed. The main methods for improving TFN membrane performance are shown in Figure 4. Membrane modification is a technique for adjusting a membrane's hydrophilicity to stop fouling from the components of process fluids. Additionally, considering that most foulant interactions with membranes are hydrophobic in nature, some claim that membrane modification can be defined as the process of adding a hydrophilic functional group to a membrane surface in order to improve the free surface energy and subsequently reduce fouling (Kumar *et al.* 2015). The active layer (skin) of the membrane controls both the separation process and the interactions between the membrane and the foulant, so membrane separation processes are in fact surface dependent. It is thought that adding a hydrophilic functional group to that surface will improve the ability of the membrane to separate waste materials from the active layer while also reducing or controlling unwelcome adhesion or adsorption interactions (Kochkodan *et al.* 2014). Several methods have been suggested to accomplish this, which may be used singly or in combination (Mohammad *et al.* 2015). Examples of surface modifications include grafting, surface chemical reactions, blending, plasma treatment, dip coating, and ion implantation (Al Aani *et al.* 2017). These methods can be applied to a variety of polymeric, organic and inorganic chemicals as well as nanoscale materials to enhance the hydrophilicity of polymeric membranes.

Membrane surface modification is also a fundamental strategy in the fouling reduction approach. Choosing an acceptable technique for modifying the membrane surface is just as crucial as selecting specific nanoparticles. Recently, the use of engineered nanomaterials (ENMs) in polymeric membrane matrices for the treatment of water and wastewater has drawn a lot of

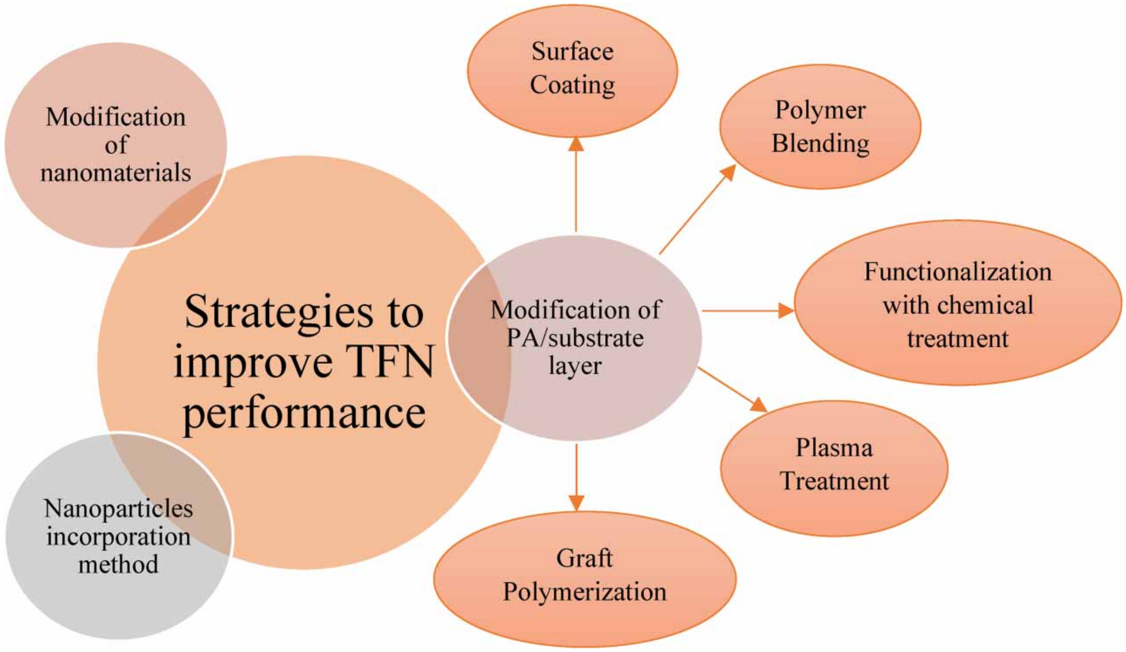


Figure 4 | Illustration of strategies available to enhance the performance of TFN membrane.

interest. The ultimate objective of membrane development is the creation of nanocomposite membranes that preserve the benefits of polymeric membranes while addressing their drawbacks through the integration of ENMs (Kango *et al.* 2013; Qu *et al.* 2013). In contrast to conventional membranes, nanocomposite membranes are a novel type of membrane made of both organic polymers and inorganic nanoscale components. Various different ENMs have been used in countless studies to create novel composite polymer membranes for water treatment applications. Over the last decade, researchers have incorporated a wide range of solid nanofillers into polyamide layers, including titanium (TiO_2), (Ag) cerium oxide, silver, GO, CNTs, aluminium (Al_2O_3), silicon (SiO_2), iron (Fe_3O_4), zirconium (ZrO_2), zinc (ZnO), clay nanoparticles, and zeolite (NaX) (Yang *et al.* 2017, 2019; Pang & Zhang 2018; Zhao & Chung 2018; Wang *et al.* 2019).

3.1. Surface engineering of nanomaterials

The surfaces have been altered with organic functionalities to prevent agglomeration and inadequate dispersion of nanoparticles in polymer matrices. Unmodified nanoparticles will cause polymer nanocomposites' properties to deteriorate without this surface modification. Surface-modified nanomaterials (SMNs) have received much attention in comparison to unmodified nanomaterials due to the outstanding interfacial interaction between the surface of the nanoparticles and polymers. Surface modification of NPs provides four primary purposes: (1) to enhance or alter magnetic nanoparticles (MNP) dispersion; (2) to boost MNP surface activity; (3) to improve MNP physicochemical and mechanical qualities; and (4) to enhance MNP biocompatibility (Zhu *et al.* 2018).

The surface-functionalization of nanomaterials involves the use of a variety of organic functional groups, such as alcohols, thiols, sulphonic, carboxylic acids, and amines. To alter the surfaces of nanomaterials, a variety of techniques have been employed, including copolymerization of functional organ silanes, macromonomers, and metal alkoxides, (ii) functionalization of organic components within sol-gel-derived silica or metallic oxides, (iii) organic functionalization of nanotubes, nano clays, or other compounds with lamellar structures, and (iv) other methods (Vengatesan & Mittal 2015). The outstanding hybrid nanocomposites produced by SMNs reinforced into polymer matrices have low weight, high strength, and improved thermal conductivity.

Adsorbents had served as vital components in TFN membranes, which are used in a variety of separation procedures. There are various advantages of using adsorbents in TFN membranes for heavy metal removal. For example, previous research (Qiu & He 2019) had applied zeolite to a PA layer in order to improve membrane water permeability. As stated in those reports, the water permeability of all TFN with different wt% of zeolite is higher compared to the TFC and the values increase with the increasing of loading (Qiu & He 2019). It is vital to note that having high water permeability while also effectively removing heavy metals may require a trade-off. Increasing permeability may reduce adsorption capacity, while decreasing permeability may increase adsorption capacity. As a result, balancing these factors based on the application's specific requirements is critical. Combining adsorbent and metal oxide to produce advanced nanocomposite materials is another approach to reduce agglomeration issues of nanoparticles. In a different study (Zhu *et al.* 2017), they created a TFN membrane by combining a PA layer with a hydrophilic nanoparticle called ZIF-8 that has been modified with poly(4-styrene sulphonate). The hydrophilicity of the surface of the PA layer increased, thereby enhancing water permeability. From those previous works, it can be said that adsorbents can help to increase the hydrophilicity of TFN membranes, allowing more water to pass through. Hydrophilic adsorbent particles can lessen the contact angle of the membrane surface, permitting water molecules to penetrate and flow more freely. This results in increased water permeability and better filtering or separation performance.

Various processing processes are used to create the nanocomposites, which normally are made up of organic polymers and inorganic nanoparticles. Metal, metal oxide, and carbon-based nanomaterials are some of the examples of nanoparticles that have been extensively used in the fabrication of hybrid polymer nanocomposites (Vengatesan & Mittal 2015). A wide variety of chemical forms and various geometric surface structures are accessible for solid materials that had been used as adsorbents. The primary characteristics of the materials that are extensively employed as conventional adsorbents for heavy metal removal from wastewater are high specific surface area, high ion exchange capacity, low cost, and their abundance in nature (Atkovska *et al.* 2018). Clay minerals (with a special emphasis on bentonite), zeolites, activated carbon, and metal oxides are some of the most often used adsorbents. The table of classification for the adsorbents was introduced by the previous researcher (Crini *et al.* 2018), as shown in Table 3.

Due to their strong chemical stability, low density, structural diversity, and applicability for field-scale applications, activated carbon-based adsorbents are extensively studied by researchers for adsorption (Crini *et al.* 2019). The distinctive properties are typically a result of their internal pore morphology, surface properties, porosity, pore volume, chemical

Table 3 | Industrial absorbents: basic types (Crini *et al.* 2019)

Carbon adsorbents	Mineral adsorbents	Other adsorbents
Activated carbon	Silica gel	Synthetic polymer
Activated carbon fibres	Activated alumina	Composite adsorbents (Mineral carbon)
Molecular carbon sieve	Metal oxides	Mixed adsorbents
Fullerenes	Metal hydroxides	
Carbonaceous materials	Zeolites	
	Clay minerals	
	Inorganic materials	

structure, and presence of functional groups from their source material, including their activation (Crini *et al.* 2019; Sonal *et al.* 2020). Because of its high specific surface area and enormous volume of micropores and mesopores, activated carbon is frequently employed to remove heavy metal ions (Atkovska *et al.* 2018). Carbons are actually one of the oldest and most commonly used adsorbents in the industry. Furthermore, commercial activated carbons have also been considered as the most effective adsorbents because of their high capacity to adsorb contaminants, they produce an excellent output if the adsorption system is developed appropriately (Crini *et al.* 2019). This ability is mainly due to their structural qualities, porous texture, which gives them a large surface area, and chemical composition, which can be easily changed by chemical treatment to vary their properties. The processes that use these widely known adsorbents are typically carried out in batch mode, either by continuously passing the contaminated solution over a packed bed of carbon or by adding activated carbon to a vessel that already contains the contaminated solution (Crini *et al.* 2019).

Another significant advantage of using commercial activated carbons is that no by-products are formed, as compared to chemical oxidation treatment. Activated carbon powder is used in conjunction with a UF membrane or other processes, such as oxidation, to provide cost-effective technology (particularly in the field of water recycling) (Crini *et al.* 2019). Although activated carbons have been used for a long time, research and development are continuously ongoing, particularly due to the growing demand for very clean water. Despite all advantages that had been mentioned, activated carbon technology also has some drawbacks. Commercially available activated carbon is quite pricey and non-selective (the higher the quality, the higher the cost). Even though the great absorbing power of active carbons no longer needs to be demonstrated, there is still the issue of disposal of spent activated carbons, as well as the disadvantage of their rapid saturation and thus their regeneration. Because of these factors, their general use is limited; in particular, small- and medium-sized businesses cannot afford such therapy (Crini *et al.* 2019).

Considering conventional treatment methods do not completely remove all contaminants, the researchers focused on developing technologies that will successfully remove these new contaminants (Atkovska *et al.* 2018). Metal oxide nanoparticles are gaining popularity among researchers as a viable alternative for wastewater treatment (Liu *et al.* 2019; Gautam *et al.* 2020; Li *et al.* 2020; Shaheen *et al.* 2020) due to the fact that metal oxide is extremely effective at removing numerous types of air, water, and soil contaminants via adsorption and photodegradation. Therefore, researchers started to focus on surface modification. Coating, stabilization, and functionalization can all be used to modify the surface of metal oxide nanoparticles. However, metal oxides are prone to agglomeration due to van der Waals forces or other interactions (Sousa & Teixeira 2020), causing a reduction in capacity and selectivity. To improve the application of nanomaterial oxides in wastewater treatment, they had been combined with an AC porous matrix. This is because magnetic adsorbents have recently received a lot of attention for water treatment because of their ease of separation and collection by a magnet. Furthermore, combining with magnetite particles can reduce particle agglomeration (Alorabi *et al.* 2020).

The addition of transition metal oxide nanoparticles to activated carbon as a result of growing research efforts has also produced synergistic benefits for the adsorptive removal of dyes from wastewater (Anjum *et al.* 2019; Nayeri & Mousavi 2020; Nasrollahzadeh *et al.* 2021). It has been reported that metal oxides, in addition to functional groups of activated carbon, provide numerous hydroxyl and oxygen linkage sites for mutual interaction, considerably improving the adsorption capacity of activated carbon-based metal oxide nanocomposite (Farooq *et al.* 2022). For example, iron oxide (Fe_3O_4) (Alorabi *et al.* 2020), copper oxide (CuO) (Peternela *et al.* 2017; Vidovix *et al.* 2019), and zinc oxide (ZnO) (Saini *et al.* 2017; Muntean *et al.* 2018) loaded activated carbon have shown a surprisingly high cationic dye adsorption capacity due to effective dye inter-diffusion. Because of its stable and varied pore structure, activated carbon (AC) has proven to be an excellent support. A previous study (Liu *et al.* 2011) has reported on Fe_3O_4/GO composites that had greater adsorption than Fe_3O_4. Another previous researcher who used Fe_3O_4 stated that it can attract water molecules in surface coatings (hydrophilicity) but does not form clusters due to particle dispersion (Jain *et al.* 2018). In that previous report a statement was also given that surface coating of iron oxide by activated carbon enhances their sorption capabilities because surface coating phenomenon aids in turning the closely packed cubic geometry of magnetic nanoparticles into compact and strong nanoparticles that helps to reduce aggregation (Ojemaye *et al.* 2017; Table 4).

Based on these findings, efforts have been made to incorporate nanocomposite metal oxide-adsorbents into membranes for heavy metal removal applications. In order to improve the stability and performance of heavy metal removal, He *et al.* (2020) developed a sulphonated graphene oxide @ metal organic framework-modified forward osmosis nanocomposite (SGO@UiO-66-TFN) membrane. The stability of the nanomaterial in the membrane was improved by the cross-linking of SGO@UiO-66 and m-phenylenediamine. Moreover, the new water channels created by SGO@UiO-66 improved the water permeability. The diffusion path of the solute was made more circuitous by the lamellar structure of SGO and the frame structure of UiO-66, which enhanced salt rejection and heavy metal removal. The hydrophilic layer of the SGO@UiO-66-TFN membrane was also capable of blocking impurities and loosen the structure of the pollution layer, helping to ensure that the membrane remained at a high removal rate. In comparison to the thin-film composite membrane, the SGO@UiO-66-TFN membrane's water flux and reverse solute flux were 14.77 LMH and 2.95 gMH, respectively, and managed to improve by 41 and 64%. Removing heavy metal ions from the membrane was another area of success. More than 99.4% of the heavy metal ions were removed in just 2 h, and more than 97.5% in just 10 h.

Zhang *et al.* (2018), stated in their study, in which MWCNTs-COOH were modified with poly(amidoamine) (PAMAM), and the as-produced MWCNTs-PAMAM were embedded into the inner polyamide skin-layer of the NF membranes. It is discovered that the rigid MWCNTs and dendrimer PAMAM molecules provide the NF membranes with outstanding porosity and hydrophilicity in their as-fabricated state. The NH_2 groups in PAMAM also offer a few positive sites in the polyamide layer. The most effective membrane PIP/MWCNTs-PAMAM (MPCP) membrane has a water flux of 12.2 $Lm^{-2}h^{-1}$, which is 1.7 times greater than that of the unaltered NF membranes, while experiencing a slight decline in Na_2SO_4 rejection from 94.9

Table 4 | Summarized previous research on metal oxides-adsorbent nanocomposites

Metal oxides	Adsorbents	Surface area (m^2g^{-1})	Adsorption capacity (mg/g)	Reference
Fe_3O_4	AC	Fe_3O_4 – 41.0 AC/Fe_3O_4 1:2 – 441.93 AC/Fe_3O_4 1:1 – 544.69 AC/Fe_3O_4 2:1 – 549.30 AC – 1045.49	Removal of Cr (VI) Fe_3O_4 – 83.33 AC/Fe_3O_4 1:2 – 250.00 AC/Fe_3O_4 1:1 – 333.33 AC/Fe_3O_4 2:1 – 500.00 AC – 500.00	Kaur *et al.* (2021)
Fe_3O_4	AC	Sunflower head waste (SHW) – 0.99 AC – 25.07 Fe_3O_4 – 47.87 AC/Fe_3O_4 – 51.10	Fe_3O_4 (Cr (VI)) – 5.50 Fe_3O_4 (Cu (II))– 2.70 Fe_3O_4 (Cd (II))– 0.09 AC/Fe_3O_4 (Cr (VI)) – 8.06 AC/Fe_3O_4 (Cu (II)) – 3.20 AC/Fe_3O_4 (Cd (II)) – 2.15	Jain *et al.* (2018)
TiO_2	Bentonite	Pure Bentonite – 78	Removal of Cd (II)	Abbasi *et al.* (2020)
ZnO		Bentonite/TiO_2 – 314.7	Bentonite/TiO_2 – 13.14	
		Bentonite/ZnO – 321.9	Bentonite/ZnO – 12.03	
GO	ZeO	ZeO – 72.739 GO/ZeO – 64.74	Removal of Cd (II) ZeO – 149 GO/ZeO – 196	Liu *et al.* (2020)
GO	SiO_2	GO – 292 SiO_2 – 522 GO-SiO_2 (water) – 252.5 GO-SiO_2 (IL) – 858	Removal of Pb (II) GO-SiO_2 – 527 Removal of As (III) GO-SiO_2 – 30	Barik *et al.* (2020)

to 92.6%. In fact, the MWCNTs-PAMAM addition created positive sites in the polyamide layer, giving the MPCP membrane a potent sulphate and metal cation rejection.

3.2. Nanoparticles incorporation methods

Even though there have been numerous studies on TFC membrane development over the past few decades, there is still a pressing need to develop TFC membranes that are both technically and economically more feasible and have excellent separation performance and low energy requirement for industrial applications. The physicochemical properties of TFN membranes, such as hydrophilicity, mechanical stability, thermal resistance, and perm selectivity, can be improved, according to recent research (Kim *et al.* 2013; Zhao *et al.* 2014). Three different types of nanoparticles are used as nanofillers in TFN membranes: one-dimensional nanotubes, two-dimensional porous NPs, and zero-dimensional metal and metal oxides (Dong *et al.* 2015). Both direct NP deposition on TFC membranes as well as encapsulating NPs inside the TFC membrane during the IP stage can be used to create TFN membranes. A post-modification method called surface deposition is frequently used to improve the antifouling properties of membranes. However, the high-pressure filtration process could cause the deposited NPs to leak. Consequently, to increase NP stability in the polymer matrix, chemical functionalization techniques such as NP surface modification are needed (Zargar *et al.* 2017).

Incorporating NPs into the TFC membrane during the IP process has the potential to be one of a promising method. Researchers in the field of membrane science have used a variety of inorganic nanofillers with various properties, such as titanium dioxide (TiO_2), GO, CNTs, TNTs, zinc oxide (ZnO), and silicon dioxide (SiO_2), to enhance the performance of TFN membranes for both pressure-driven and osmotically driven filtration processes (Ji *et al.* 2017; Lee *et al.* 2019). Zeolite-A NPs (50–200 nm) had been incorporated into the polyamide (PA) layer *in-situ* by earlier researchers, who had created the first TFN membrane. These zeolite-incorporated TFN membranes showed improved separation performance and fouling resistance (Jeong *et al.* 2007). In the membrane matrix, NP stability and dispersion play a key role in the long-term structural and performance improvement of TFN membranes (Kang & Cao 2012). It is anticipated that these NPs added via IP will be more stable overall than those added via deposition. This is due to the fact that during the IP process, a large number of NPs are partially or entirely enclosed within the PA thin film layers (Zargar *et al.* 2017).

One of the key strategies in the fouling reduction method is membrane surface modification. As important as choosing certain nanoparticles is choosing an acceptable strategy for changing the membrane surface. In order to incorporate nanoparticles in the membrane surface modification shown in Figure 5, two methods – (i) the conventional approach and (ii) the pre-seeding IP method – are used. There are two distinct types of conventional methods, depending on whether the nanoparticles are added to the trimesoyl chloride (TMC) solution or the MPD solution. When the nanoparticles are added to the TMC solution, an IP zone forms, as shown in Figure 5(i) (a). Considering that they are found in the topmost layers of the surface, the nanoparticles can leach and agglomerate. As shown in Figure 5(b), an IP zone develops when nanoparticles are added to the MPD solution, and then a polyamide layer follows. Fouling will be more common now that the polyamide layer is on the top surface (Lau *et al.* 2015).

In a previous research report, FeO nanoparticles have been used to prepare surface-modified nanocomposite membranes. However, one of the main drawbacks of using FeO nanoparticles is their rapid aggregation during membrane preparation, which decreases their hydrophobic properties, obstructs surface pores, and worsens membrane fouling. In order to prevent FeO nanoparticles from aggregating, an intermediate pre-seeding step is carried out. This step involves introducing a hexane solution containing ethanol, nanoparticles, and TMC at a low concentration between the MPD and TMC layers. This helps to ensure that FeO nanoparticles are properly dispersed on the membrane surface (Lakhotia *et al.* 2019). As demonstrated in Figure 5, this results in an IP zone at the same layer of the membrane where the nanoparticles are present (neither above nor below the nanoparticles).

In another previous research that had been incorporating NPs into the TFC membrane (Soo *et al.* 2020), they used TNT-Fe_3O_4 as nanoparticles to remove cadmium (Cd) and lead (Pb). The results of the work showed that all of the membranes had rejection rates of more than 98% for both Cd and Pb heavy metals. The theoretical transport model states that membrane selectivity is dependent on mechanisms such as sieving and charge repulsion (You *et al.* 2017). Particularly, the PA layer played a role in the rejection of heavy metals by TFNs. The dissociation and protonation of active functional groups, like amine groups, produce the charges on the surface and pore structure of the PA layer. These charges improve separation efficiency by electrostatically repelling co-ionic species from the membrane surface (Sum *et al.* 2019). In addition,

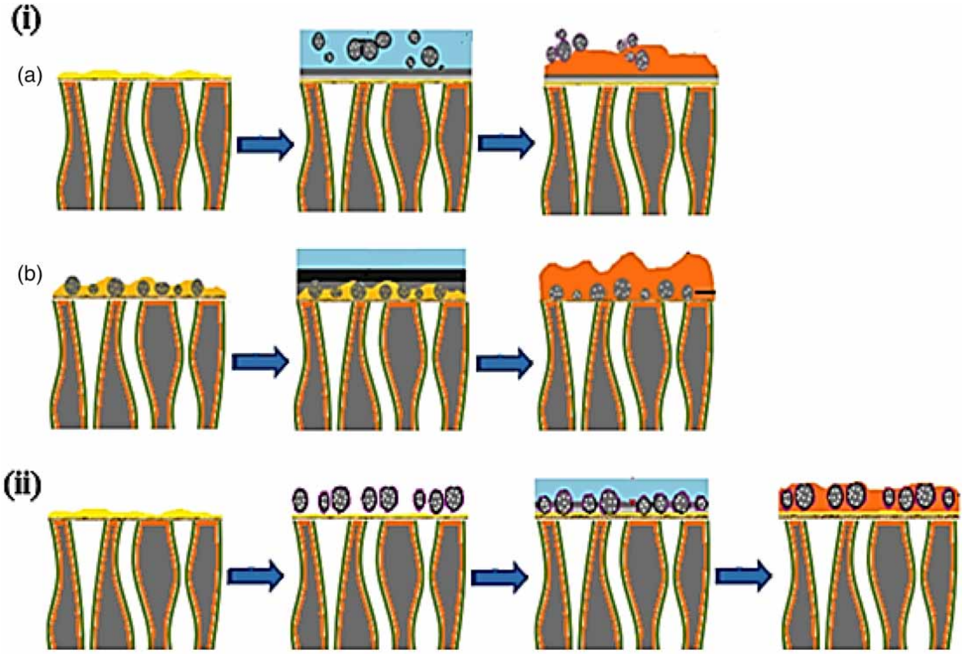


Figure 5 | (i) Conventional method: (a) by dispersing NPs in TMC solution and (b) by dispersing NPs in MPD solution and (ii) pre-seeding interfacial polymerization method (Lakhotia *et al.* 2019).

TFNs incorporated with TNT-Fe_3O_4 hybrid nanoparticles demonstrated the maximum rejection of Cd^{2+} and Pb^{2+} heavy metals, with 99.81 and 98.84%, respectively.

3.3. Surface modification of PA layer or substrate layer

Membranes successfully remove impurities from drinking water; however, fouling will lead to a rise in operating costs and limits the applicability of membrane process. According to the definition of membrane fouling, it is 'a condition that occurs when the membrane is blocked or coated by a component present in the processed stream, causing a reduction in flux'. Membrane separation is a phenomenon that occurs on surfaces, and the top selective layer is vital (Saqib & Aljundi 2016). Consequently, it is normal to see a lot of research projects with a membrane surface modification focus. These initiatives had specific objectives, like increasing permeate flux and/or rejection (Wang *et al.* 2015; Ma *et al.* 2016). Nevertheless, reducing membrane fouling is the most important objective (Ray *et al.* 2015; Shafi *et al.* 2015; Wu *et al.* 2015; Matin *et al.* 2016). Since many foulants are naturally hydrophobic, membranes that are more hydrophilic are believed to be more resistant to fouling because stronger hydrogen bonds develop between the membrane surface and the nearby water, forming a protective water-layer from foulants (Saqib & Aljundi 2016).

'The plane of membrane ends' or 'the last layer of atom before the next phase begins' are two definitions given for a surface (Xu *et al.* 2009). However, the magnitude of both a short-term and long-term flux reduction is greatly influenced by membrane surface properties in the membrane transport system. As previously mentioned, interactions between surface and foulant particles can be whittled down by cleaning the membrane with chemicals like sodium hypochlorite solution. Regrettably, the use of chemicals may cause the polymeric membrane material to instantly deteriorate, shortening the lifetime of the membrane (Ayyavoo *et al.* 2016). By using efficient surface modification techniques, the complexity and high energy consumption of the pressure-driven membrane process (MF, UF, and NF) can be prevented. Modifying membrane characteristics that prevent membrane fouling can be made easier, including their surface hydrophilicity, charge, roughness, and functional groups. The development of completely fouling-free membranes appears to be highly complicated, but it is doable and has been accomplished through numerous modification methods (Ayyavoo *et al.* 2016) and many studies have shown that reducing fouling on the membrane has a positive effect (Choi *et al.* 2012; Kwon *et al.* 2012).

In previous research work (Soo *et al.* 2020), a novel TFN forward osmosis (FO) membrane with a positively charged and nano functional substrate layer has been developed for efficient removal of heavy metal ions. Titanium nanotubes and magnetite oxide hybrid nanoparticles (TNT-Fe_3O_4) are incorporated to the PSF matrix in order to form the substrate layer. The addition of nanoparticles enhanced the hydrophilicity and loose structure of the substrate layer. The modified substrate layer also increased the affinities between the polymer matrix and the nanofillers, maintaining the membrane selectivity. The modified substrate hydrophilicity, which has significantly decreased the internal polarization concentration (ICP), was primarily responsible for the improvement. The membrane with the best performance increased water flux by 73% when compared to TFC and displayed a high level of Cd^{2+} and Pb^{2+} heavy metal ion rejection of $>$98%. This study demonstrated the viability of improving the performance of FO membrane for treating heavy metal wastewater using a quick and easy technique by designing the substrate layer (Soo *et al.* 2020).

In order to modify the surface properties of antifouling membranes, several modification approaches have been developed. These modifications are classified as either physical (coating, blending, and employing composite membranes) or chemical (functionalization of polymers, plasma treatment, and graft polymerization) (Ayyavoo *et al.* 2016).

3.3.1. Surface coating

Surface coating refers to the thin selective layer that is straightforwardly deposited on the top layer of the membrane surface. The three theoretical mechanisms by which hydrophilic functional materials are physically deposited on membrane surfaces are: (1) adhesion/adsorption, in which the binding energy is enhanced by multiple interactions between functional groups in the macromolecular layer and on the hard surface; (2) interpenetration, in which the functional material and base polymer are combined in an interphase; and (3) macroscopic entanglement of functional group and pore structure of membrane. The coating procedure typically entails submersion in a coating solution followed by the evaporation of any remaining solvent at the proper temperature to produce the coating layer. Performance of the membrane is significantly influenced by the preparation conditions (flux and rejection) (Xu *et al.* 2013).

Ni *et al.* (2014) improved the chlorine resistance and antifouling performance of a polyamide TFC RO membrane by coating it with a novel random terpolymer poly(methyl-acryl-oxy-ethyl-dimethyl benzyl ammonium chloride-r-acrylamide-r-2-hydroxyethyl methacrylate) (P(MDBAC-r-Am-r-HEMA) as shown in Figure 6. The coated TFC membrane, which is 7–10 times more resistant to chlorine exposure than a pure membrane, showed exceptional tolerance to exposure levels above 16,000 ppm h. In addition to having antibacterial properties, the coated membrane also demonstrated an increase in surface hydrophilicity, which is advantageous to the membrane's antifouling performance.

3.3.2. Polymer blending

Polymer blending has become a widely known, effective, and flexible method for improving membrane properties for a variety of applications. In the preparation and processing of materials, blending is a common method for distributing liquid-state powders that effectively mixes molecules at the molecular level (Ayyavoo *et al.* 2016). The basic transport properties of the underlying polymer must be combined with the necessary qualities in order to create a polymer blend membrane. For all pressure-driven membranes, the proper choice and combination of polymeric components in a precise ratio can produce a blend that has advantageous properties for antifouling membranes (Ayyavoo *et al.* 2016). According to previous studies, the presence and concentration of hydrophilic PEG 600 have a significant influence on changing membrane properties like porosity and pore size. The recently founded membranes were more effective at removing metal ions and proteins from aqueous streams (Nagendran & Mohan 2008).

3.3.3. Functionalization through chemical treatment

The surface of membranes with different functional groups (such as hydroxyl, amine, carboxyl, and sulphone) can be altered chemically, which is a common procedure. The primary chemical treatment techniques are hydrolysis, substitution, addition, and oxidation; bulk modification also uses these techniques (used before membrane formation, not on membrane). Direct application of bulk modification techniques to the polymer solution is simple and efficient (Ayyavoo *et al.* 2016). Typical bulk modification techniques used to increase surface hydrophilicity include carboxylation, sulphonation, amination, and epoxidation of aromatic polymer backbones. The modified membrane surface still has the original membrane's mechanical characteristics because it is moderately stable. The different functional groups that are attached to polymer or membrane surfaces activate them to produce superior properties (Ayyavoo *et al.* 2016).

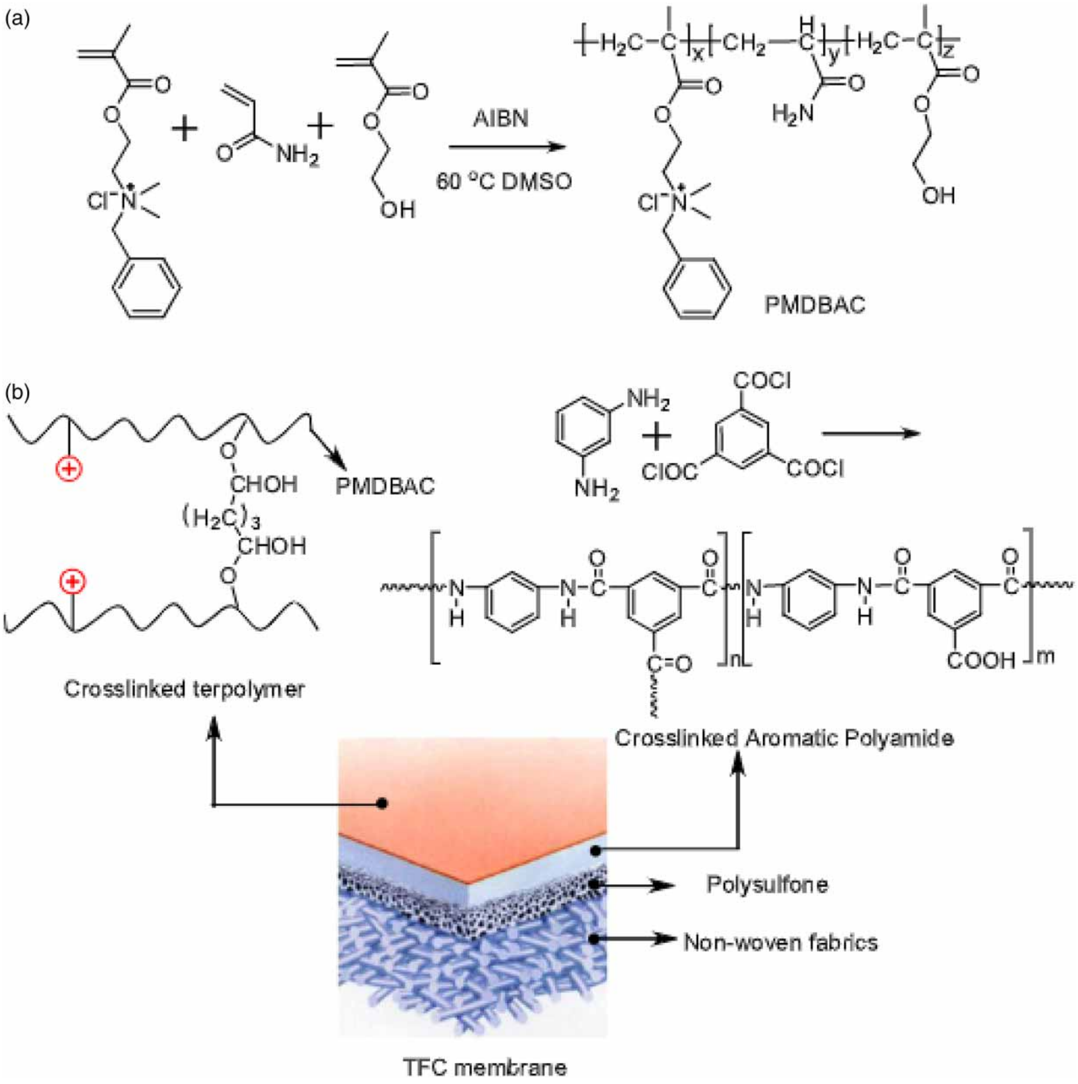


Figure 6 | Schematic diagram for synthesis of the terpolymer P(MDBAC-r-Am-r-HEMA) (a) and surface modification of RO membranes (b) (Ni *et al.* 2014).

3.3.4. Plasma treatment

Interaction with highly excited atomic, molecular, ionic, and radical species is required for surface modification with plasma. The exchange of ions and atoms in materials brought on by elastic and inelastic collisions is known as plasma sputtering. As the process progresses, inert gases are activated to create plasma. When hydrogen is removed from polymer chains during the plasma implantation procedure, radicals are produced at their midpoint. The oxygen or nitrogen on the polymer chains is formed when these radicals react with other simple radicals produced by plasma gas. Plasma gas produced from $CHCl_3$ and CCl_4 increases the surface hydrophilicity of the membrane surface. Moreover, compared to hydrophobic surfaces, hydrophilic membrane surfaces have higher permeability and reproducibility. Inserting sprayed materials into the plasma region of a plasma torch with a high temperature and flux velocity is known as plasma spraying. However, these techniques are not frequently applied in the formation of fouling-resistant membranes (Ayyavoo *et al.* 2016). Figure 7 shows a schematic illustration of plasma therapy.

Based on previous research (Khoo *et al.* 2022) that was inspired by the benefits of surface coating and nanoparticle incorporation, this study aims to integrate both techniques to produce TFN membrane with minimal surface defects for RO

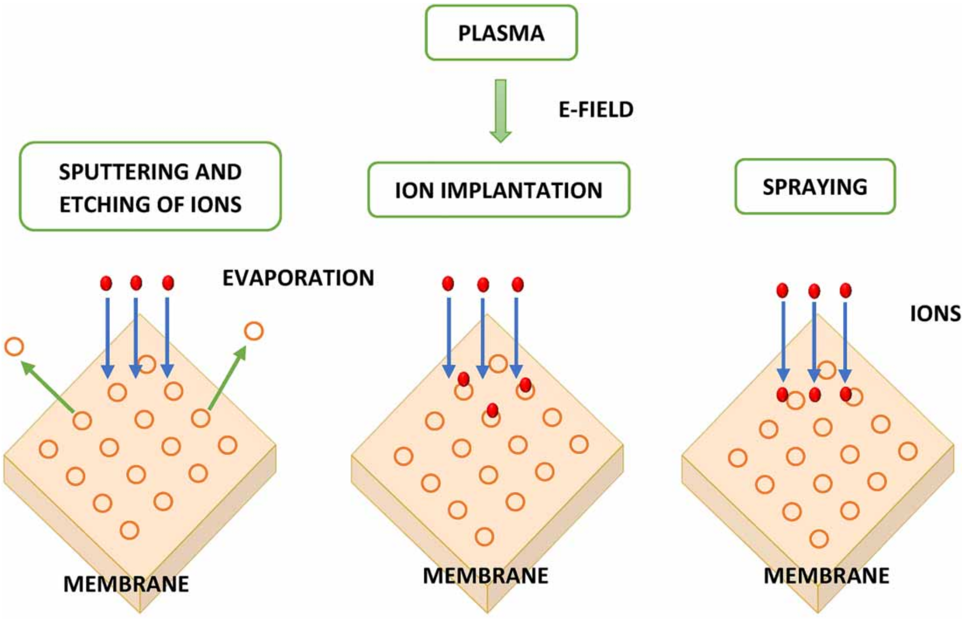


Figure 7 | Schematic representation of plasma treatment (Ayyavoo *et al.* 2016).

application by employing a rapid surface deposition technique – plasma enhanced chemical vapour deposition (PECVD) to form a hydrophilic thin layer atop nanofiller-incorporated PA layer. This coating method is expected to prevent TNT leaking from the membrane. The PECVD approach is used for surface modification of nanomaterials and TFN membranes because it can change the material surface functionality (Hassan & Carr 2019) with its lower degree of plasma ionization without causing damage to the bulk material. In addition, unlike conventional surface grafting and coating processes, this technology has a quick reaction time and does not require any hazardous ingredients (Khoo *et al.* 2020).

3.3.5. Graft polymerization

By grafting monomers together, graft polymerization produces distinct properties while shielding the membrane surface from external agents. It is the best and most efficient method for surface modification. Grafting-to and grafting-from reactions are the two main categories used to categorise grafting reactions. A grafting-to procedure involves covalently attaching reactive functional polymer chains to the membrane surface. For grafting-from, the surface-based monomers are first polymerized by the active species on the polymer backbone (Ayyavoo *et al.* 2016). Multiple types of reactive group propagation occur after the grafting-from process, which is started by chemical, radiation, photochemical, and plasma-induced mechanisms. By using initiators and copolymerizing monomers on the polymer backbone, the chemical grafting technique creates free radical and ionic active sites for a variety of functional groups on the membrane surface (Ayyavoo *et al.* 2016). The acrylic acid (AA) monomer was successfully free radical polymerized onto polyamide (PA) by prior researchers (Makhlouf *et al.* 2007) and grafting was produced as a result of heat cleaving the peroxide group (Benzoyl peroxide) (Makhlouf *et al.* 2007).

All of the aforementioned membrane surface modifications were carried out in an attempt to avoid or lessen fouling by altering the surface's charge, hydrophilicity, functional groups, and roughness. The elimination of unwanted interactions and the creation of cutting-edge separation functions are made possible by modifications to membrane surfaces. Graft polymerization that is initiated by photochemical or redox reactions is more practical, less complicated, and much less expensive in commercial settings (Ayyavoo *et al.* 2016). Numerous studies on fouling have revealed that modified polymeric membranes are more impervious to foulants of all kinds than virgin membranes. Colloidal deposition can be effectively avoided by creating a fouling-resistant coating on the membrane surface using blending, photochemical grafting, and chemical grafting. Membrane washing is necessary to prevent foulants from accumulating on the membrane, and fouling resistance can be improved by incorporating membrane module design (Ayyavoo *et al.* 2016).

4. CONCLUSION

Given their high toxicity, heavy metals are known to be extremely dangerous to the environment and human health if released directly. Heavy metals in industrial wastewater should be treated carefully to meet the discharge standard and prevent any negative effects. It has been reported that heavy metal removal can be succeeded in using membrane-based processes, such as pressure-driven membrane. Despite their effectiveness, laboratory-scale tests were still conducted to examine the majority of heavy metal removals by membranes. At the pilot or commercial scale, membrane durability, scaling and fouling formation, and long-term performance must be assessed for future applications. Many industries and sciences require a low cost, dependable, and high yield technology for separation and manufacturing of high-quality materials, and TFN membrane can prepare the perfect setting for these purposes. Membranes are ideal due to their great selectivity and other unique properties, despite the fact that many laboratory size projects have yet to be commercialized. In recent years, advancement has been made in the fabrication and development of high-performance TFN membranes using functionalized fillers derived from GO, CNT, TiO_2, Ag-TiO_2, metal organic frameworks (MOFs), and organic fillers for water purification applications using membrane separation processes such as NF, UF, and RO. The nanofiller is then applied to develop TFN membranes through IP between an organic solution of the monomers in non-polar solvents and an aqueous-solution confined nanofiller. The kind of functionalized nanofiller used and how much is loaded into the PA-selective layers of the TFN membranes affect how well water purification and water treatment work.

However, agglomeration of nanofiller in the selective layer of matrix of the membranes at high loading concentrations is one of the major barriers to large-scale production of TFN membranes and how they are used in the filtration of water. In order to prevent the agglomeration of functionalized nanofiller in the selective layers at high loading quantities, new types of functionalized nanofiller that work better with the membranes' selective layers should be developed. As a result, future research should concentrate on developing high-performance TFN membranes through the use of surface engineered nanofiller or surface modification of the PA and/or substrate layer to achieve high permeate flux and/or rejection. The development of TFN membranes made from functionalized nanofiller from metal oxide-adsorbent nanocomposite can be an interesting area of scientific or industrial study for those involved in the low-cost separation and removal of heavy metals from wastewater and aqueous solutions.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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