Recent progress in nanomaterial-functionalized membranes for removal of pollutants

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SUMMARY

Membrane technology has gained tremendous attention for removing pollutants from wastewater, mainly due to their affordable capital cost, miniature equipment size, low energy consumption, and high efficiency even for the pollutants present in lower concentrations. In this paper, we review the literature to summarize the progress of nanomaterial-modified membranes for wastewater treatment applications. Introduction of nanomaterial in the polymeric matrix influences membrane properties such as surface roughness, hydrophobicity, porosity, and fouling resistance. This review also covers the importance of functionalization strategies to prepare thin-film nanocomposite hybrid membranes and their effect on eliminating pollutants. Systematic discussion regarding the impact of the nanomaterials incorporated within membrane, toward the recovery of various pollutants such as metal ions, organic compounds, dyes, and microbes. Successful examples are provided to show the potential of nanomaterial-functionalized membranes for regeneration of wastewater. In the end, future prospects are discussed to develop nanomaterial-based membrane technology.

INTRODUCTION

The wastewater problem has become a severe global issue driven by sundry pollution such as domestic, industrial, and agricultural activities (Connor and Uhlenbrook, 2017). In addition, with the drastic growth of population, the water demand will increase by 55% in 2050, and the global water deficit will be estimated up to 40% in 2030 (Bielawski, 2020). Approximately two to four billion people in Asia, Middle East, Africa, and Latin America either do not have safe drinking water at home or experience water scarcity at least once every year (Pavon, 2019). Besides, severe climate conditions have even raised the demand for wastewater regeneration (Tetteh et al., 2020). To achieve the sustainable use of water, methods for wastewater treatment were developed to improve the issue of water demand.

Traditional methods for wastewater treatment include coagulation and flocculation. It is impossible to find a universal flocculent, whereas inorganic flocculent often produces large quantities of sludge (Kimura et al., 2013). Precipitation techniques are limited by toxic byproducts such as H2S fumes and other colloidal sulfides (Fu and Wang, 2011; Peters and Kim, 1985). Ion-exchange-based treatments are very advantageous for selective recovery of metal at high concentrations (>100 mg L⁻¹) (Kurniawan et al., 2006). Adsorption processes have been the most economical method for pollutant removal from wastewaters; however, pretreatment of sorbent is usually required to achieve high efficiency (Owlad et al., 2008). Although the aforementioned strategies are employed to lower the concentration of pollutants in wastewater to match the minimum regulatory required levels, they are certainly not recommended for drinking purposes (Zinicovscaia and Cepoi, 2016). Alternatively, electrochemical methods work on the principle of metal ions deposition on a cathode surface and their subsequent recovery in the elemental state (Brillas and Sires, 2012; Fu and Wang, 2011). Despite their wide industrial application, these physico-chemical methods have their own demerits; some lead to secondary water pollution, whereas others are nonprofitable or inefficient in higher concentration ranges (Zinicovscaia and Cepoi, 2016). Thus, developing inexpensive yet efficient, broad-spectrum but ecofriendly, selective, and scalable methods for wastewater treatment is a colossal challenge.

Over the past couple of decades, membrane technology has gained tremendous attention for its employability in water and wastewater treatment, mainly due to its affordable capital cost, miniature equipment
Nanotechnology is considered to have the most potential and can circumvent the challenges associated with the removal of pollutants via conventional membrane processes. Nanomaterials provide superior adsorption capacity attributed to large surface area, copious adsorption sites, and tunable pore size. It can effectively adsorb pollutants with functional groups anchored on nanomaterials such as amine, hydrogen bonds, hydroxyl, carbonyl, and carboxylic groups by hydrophobic interaction, π–π stacking, electrostatic interaction, and van der Waals interactions (Cai et al., 2018). In addition to chemical adsorption, several metal-oxide-based nanomaterials offer properties of photocatalysis and disinfection that allow these nanomaterials to remove biological and chemical pollutants (Hyder and Mir, 2021; Manikandan et al., 2022). Since the early 2000s, various polymeric, carbon, or metallic nanomaterials with well-defined structures have been employed to design state-of-the-art membrane-based wastewater purification systems (Saleh and Gupta, 2016). One or more dimensional nanomaterials such as gold-, titanium-, and carbon-based nanostructures have been prepared and used in various applications such as sensing, catalysis, and energy (Chang, 2021; Chang et al., 2014; Chen et al., 2013, 2015, 2016; Lin et al., 2013, 2021; Roy et al., 2013, 2015; Unnikrishnan et al., 2021; Wu et al., 2020a, and Wu et al., 2020b; Xu et al., 2020). Nanoparticles (NPs), metal-organic framework (MOFs), nanofibers (NFs), nanowires (NWs), nanotubes (NTs), and two-dimensional (2D) nanosheets (NSs) functionalized membranes have been demonstrated to detect and remove organic dyes, heavy metals, macromolecule, bacteria, and other effluents from wastewater (Anjum et al., 2019; Barman et al., 2018; Nain et al., 2017, 2020a, and Nain et al., 2020b; Wei et al., 2020; Hyder and Mir, 2021; Manikandan et al., 2022). Incorporating nanomaterial with existing membranes will boost wastewater treatment efficiency because they have exclusive characteristics such as hydrophilicity, thermal stability, surface roughness, hydraulic stability, higher permeability, fouling control, and higher selectivity (Anjum et al., 2019; Chu et al., 2020). For example, Jaafar’s group prepared polycrylonitrile (PAN)/graphitic carbon nitride (GCN) photocatalytic nanofiber-coated alumina (Al2O3) hollow fiber membrane, which has been used to overcome the severe problem of fouling associated with the oil droplet in the treatment-oilfield-produced wastewater (Alias et al., 2019). Previously, our group prepared polymer/reduced graphene oxide composite functionalized superabsorbent for oil removal and its recovery (Periasamy et al., 2017). In another report, antimicrobial zinc oxide NPs were functionalized onto polyvinyl chloride membrane for remediating actual hospital wastewater (Alsuhay et al., 2018). Despite being the most exploited feature, antifouling is not the only importance of nanomaterial-modified membranes. Recently, Wei et al. employed graphene oxide nanosheets to modify N+-nylon membranes to extract toxic effluents. The developed membrane also served as a substrate for mass spectrometric detection of highly toxic disinfectant in fish meat i.e., malachite green (Wei et al., 2018). Polyethersulfone (PES) is a commonly employed material for ultra- and/or nano-filtration membranes; however, it is hydrophobic and prone to
contamination. Recently, Liang et al., developed zwitterion (2-methacryloyloxy ethyl dimethyl (3-sulfo-propyl)-ammonium hydroxide sulfobetaine methacrylate)-coated molybdenum disulfide NSs and incorporated with PES via phase inversion technique to manipulate the wettability of the membrane, which led to the efficient and selective separation of dye/inorganic salt from industrial effluents (Liang et al., 2019). Another group prepared titania NWs functionalized polyetherimide (PEI)/P25 TiO2 NPs hybrid membranes for the photodegradation of rhodamine B in water using ultraviolet (UV) light (Jiang et al., 2018a). In addition, UV light treatment showed superior water flux recovery ratio (FRR; 88%), revealing significant reduction in fouling compared with water-rinsed ones. Merits of nanomaterial-modified membranes include, but not limited to, pollutant degradation and antifouling.

Employing nanostructures to modify membranes is not an invention; the deteriorating wastewater quality due to complexities in effluents makes room for further improvement in terms of efficiency, selectivity, energy consumption, permeation, and cost-effectiveness. Herein, we review the merits and demerits of nanomaterial-functionalized membranes for removal of pollutants. This paper covers the general idea of membrane technology, fabrication, and characterization of various nanomaterial-modified membranes, the influence of nanomaterials in water remediation, and the additional functionality they bring along.

FABRICATION STRATEGIES OF MEMBRANES

Polymer-nanomaterial composite membranes attempted to solve some of the issues related to permeability, selectivity, biofouling, and mechanical strength in water treatment. Nanomaterials have high degree of functionality. Therefore, it can improve the overall performance of conventional membranes used in environmental applications. The properties required for membrane separation can be achieved by choosing appropriate materials and fabrication methodologies. The functionalization process of nanomaterials is crucial for determining the membrane properties. The efficiency of effluent removal largely depends on the successful implementation of the method employed and in situ dispersion or interaction in the polymeric matrix. Typically, nanomaterials can be incorporated either in the bulk/support layer and/or surface/active layer of the membrane. The widely employed methods include phase inversion, electrospinning, interfacial polymerization, and track etching. The fabrication of membranes against pollutants in wastewater in combination of nanomaterials is strategized as shown in Figure 1. These approaches can be executed individually or simultaneously in a fabrication process to achieve desired characteristics. Below we will discuss the influence of nanomaterial on the traditional membrane fabrication strategies.

Phase inversion method

Phase inversion method is the most common procedure for preparing asymmetric membranes with either thin and dense surface layers and suitable for a large number of building blocks of polymer. In a typical process, polymer undergoes phase transition from a solution to a solid-state, which is usually achieved through immersion precipitation. Figure 2A schematically depicts the principle of the non-solvent-induced phase-inversion methods (Díez and Rosal, 2020; Eykens et al., 2017; Sadrzadeh and Bhattacharjee, 2013; Wang et al., 2013). This procedure is based on a transition between two phases, caused by a change in polymer solubility. A change in composition or conditions causes the mixture to transfer into polymer-rich and polymer-poor phase to form a homogeneous mixture. Other ways to yield highly efficient polymeric membranes for water treatment are precipitation by controlled evaporation and thermal precipitation of the vapor phase (Guo et al., 2021). Key factors influencing phase inversion include solvent, polymer solution, non-solvent system, and the composition of coagulation bath (Urducea et al., 2020). Phase inversion strategy is quick, simple, and currently being employed for commercial manufacturing; however, interaction among solvent and non solvent system, nonuniform distribution, and hydrophobic nature of polymeric matrix is still a major challenge. In addition, smooth and inactive polymer surface does not allow the in situ protraction of pollutants.

In the past decade, efforts have been made toward the modification of membrane surfaces to enhance the water flux, rejection rate, and other surface properties. For instance, in order to improve solvent resistance and filtration performance of nano-filtration membranes, different kinds of organic phenols such as quercetin, dopamine, tannic acid, morin, etc., were coated onto various loose asymmetric membrane supports made of polyimide (PI), PAN, polysulfone (PSF), polyvinylidene difluoride (PVDF), polybenzimidazole (PBI), or polydimethylsiloxane (PDMS) through oxidant-induced polymerization (Fei et al., 2019). Alternatively, PVDF membranes were incubated in an alkaline solution to further immobilize Al2O3 NPs (Liu et al., 2011). Formation of PVDF-conjugated double bonds in the process endowed its direct interaction with...
Al₂O₃ NPs through acid-catalyzed grafting reactions. By employing a modified blending phase inversion method, aqueous phase-triggered precipitation of the hydrophilic bismuth oxychloride (BiOCl) nanocomposite into PVDF phase can be achieved (Figure 2B). A plausible mechanism was proposed for the modified blending-phase inversion method, with an emphasis on the interactions between PVDF and BiOCl. Such nonsolvent induced phase inversion methods enable simultaneous precipitation of nanomaterial and PVDF in the coagulation bath. The precursors of BiOCl (KCl and Bi(NO₃)₃) were readily dissolved in ethylene glycol (EG) and N-methylpyrrolidone (NMP) to obtain a clear solution (Figure 2B). This resulted in surface concentrated BiOCl, as water is rich in the PVDF-H₂O interface (Deng and Li, 2021). On the other hand, incorporation of fillers (e.g., TiO₂ NPs) into PS membrane dissolved in N-methyl-2-pyrrolidinone solution showed a huge impact on the membrane structures. Cross-sectional membranes in SEM are shown in Figure 2C (Kusworo et al., 2020). The finger-like voids of PSF/TiO₂ NPs composites membrane are more significant, with increasing TiO₂ NPs loading concentration. The flux through such porous composite membranes can be significantly increased, whereas the retention remains nearly constant. Similarly, Xia’s group demonstrated the tunable pore size and structure of silicon rubber microporous membranes by varying casting temperature and the concentration of liquid paraffin (Zhao et al., 2013). The intrinsic biocidal properties of Bi contributed to anti-biofouling resistance of the membrane. In addition, there are reports that nanomaterial functionalization also enhances the filtration membrane’s water flux, ductility, and mechanical strength (Hashim et al., 2011). For example, SiO₂ NPs were precipitated along with PVDF through a conventional immersion precipitation method. The NPs dispersed in the membrane matrix were completely etched out by NaOH or HF treatment to form hollow fiber membranes. Another type of membrane, i.e., PES, was hybridized with β-cyclodextrin-functionalized multi-walled carbon nanotubes (β-CD/MWCNTs)
through the wet-phase inversion method to prepare polymeric/nanocomposite membranes (Rahimi et al., 2020). Conventional phase inversion strategy to incorporate nanomaterial can be further improved; for example, Wang et al. demonstrated graphene oxide (GO) into PES phase via direct-current-induced electric-field-assisted phase inversion method. The GO particles migrated toward the anode and were uniformly distributed in the casting solution (Wang et al., 2019a). These methodologies are new and rarely investigated, opening a new way to enhance hydrophilicity, charge density, separation performance, and the antifouling ability of mixed matrix membranes.

Electrospinning method

Electrospinning is a robust and versatile technique that allows the fabrication of nano to macro-scale fibers from solutions or melts using an electrically forced fluid jet (Ghosal et al., 2018; Luo et al., 2012). Characteristics of electrospun fibers such as porosity, surface-to-volume ratio, disposition arrangements, and morphology can be controlled by varying operation parameters and polymer solution (Ghobeira et al., 2018; Ruhela et al., 2021). A schematic diagram of the electrospinning experimental set up to prepare nano-fibrous membrane is shown in Figure 3A (Suja et al., 2017). Reneker’s group controlled the branching and bending of the charged polymer jet by varying the applied electric field to form “garland-like” columnar networks of polycaprolactone and glycine-melamine complex nanofibers (Reneker et al., 2002). Another report has also demonstrated electrospinning to form flat ribbons instead of round fiber (Du et al., 2013; Yadav et al., 2021). Due to the precise control over the fiber size, shape, and morphology, electrospun fibrous membranes have been used for membrane filtration processes (Lee et al., 2020).

Electrospinning offers several advantages such as ease of operation, material selectivity, and low cost. Although different sizes of membranes can produce jet instability, super hydrophobicity, random pore size, unpredictable polymer properties, use of toxic solvents, and adjustment of various parameters are still major pursuits (Bjorge et al., 2009; Pervez et al., 2020). Recently, Khalaf et al. developed single-walled (SW)
CNTs functionalized poly (acrylonitrile-co-vinyl acetate) nanocomposite fibrous membrane for oil/water separation. Hydroxyl groups from carboxylated SWCNTs drastically reduced the hydrophobic nature of membrane (contact angle from $160^{\circ}$ to $89^{\circ}$), thereby achieving 97.5% of rejection efficiency, which is much better than bare polymer (Figure 3B) (Khalaf et al., 2020). Although it is desired to have hydrophilic characteristics for higher rejection, condition is slightly different when it comes to oil-based pollutants. Recently, Zhong et al. have attempted to fabricate hierarchical SiO$_2$ NPs-embedded polytetrafluoroethylene (PTFE) nanofibers via electrospinning of SiO$_2$ NPs containing shell solution, PTFE emulsion as core spinning solution, and 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (Zhu et al., 2020). As a result, nanofibrous membrane produced with core-shell electrospinning exhibited super hydrophobicity and oleophobicity with contact angles of $173^{\circ}$ and $134^{\circ}$, respectively (Figure 3C (a, b)). Minimum viscosity requirements vary with the choice of polymer and their molecular weight. Poly (D,L-lactic acid) (PDLA) solution containing salts such as NaCl, sodium phosphate, or potassium phosphate could yield the smallest average fiber diameter as shown in their surface topography observed by atomic force microscopy (AFM) (Figure 3C (c, d)) (Zhu et al., 2020; Zong et al., 2002). Other than size and shape of nanofibers, thermal and mechanical strength can also be influenced by polymer solution composition. Xu et al. discussed the formation of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/polyethylene oxide (PEO) NF using different solvent systems such as ethanol, chloroform, and dichloromethane. Results indicated that binary-solvent system (dichloromethane/ethanol) generated defect-free fibers with high conductivity, thermal resistance, and mechanical properties compared with mono-solvent system (Xu et al., 2017a, and Xu et al., 2017b).

**Interfacial polymerization method**

Interfacial polymerization (IP) is a polymerization process that occurs at the interface of two immiscible liquids to form variety of polymer topologies, mainly polyamide thin-film composite membranes. In a typical IP reaction, microporous support membrane formed via phase separation acts as a platform to collect the precipitate obtained after soaking the polymer dissolved in one solvent into a nonsolvent phase (Werber et al., 2016). This process often yields a porous membrane structure; however, precise control of
Figure 4. Interfacial polymerization method of synthesizing nanomaterial-functionalized membranes

(A) Typical process of interfacial polymerization to fabricate thin-film composite membranes. Reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) occurs at the surface of a microporous polysulfone support to form a thin polyamide layer. Reproduced with permission from Lu and Elimelech (2021), Copyright 2021, Royal Society of Chemistry.

(B–D) Schematic illustration of formation of nanoparticle-induced crumpled polyamide nano-filtration membrane. SEM images of (b) SWCNTs/PES composite membrane and (c) PD/ZIF-8 NPs-loaded SWCNTs/PES composite membrane. (d–g) Morphology change of the membrane immersed into water in different time after interfacial polymerization reaction on PD/ZIF-8 NPs-loaded SWCNTs/PES composite membrane (scale bar: 1 μm). Reproduced with permission from Wang et al. (2018), Copyright 2018, American Chemical Society. Mechanism of (C) Ag NPs and (D) hydrophilic silica induced nanochannels in the PA layer for efficient water transport. Reproduced with permission from Yang et al. (2019a, 2019b) and Yin et al. (2020), Copyright 2019 and 2020, American Chemical Society.
microporous support is still a major pursuit. IP can be performed at a free interface between an organic and an aqueous phase (Jiang et al., 2018a, and Jiang et al., 2018b). Such a strategy allows facile isolation of polyamide layers for advanced structural characterization, mainly due to weaker interaction between polyamide and support than those of solid support. In addition, poor mechanical strength also restricts the integration of such free-standing films into membrane modules for operation in high-pressure or high-cross-flow conditions. Constructing a sacrificial interlayer made from nanomaterials may endow unique physicochemical properties (e.g., wettability, roughness, and charge), which can effectively modify the support layer before IP. For example, needle-like cadmium hydroxide nanostrands were deposited on porous support to keep the interfacial reaction away from the platform to achieve a thin, smooth polyamide film (Karan et al., 2015). This strategy was first demonstrated to fabricate membranes used in organic solvent separation; however, similar methods have recently been applied for treatment of wastewater. Different from nanostrand layers, Wang et al. developed PD/ZIF-8 MOFs NPs as a sacrificial template, as illustrated in Figure 4B(a). Then to prepare a composites membrane, PD/ZIF-8 MOFs were loaded onto SWCNT/poly-ether sulfone/polyamide membrane for desalination. After the interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMS), a rough polyamide active layer with crumpled nanostructures was formed (Figure 4B (b-g)). Such crumpled texture enhanced water permeability without compromising effluent rejection efficacy (Wang et al., 2018).

Another approach is to embed fillers in the polyamide selective layer to fabricate high-performance thin-film composite membrane fabrication (Pendergast and Hoek, 2011). Early efforts mainly focused on using different kinds of nanofillers to combine with polyamide layer to prepare thin-film nanocomposite membranes. For example, Yang et al. recently demonstrated the formation of nonselective defect channels (~2 nm) between a nanofiller, i.e., Ag NPs and polyamide matrix, which are detrimental to membrane water–salt selectivity (Figure 4C) (Yang et al., 2019b). Although high water permeance, hydrophilicity, and (bio)fouling resistance are achieved, real-time deployment of nanocomposite membranes is still limited by several challenges, raising doubt about their potential applicability. The most crucial factor is the inevitable formation of defects at the interface between fillers and the polyamide matrix, attributed to either low miscibility or less cross-linked polyamide regions due to inhibited IP reaction (Hoek and Tarabara, 2013). Figure 4D shows that introducing hydrophobic materials may improve their dispersibility in the polyamide matrix, thereby inhibiting the formation of the defect channels, and thus the high liquid entry pressure in these hydrophobic nanofibers would provide additional resistance to water transport (Yin et al., 2020). Although hydrophobic mesoporous material (~4 nm) is another option to avoid defects, a required pressure of 138 bar is simply beyond the maximum operating pressure in typical RO systems (i.e., ~80 bar) (Lu and Elimelech, 2021). Despite the wide use of IP process to fabricate membranes for wastewater treatment, several technical obstacles have hampered the use of IP methods, which largely stem from the inherent limitations of the polyamide chemistry and reaction mechanisms.

**Track etching method**

It is a two-step (tracking (Figure 5A(a)) and chemical etching (Figure 5A(b))) membrane fabrication technology that uses nuclear tracks on polymer films for the production of porous membrane. There are two methods to produce latent tracks: using high-energy ion beams from accelerator or irradiating with fragments of nuclear fission (californium or uranium) (Ferrante, 1964; Lück et al., 1990). Chemical etching is a process of removing damaged zone of the tracks to form a hollow channel and is a crucial stage for determining the pore size/shape of the membranes. Despite the lower particle flux stability, the accelerator-based tracking method has become more common, mainly due to easier control of impact angle and production of high-density track arrays. Major constraints in the fabrication of track-etched membranes are radioactive contamination and limited energy range.

Although polyethylene terephthalate (PET) is one of the popular polymer choices for track etching technology, other polymers such as polycarbonate (PC), PI, PVD, and polypropylene (PP) have also been used to design track-etched membrane (Korolkov et al., 2018; Kumar et al., 2016; Kuo et al., 2008; Muench et al., 2014; Song et al., 2007). After chemical etching, cone-shaped nanopores in PET possess carboxylate moieties that are ideal for further chemical functionalization and polyelectrolyte adsorption. SEM images of conical pores and the etching procedure of pores were presented in Figure 5B. (Apel, 2001; Siwy et al., 2003). PC-based membrane with cylindrical nanopores offers hydrophilicity and lower resistance to organic solvents, whereas PI exhibits thermal stability (Ma et al., 2020). Because of high chemical stability, hydrophobic materials such as PP can withstand alkaline solutions, strong oxidizers, and inorganic acid filtration.
Other potential membrane materials explored to produce heterogeneous membranes through track-etched nanopore designing technology are mica, graphene, and graphene oxide (Nehra et al., 2017; Zhang et al., 2018). Because of the hydrophobic nature of track-etched membrane, prior surface functionalization is essential, not just to introduce novel features but also to produce highly uniform nanopores or nanochannels. Recently, atomic layer deposition (ALD) is employed to modify track-etched PC membrane surfaces using Al₂O₃-, SiO₂-, and TiO₂-derived nanomaterials (Spende et al., 2015; Ulrich et al., 2021). For instance, Balme group demonstrated the formation of biological/artificial nanopores by using the concept of high-energy particle tracks and chemical etching (Cabello-Aguilar et al., 2013). Deposition of Al₂O₃/ZnO nanocomposite layer can reduce the diameter from 75 to sub-10 nm for α-hemolysin and Gramicidin A insertion (Figure 5C) (Abou et al., 2013; Cabello-Aguilar et al., 2013). Typically, the deposition occurs at lower temperature (<100 °C) in order to maintain the membrane structure, which further limits the material choice and their phases.

Layer-by-layer method
The layer-by-layer self-assembly (LBL assembly) process involves forming multiple layers in the membrane device. It is possible to control the internal thickness and composition of layered membranes with the help of various interlayer forces, including hydrogen bonding, electrostatic attraction, and chemical bonding (Rawtani and Ageawal, 2014; Gu et al., 2013). The concept of LBL assembly has been widely used in layered film assembly by the sequential interaction of absorption between oppositely charged species. In addition, the utilization of nanomaterials on multilayer films enhances the stability and durability of the membrane (Rawtani and Agrawal, 2014; Jia et al., 2020). For example, Jia et al. constructed an anhydrous proton exchange membrane (PEM) by the sequential deposition of positively charged polyurethane (PU), negatively charged GO, and poly(diallyldimethylammonium chloride) (PDDA) with positive charge on a glass substrate with negative charge (Jia et al., 2020). The hybrid membrane was fabricated by repeating the LBL assembly process 200 times. (PU/GO/PDDA/GO)₂₀₀ exhibited high and stable proton conductivity of 1.83 × 10⁻² S/cm at 150 °C in 60% phosphoric acid. Thus, the component and mechanical stability of the hybrid membrane were obtained to be 1.47 × 10⁻¹ S/cm at 120 °C and 1.83 × 10⁻¹ S/cm at 140 °C, respectively. Similarly, Woo et al. developed a hierarchical composite membrane through LBL self-assembly by
negatively charged silica aerogel (SiA) and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FTCS) on a PVDF phase inversion membrane. And the membrane was interconnected with positively charged poly(diallyldimethylammonium chloride) (PDDA) via electrostatic interaction (Woo et al., 2018). The composite membrane showed increased surface roughness and the property of oleophobicity. A stable water vapor flux of 11.22 L/m²·h was obtained with a salt rejection of almost 100%. In addition to the utilization of GO, molybdenum disulfide (MoS₂), a graphene-like nanomaterial, also showed the superiority for nanofiltration (Wang and Mi, 2017). Zhou et al. developed a ceramic composite membrane composed of poly(diallyldimethylammonium chloride)-modified MoS₂ nanosheets (PDDA@MoS₂ nanosheets) and deposited by poly(sodium 4-styrenesulfonate) (PSS) in a ceramic tube (Zhou et al., 2019). For the separation of dyes from aqueous solution, the ceramic composite membrane rejected 97.2% of 0.2 g/L methyl blue dye solution with a flux rate of 163.2 L·m⁻²·h⁻¹·MPa⁻¹. The flux efficiency was approximately 2.4 times higher than pure PSS/PDDA membrane (flux rate: 68.0 L·m⁻²·h⁻¹·MPa⁻¹) without the modification of MoS₂.

Self-assembly method

Self-assembly is a method of fabricating large-scale aggregates from small components by a spontaneous reaction. During this process, molecules and nanoscale entities may form into structured aggregates, networks, or patterns through various interactive mechanisms, such as surface properties, and electrostatics, through other mediating agents. Coating nanoparticles on membrane surfaces by self-assembly is often used to incorporate nanoparticles into membrane complex. The mechanisms by which self-assembly of molecules occurs include chemical interactions, self-assembly methods (Min et al., 2008), and electrostatic surface forces (Lindgren et al., 2018). With the self-assembly strategy, membranes were fabricated that possessed various properties attributed to the modified nanoparticles (Li et al., 2014; Zhang et al., 2015; Xu et al., 2017a, and Xu et al., 2017b; Koh and Lee, 2021).

Li et al. established self-assembled TiO₂ nanoparticles (3–5 nm) surrounding PES ultra-filtration membrane pores. The wettability enhancement in the pore channel provides higher hydrophilicity of the PES membrane after the modification of TiO₂ nanoparticles. This hybrid PES membrane exhibited better antifouling performance and reusability (FRR: 1st cycle: 83.9%; 2nd cycle: 78.5%) than conventional PES membrane (FRR: 1st cycle: 62.5%; 2nd cycle: 51.5%) (Li et al., 2014). Zhang et al. report an RGO/AgNP hybrid membrane by the self-assembly of AgNPs onto the surface of RGO upon the combination of simultaneous reduction and a thermal evaporation-driven self-assembly process. The obtained hybrid membrane provided antibacterial property inherited by AgNPs and higher hydrophilicity with a decrease in contact angle of a water droplet to approximately 18° compared with bare GO (27°) and RGO (24°) (Zhang et al., 2015). Xu et al. developed an ultrathin GO membrane through single-layer graphene oxide (SLGO) self-assembly. The study found that a slow deposition rate produced narrow hydrophobic nanochannels from oxygen-containing groups between two adjacent SLGO flakes, whereas a fast deposition rate produced a random arrangement. Furthermore, the GO membrane formed by slow deposition possessed 1.8–4-fold higher salt rejection and 2.5–4-fold higher water flux than the GO membrane fabricated by fast deposition (Xu et al., 2017a, and Xu et al., 2017b). Koh et al. utilized the self-assembly of hydrophobic nanoparticles to construct a nano-fiber membrane. The hydrophobic nanoparticles were formed by the graft of a polyvinylidene fluoride (PVDF) and trichloro(1H,1H,2H,2H-perfluorooctyl) silane (F-POSS). The hydrophobic coating membrane exhibited lower water flux (8.7 LMH) and possessed omniphobicity with the contact angle of 149°, which was higher than the membrane without omniphobic modification (~71°). In the application, the rejection rate of ethylene glycol can achieve 100% by this membrane, and the water flux can maintain up to 20 cycles (Koh and Lee, 2021).

Alternatively, electrochemical and vapor deposition techniques were also considered for membrane preparation, mainly in order to introduce inorganic layers in the pores or on the membrane surface. These modifications are useful to change pore surface properties and pore size (Asatekin and Gleason, 2011; Kelkar and Wolden, 2017). Electrochemical deposition is a process in which metals, oxides, or salts are deposited from a solution onto an electrically conducting surface by electrolysis. For the desired layer thickness and the synthesis of homogeneous coating, it is important to optimize multiple parameters such as electrolyte composition, pH of electrolytic, deposition time and temperature, and applied voltage, as well as anode and cathode materials (Arulmani et al., 2018; Gunputh and Le, 2017). Zhao et al. prepare electrocatalytic micro-filtration CuO/carbon membrane by a simple-step dynamic electodeposition method to remove the organic pollutants such as rhodamine B, and its removal efficiency can reach 99.96%. The CuO/carbon membrane shows the higher permeability than carbon membrane (Li et al., 2020a, and...
500 ppm was achieved, relative to pristine PPY membrane (Yang et al., 2020). Alternatively, ultra-filtration is known to significantly lowered down the salt rejection rates by 95% (Yang et al., 2020). The initial chemical vapor deposition (CVD) process translates free radical polymerization into a chemical vapor deposition process. It was employed to functionalize track-etched membranes to tune surface hydrophobicity for separation applications (Asatekin and Gleason, 2011). Alternatively, an electrodeless plating method for the controlled deposition of metallic layers onto the polymeric surface has also been developed (Ma et al., 2020).

**WASTEWATER TREATMENT**

It has been well documented that unmodified membranes can eliminate various pollutants from small ions to macromolecules through adjustments in the pore size or in combination with coagulation or flocculation. The advancements in the fabrication technology and material choice for membrane preparation discussed in the previous sections have allowed conventional membranes to feature favorable hydrophobicity, tunable pore size, effluent-specific modification, and faster water efflux to for the removal of a wide range of pollutants. Further nanomaterial functionalization has endowed huge surface area, photo (catalytic) properties, and enhanced fouling resistance, thus making membranes multifunctional and highly efficient for several toxic effluents. These types of nanomaterials and their applications include removing dye molecules, metal ions, microbes, biomass, or other toxic sulfur-/nitrogen-containing organic molecules as summarized in Table 1.

**Dye molecules**

Wastewater produced from textile dyeing is a huge pollutant and accounts for most dye pollution (Lellis et al., 2019). In some cases, these dyes are never degraded in water bodies and some even generate toxic byproduct as they decompose. Dyes present in a small amount also reduce the transparency (sunlight penetration) and water aeration, directly affecting photosynthesis by lowering dissolved oxygen levels (Pereira and Alves, 2012). Once the dye molecules make their way up in the food chain, they cause bioaccumulation and possess severe toxicity, mutagenicity, and carcinogenicity (Kant, 2012). Dyes not only deteriorate water quality but also seriously affect the aesthetic value. Thus, it is of great importance to remove dye-based industrial effluents.

It is widely reported that nano-filtration is the most explored membrane type separation process for dye wastewater (Li et al., 2019; Moradihamedani, 2021). Membranes in nano-filtration show higher rejection of inorganic or divalent salts, which reduces water permeability (blocked pore size), limiting their practical use (Tavangar et al., 2020). Lately, nano-filtration can conquer these challenges by incorporating nanomaterials. For instance, embedding cerium oxide CeO2 NPs into PES membrane via phase inversion process notably improved the contact angle (65.5° → 48.1°) and water flux (31.8 versus 131.2 L/m²-h), which significantly lowered down the salt rejection rates by ~6-fold (Figure 6A). Increased surface charge and hydrophilicity of the composite membrane resulted in high fluxes (19.1–105.2 L/m²-h) and excellent rejections (~99.36%) of Direct Red 23, Congo Red, and Direct Red 243 (Figure 6A) (Tavangar et al., 2020). In another study, Yang et al. employed ZIF-67 MOFs to prepare polyvinylpyrrole (PPY) membranes for the removal of Congo Red (Figure 6B). As-expected high-performance permeability (12.57 versus 1.62 L h⁻¹ m⁻² bar⁻¹) at 500 ppm was achieved, relative to pristine PPY membrane (Yang et al., 2020). Alternatively, ultra-filtration is a membrane separation technique with 1–100 kDa molecular weight cutoff membrane, which is apparently much higher than dyes, resulting in lower efficiency (Ouni and Dhahbi, 2010). Recently, Heng et al. demonstrated that PSF membrane modified with carbon dots (CDs) and silica (SiO2) contributed to favorable hydrophobicity, porosity, and permeability. As we can see, pore size for all the membranes was observed in the approximate diameter range of 3–6 μm (Figure 6C(a–e)). Depending on the surface charges present on both the membrane surface and the dye particle, the degree of rejection could be varied. The rejected tartrazine dye solutions were ~3.5 times higher than the nonmodified PSF membrane (Figure 6C(f)) (Heng et al., 2021). Because tartrazine is an anionic dye, membranes with negative surface charges exhibit excellent degrees of repulsion (Banerjee and Chattopadhyaya, 2017).

Among membrane technology, micro-filtration process is operational under low pressure to provide high water permeability (Charcosset, 2012). Mainly due to its macro-sized pores (0.1–10 μm), these membranes are rarely applied alone to remove dyes from wastewater. For example, Januário et al. combined a hybrid...
| No. | Membrane | Nanomaterial | Fabrication method | Unique feature | Rejection mechanism | Effluent | References |
|-----|----------|--------------|-------------------|----------------|----------------------|---------|------------|
|     | Dye molecules |                        |                    |                |                      |         |            |
| 1   | PDA/PEI/TiO₂ | Ag NPs        | Deposition method  | High water permeability | Vacuum filtration, Size exclusion, Electrostatic effect | Congo red, Reactive black 5, and Reactive orange 16 (>96%) | (Li et al., 2019) |
| 2   | PES       | CeO₂ NPs      | Phase separation   | Salt permeation, Antifouling | Surface adsorption, Electrostatic separation | Direct Red 23, Congo Red, and Direct Red 243 (>99%) | (Tavangar et al., 2020) |
| 3   | PI/PPY   | ZIF-67 MOF    | Phase inversion    | Flux enhancement, Long-term stability, Porous support | Size exclusion | Rose Bengal, Methyl Blue, and Congo Red (>98%), bromothymol blue (BTB) (80.2%) | (Yang et al., 2020) |
| 4   | PAN      | UIO-66-NH₂ MOF | Phase inversion    | High water flux, Long-term stability | Size exclusion, Electrostatic repulsion | Rhodamine B (92%) | (Aghili et al., 2020) |
| 5   | CS/PVA   | SiO₂          | Electrospinning    | Fouling resistance, High water flux, Increased compaction resistance | Electrospinning, Electrostatic interactions | Direct Red 23 (98%) | (Hosseini et al., 2018) |
| 6   | PANI     | MoSe₂         | In-situ polymerization | Photocatalytic | Photodegradation | Methylene blue (65%) and Methyl orange (94%) | (Mittal et al., 2019) |
| 7   | PAN      | GO, and O-CNTs | Layer-by-layer self-assembly | Low irreversible fouling ratio, Long-term stability, High water flux | Size exclusion | Methyl blue (>99%) | (Kang et al., 2018) |
|     | Metal ions |                        |                    |                |                      |         |            |
| 1   | PVDF     | SnO₂ NPs      | Phase inversion    | Complexations and electrostatic with metal ions | Ion exchange/adsorption, Inner-sphere complexations | Pb²⁺ (93%), Cu²⁺ (92%), Zn²⁺ (82%), Cd²⁺ (70%), and Ni²⁺ (63%) | (Ibrahim et al., 2020) |
| 2   | PS       | g-C₃N₄ NSs    | Phase inversion    | Hydration layer formation, Antifouling | Electrostatic attraction | Pb²⁺ (95%), Cd²⁺ (80%), and As³⁺ (70%) | (Nadig et al., 2021) |
| 3   | PVDF/PVP/NMP | MWCNTs       | Phase inversion    | Enhanced water flux | Sieving mechanism | Pb²⁺ (98%), Hg²⁺ (76%), and Cd²⁺ (72%) | (Chandrashekar Nayak et al., 2020) |
| 4   | PETI     | POSS NPs      | Phase inversion    | Enhanced water flux, Higher rejection rate | Adsorption | Pb²⁺ (85%), Cu²⁺ (86%) | (Bandehali et al., 2019) |
| 5   | SiO₂/TiO₂ NFM | MoS₂         | Electrospinning    | Excellent adsorption capacity, Reusability | Affinity of Pb²⁺ to the sulfur atoms from MoS₂, Surface adsorption | Pb²⁺ (96%) | (Mercante et al., 2020) |

(Continued on next page)
| No. | Membrane | Nanomaterial | Fabrication method | Unique feature | Rejection mechanism | Effluent | References |
|-----|----------|--------------|-------------------|----------------|-------------------|---------|------------|
| 6   | PES      | Fe$_2$O$_3$ NPs | Liquid-induced phase separation | High permeability and separation efficiency Multifunctional | Selection adsorption Pb$^{2+}$, Cd$^{2+}$, and Ag$^+$ (>90%) | (Zhang et al., 2020a, 2020b) |
| 7   | HECE     | CuO NPs      | Slurry casting method | Reduced pore size Good stability | Pressure ultra-filtration Active site adsorption Electrostatic repulsion Cr$^{4+}$ (91.44%) Pd$^{2+}$ (97.14%) | (Roy et al., 2018) |
| 8   | PA       | SGO NPs      | Interfacial polymerization | High hydrophilicity, water flux, salt rejection, and antifouling properties | Size exclusion Electrostatic repulsion MgSO$_4$ (>95%) Na$_2$SO$_4$ (>95%) NaCl (>75%) | (Kang et al., 2019) |
| 9   | PS       | ZIF-8        | Interfacial polymerization | In-situ growing process High water flux and salt rejection Antifouling | Size exclusion MgSO$_4$ (>85%) Na$_2$SO$_4$ (>95%) | (Yang et al., 2019a, 2019b) |

Organic compounds

| No. | Membrane | Nanomaterial | Fabrication method | Unique feature | Rejection mechanism | Effluent | References |
|-----|----------|--------------|-------------------|----------------|-------------------|---------|------------|
| 1   | PA       | Aromatic NPs | Interfacial polymerization | High stability Antifouling | Size exclusion | Perfluorohexanoic acid, salicylic acid, ibuprofen, and bisphenol A (>99%) | (Ji et al., 2021) |
| 2   | Al-HF    | PAN/g-C$_3$N$_4$ NFs | Electrospinning | Photocatalytic degradation | Photodegradation | Oilfield produced water (97%) | (Alias et al., 2019) |
| 3   | TP-AI    | Fe$_3$O$_4$ NPs | In situ chemical deposition | Catalytic degradation | Catalytic Fenton reaction | Diclofenac (65%) | (Plakas et al., 2019) |
| 4   | PA       | MOFs (ZIF-93 and HKUST-1) | Interfacial polymerization | MOF porosity Hydrophilicity Surface roughness | Size exclusion | Diclofenac and Naproxen (98%) | (Paseta et al., 2019) |
| 5   | PS       | Fe-TiO$_2$ NPs | Phase inversion | Self-cleaning Photoresponsivity Enhanced mechanical capacity | Photodegradation | Bisphenol A (>90%) | (Wang et al., 2017) |
| 6   | NCE      | Ag NPs       | Gravimetric filtration | In situ formation High water permeability Catalytic activity | Vacuum filtration Catalytic reduction | 4-nitrophenol (>95%) | (Das et al., 2021) |
| 7   | PDES     | MWCNTs       | Solution casting method | Improved water permeability Practical for food recovery | Sorption-diffusion via pervaporation | Linalool (85.80%), MetSa (90.84%), and β-Ionone (83.40%) | (Li et al., 2021) |
| 8   | PAN      | Fe-based NPs | Phase inversion | Significantly enhanced antifouling features Antibiotic separation and degradation with high performance | Fenton reaction | Amoxicillin (92.3%) | (Karimnezhad et al., 2020) |

(Continued on next page)
| No. | Membrane | Nanomaterial | Fabrication method | Unique feature | Rejection mechanism | Effluent References |
|-----|----------|--------------|-------------------|---------------|-------------------|-------------------|
| 1   | Microbes | PS TiO<sub>2</sub> NPs | Phase inversion | Antifouling<br>Enhanced flux<br>Removal ratio | Surface adsorption | E. coli<br>(Azhar et al., 2021) |
| 2   | PES      | NCDs         | Phase inversion | High water flux<br>Desalination<br>Broad-spectrum antimicrobial | Sharp edges<br>Hydroxyl radicals | E. coli and S. aureus<br>(Kouliivand et al., 2020) |
| 3   | CS-CE    | Ag NPs       | Coagulation      | In situ synthesis of Ag NPs | Ag<sup>+</sup> release from the Ag NPs | E. coli (96.7%) and S. aureus (91.8%)<br>(Chook et al., 2017) |
| 4   | PA       | Ag-based MOF | Interfacial polymerization | Antimicrobial<br>Antibiofilm | Ag<sup>+</sup> release from the MOFs | E. coli (96%) and S. aureus (90%)<br>(Zirehpour et al., 2017) |
| 5   | PS       | p-AP-GO      | Interfacial polymerization | High water flux<br>Salt rejection<br>Improved hydrophilicity | Sharp edges<br>Phenolic functional groups on mGO | E. coli (96.8%) and S. aureus (95.3%)<br>(Zhang et al., 2020a, 2020b) |
| 6   | PES      | Ag@ZnO core-shell NPs | Interfacial polymerization | Long-term activity<br>Antifouling<br>High flux recovery rate | Ag<sup>+</sup> release | E. coli (>99.9%) and S. aureus (>99.9%)<br>(Huang et al., 2020) |

AgNPs: silver nanoparticles; Al: aluminum; CeO<sub>2</sub>: cerium dioxide; CS: Chitosan; CuO: copper oxide; Fe<sub>3</sub>O<sub>4</sub>: iron oxide; g-C<sub>3</sub>N<sub>4</sub>: graphitic carbon nitride; GO: graphene oxide; HECE: hydroxyethyl cellulose; HF: hollow fiber; MOF: metal organic framework; MoS<sub>2</sub>: molybdenum disulfide; MoSe<sub>2</sub>: molybdenum selenide; MWCNTs: multiwall carbon nanotube; NCDs: nitrogen-doped Carbon Dots; NCE: nanocellulose; NFM: nanofibrous membranes; NMP: 1-methyl-2-pyrrolidone; NSs: nanosheets; O-CNTs: oxidized carbon nanotube; NFs: nanofibers; PA: polyamide; PAN: polyaniline; p-AP: p-aminophenol; PDA: polydopamin; PDES: polydimethylsiloxane; PEI: polyethylenimine; PES: polyether sulfone; PEI: polyetherimide; PI: polyimide; POSS: polyhedral oligomeric silsesquioxane; PPY: polypyrrole; PVA: poly(vinyl alcohol); PVDF: polyvinylidene fluoride; PS: polysulfone; PVP: polyvinylpyrrolidone; PVS: polyphenylsulfone; SGO NPs: sulfonated graphene oxide nanoparticles; SiO<sub>2</sub>: silicon dioxide; SnO<sub>2</sub>: tin oxide; TiO<sub>2</sub>: titanium oxide; UiO-66-NH<sub>2</sub>: NH<sub>2</sub>-functionalized zirconium carboxylate MOF; ZIF: zinc imidazole framework; ZrO<sub>2</sub>: zirconia oxide.
coagulation/flocculation and a micro-filtration process to effectively remove solophenyl blue from waste-water (Figure 6D). Interestingly, potato starch acts as a nontoxic coagulant and can form denser flakes with the dye, thereby reducing the dye flow and inducing the dye’s protonation. Furthermore, incorporation of TiO2 NPs in the membrane significantly reduced fouling and boosted the flow recovery rate (1.06%–36.35%), which eventually removed ~100% of the solophenyl blue (Januário et al., 2021).

**Metal ions**

Potential metal pollutants such as cadmium, mercury, chromium, lead, etc., pose a serious threat on aquatic system and human health. Accumulation of these metals in human beings can actively contribute in physical and neurological disorders including Parkinson disease, multiple sclerosis, and Alzheimer...
disease (Sonone et al., 2020). Shockingly, 8% of the world’s population (the United States, Germany, and Russia) consume about 75% of the world’s most widely used metals. To date, adsorption (Kyzas et al., 2019), chemical precipitation (Zhang et al., 2020a, and Zhang et al., 2020b), ion exchange (Bashir et al., 2019), and membrane-based processes (Kavaiya and Raval, 2021; Lam et al., 2018; Yang et al., 2021) have been employed for the removal of these metals. Among all, membrane technology has maximum heavy metal removal efficiency; however, selective permeability, low water flux, hydrophobicity, and biofouling have limited their application in wastewater treatment. A series of efforts have been made to achieve maximum recovery of these metals from industrial effluents by modifying the conventional membranes with nanomaterials to achieve desirable porosity, tensile strength, hydrophilicity, and fouling resistance. For instance, MWCNTs-incorporated polyphenylsulfone (PPSU) ultra-filtration membrane was fabricated via phase inversion technique for the removal of heavy metals (Pb^{2+}, Hg^{2+}, and Cd^{2+}) from aqueous solution (Figure 7A). According to the contact angles corresponding to the loading of MWCNTs, small contact angles mean low interfacial energy and high hydrophilicity of PPSU membranes (Figure 7B) (Chandrashekhar Nayak et al., 2020). The optimal number of nanotubes (0.3 wt%) in a polymer matrix offered greater permeability due to altered pore size and significant improvement in water flux, from 41.69 L/m² h to >185 L/m² h, which led to the enhanced metal recovery. Hasan et al. also showed that the water flux in SnO2 NPs-decorated PVDF ion exchange membranes was improved by 10-fold, compared with the pristine membrane (Figure 7B) (Ibrahim et al., 2020). Interestingly, the point of zero charges
flaws in the phase interface. As a result, several investigations have demonstrated that the desalination capacity of nanocomposite membranes is dropped due to nanoparticle aggregation and the creation of nonselective interfacial polymerization process to boost its membrane practicality (Kang et al., 2019). Because of the addition of 1.86 mM H2SO4 to manufacture sulfonated graphene oxide (SGO) and incorporated SGO into NF membranes using an aqueous medium and thus the membranes act as anion/cation exchanger for efficient removal of heavy metal ions.

Another study demonstrated that graphitic carbon nitride nanosheets (g-C3N4) embedded into the PSF membranes via nonsolvent-induced phase inversion significantly improved the hydrophilicity of the membrane surface, water uptake was increased to 255%, and contact angle was reduced to ~54°, compared with the pristine membrane (74.5°) (Figure 7C) (Nadig et al., 2021). As-prepared thin-film composite membrane showed much higher rejections for Pb2+ (>95%), Cd2+ (>80%), and As3+ (>70%), relative to those of PSF membranes, mainly due to obvious increase in hydrophilicity and the formation of hydration layer on the membrane induced by (–NH2) amide rich hydrophilic of g-C3N4 surface. Further, antifouling properties of g-C3N4/PSF membrane were also enhanced by the g-C3N4, which in turn prevented the interactions between membrane surface and foulant, i.e., bovine serum albumin (BSA). Along with improvements in wettability and antifouling properties, curcumin-functionalized boehmite NPs achieved maximum efficiencies (>98%) for the removal of metals, including Fe2+, Cu2+, Pb2+, Mn2+, Zn2+, and Ni2+, which were <16% for unmodified PES membranes (Moradi et al., 2020).

Except for efficiently decreasing heavy metal pollutants, removing other less hazardous metals and mineral salts is equally important. It involves a variety of practical applications, such as seawater desalination, dairy demineralization, and dialysis separation in purified peptides or drug-binding studies (Kidambi et al., 2017; Salehi, 2014; Zhao et al., 2020). Reverse osmosis (RO), forward osmosis (FO), nano-filtration (NF) are three membrane techniques widely employed for the aforementioned treatment (Werber et al., 2016). Although membrane separation with RO is one of the most effective methods for desalination treatment, energy consumption remains a major drawback. More so than RO, FO does not require high pressure for separation, allowing for lower energy consumption and fouling propensity. However, the draw solution recovery step in FO still necessitates significant energy consumption and a lower amount of freshwater per unit of water treated in FO compared with RO (Mazlan et al., 2016). Nano-filtration is the most important approach for demineralization treatment and antifouling (Eläikkiä et al., 2021). Kang et al. modified GO with sulfonic acid to manufacture sulfonated graphene oxide (SGO) and incorporated SGO into NF membranes using an interfacial polymerization process to boost its membrane practicality (Kang et al., 2019). Because of the amount of oxygen functional groups, the ideal SGO doping at 0.3% can successfully increase wettability, negative charge, and surface roughness and lower the thickness of the polyamide layer. Furthermore, the modified membrane outperformed the pristine membrane in terms of application potential, with a water flux of 11.86 L m−2 h−1 (an increase of 87.3%) and a lower fouling propensity than the pristine membrane, while preserving its desalination performance (Na2SO4> 96%). However, the desalination of directly generated composite membranes is dropped due to nanoparticle aggregation and the creation of nonselective flaws in the phase interface. As a result, several investigations have demonstrated that in situ synthesis can minimize the major issues associated with nanocomposite membranes, such as potential agglomeration and interfacial defects (Ang et al., 2019; Zhai et al., 2019). Yang et al. reported in situ growth of zinc imidazole framework (ZIF) nanocrystals in large nanopores of about 4.3–8.0 Å in size formed during interfacial polymerization (Yang et al., 2019b). Not only do these novel membranes have 3–4 times the water flow of original membranes but they also have comparable salt rejection and antifouling resistance. They also compared directly generated (TFN-CM) and in situ grown (TFN-ZIF-8) ZIF composite membranes. TFN-CM had a larger water flow (about 5–10% increase) due to the creation of interfacial defects, but a significantly poorer desalination capacity (roughly 60% drop), highlighting the necessity of the in situ synthesis.

Organic compounds

The demand for nitrogen- or sulfur-containing organic compounds in chemical industries, pesticide factories, pharmaceutical sectors, and personal care products increases enormously every year (Zambianchi et al., 2017). Inadequate treatment of such wastes can be life-threatening, even at low concentrations (Fonseca Couto et al., 2018). For instance, disulfoton, an organophosphate acetylcholinesterase inhibitor and used as a pesticide for various vegetables, is lethal to humans at ≥ 5 mg kg−1 (Bingham et al., 2001). Similarly, the overdose of diphenhydramine, an allergy medication, can lead to severe dizziness, coma, and even death in some cases (Nishino et al., 2018). Thus, it is imperative to eliminate these harmful organic pollutants. Conventional wastewater treatment strategies employed adsorption, bio-oxidation, coagulation, and sedimentation to eradicate organic substances, and the efficiency is unsatisfactory. Both micro-filtration and ultra-filtration methodologies employed to remove the organic effluent are no
longer effective due to larger pore size and molecular weight cutoff (Petrie et al., 2015). On the contrary, nano-membrane separation processes are low cost, consume less energy, and possess excellent permeate flux, thus eliminating the risk of increasing poisonous compounds (Khanzada et al., 2020). The removal efficiency of bare membranes toward organic molecules with high solubility and small molecular weight is extremely poor. However, the introduction of nanomaterials into the membrane has widened the effluent domain and attained impressive removal rate while maintaining the original high flux. For example, Plakas et al. reported in situ grown iron oxide (Fe₃O₄ NPs) into tubular porous alumina (α-Al₂O₃) membrane for oxidation-induced elimination of pharmaceutical diclofenac (Plakas et al., 2019). Other than improvements in hydrophilicity and water flux, as explained in earlier sections, this report demonstrated a catalytic feature of Fe₃O₄ NPs/α-Al₂O₃ membrane. The Fenton-like reaction assisted diclofenac degradation (∼65%, pH = 3) by transforming the hydrogen peroxide into highly reactive hydroxyl free radicals (Figure 8A). In another report, bisphenol A was degraded by Fe-TiO₂/PSF membranes upon visible-light-irradiation-induced generation of $\cdot$O₂⁻ and $\cdot$OH radicals (Figure 8B) (Wang et al., 2017). Moreover, photoactive TiO₂ NPs greatly improved the self-cleaning ability of the ultra-filtration membranes due to their intrinsic antifouling properties.

Despite high energy consumption and low water flux under high pressure, nano-filtration and reverse osmosis are widely used to treat organic molecules in wastewater (Fonseca Couto et al., 2018). Tellez’s group fabricated polyamide/metal-organic framework (MOF) bilayered composite nano-filtration membranes through interfacial polymerization for the removal of pharmaceutical grade chemicals (diclofenac, naproxen, paracetamol, etc.). Parameters including polyamide layer thickness, MOF porosity, hydrophilicity, and surface roughness contributed to the increment in water flux from 6.8 to 33.1 L m⁻² h⁻¹ bar⁻¹, without sacrificing rejection efficiency (>98%) (Figure 8C) (Paseta et al., 2019). Moreover, Ji et al. reported the self-assembled aromatic nanoparticles controlled interfacial polymerization method to prepare state-of-the-art polyamide reverse osmosis membranes to efficiently remove organic micro pollutants (Ji et al., 2021). As-prepared asymmetric membranes (loose and crumpled front surface and smooth rear surface) exhibited

![Image](https://i.imgur.com/3Q5Q5Q5.png)

**Figure 8. Removal of organic compounds by nanomaterial-functionalized membranes**

(A) Illustration of in situ grown Fe₃O₄ NPs-modified tubular porous α-Al₂O₃-membrane-based pH sensitive elimination of pharmaceutical diclofenac through Fenton-like reaction. Reproduced with permission from Plakas et al. (2019), Copyright 2019, Elsevier.

(B) Photocatalytic Fe-doped TiO₂/PSF composite UF membranes for the removal of bisphenol A and their possible energy band diagram and reaction mechanisms. Reproduced with permission from Wang et al. (2017), Copyright 2017, Elsevier.

(C)Comparison in water permeability, rejection efficiency (diclofenac, naproxen, paracetamol, etc.), and surface morphologies of thin-film composite (TFC, PA), thin-film nanocomposite (TFN, MOFs), and PA/MOFs bilayer thin-film composite nano-filtration membranes (BTFN). Reproduced with permission from Paseta et al. (2019), Copyright 2019, Elsevier.
ultra-high water flux $\sim 67.8 \text{ L m}^{-2} \text{ h}^{-1}$ and satisfactory rejection ($>99.4\%$) of perfluorohexanoic acid, salicylic acid, ibuprofen, and bisphenol A. Facile tunability of membrane texture provided enhanced separation, chlorine resistance, and desalination ($\text{NaCl} > 98.3\%$) performances, with a great potential for a variety of applications. In recent years, it has become clear that the deadly impact of pharmaceutical effluent on the environment, particularly the widespread overuse of antibiotics, would have unforeseen repercussions (Le et al., 2018; Wang et al., 2019b.b). As a result, several researchers have presented a strategy against antibiotic waste via the composite membrane (Shakak et al., 2020; Yang et al., 2019a, 2019b). Karimnezhad et al. suggested incorporating iron-based nanoparticles into the polyacrylonitrile (PAN) framework, effectively coupling the Fenton process with nanofiltration membranes to improve amoxicillin (AMX) rejection and antifouling properties (Karimnezhad et al., 2020). The composite membrane outperformed the raw PAN membrane in AMX removal (92.3%, approximately 20% increase) and permeate flux (23.2 L m$^{-2}$ h$^{-1}$, about a 3.8-fold increase). Furthermore, the antifouling properties of the composite membranes were significantly improved by separating and degrading into lighter products in the presence of the Fenton reaction (FRR = 97.3%, a 30% growth), increasing the practical utility and having the potential to remove other antibiotics.

Microbes

Although aforementioned pollutants undoubtedly possess severe toxicity, they rarely contribute to membrane biofouling. The overgrowth of bacteria mainly causes biofouling due to inhabitable environment in the wastewater. The formation of biofilms on the polymeric surface significantly decreases membrane lifetime, durability, and performance by blocking the surface’s active site and pores (Huang et al., 2020) (Aryanti et al., 2017). In addition, after a while, bioaccumulation initiates the release of bacteria, which is a serious concern for aquatic animals or humans (Uddin et al., 2020). In the past, membranes were pretreated with chlorinated for efficient disinfection; however, chlorine and their derivatives often cause membrane degradation and produce harmful byproducts (Yu et al., 2014). Recently, many reports have demonstrated that incorporation of metal/metal oxide/metal sulfide, carbon-based nanomaterials into the membrane is an effective strategy to circumvent the issues related to biofouling of membrane, thereby restoring the enhanced separation performance in terms of rejection and stability (Azhar et al., 2021; Liu et al., 2017; Nain et al., 2020b; Rajakumaran et al., 2020; Zhao et al., 2021). Ag NPs are one of the widely explored antibacterial agents, and the formation of aggregates and toxicity of the released metal ions have limited the application. Thus, Park et al. proposed a novel stagey of immobilizing AgNP@SiO2 particles onto polyamide membranes by forming multiple Ag-S chemical bonds between the particles and the membrane surface, which prevented the leaching of Ag$^+$ ions (Figure 9A (a)) (Park et al., 2016). The SiO2 NPs (~400 nm) decorated with AgNPs (~30 nm) indicated broad-spectrum antibacterial activity against commonly found waterborne pathogens such as E. coli (92.7 ± 1.8%), P. aeruginosa (99.5 ± 0.3%), and S. aureus (73.3 ± 5.5%), thereby protecting the fouling of membrane without compromising rejection efficiency (Figure 9A (b)). In another report, tannic acid-stabilized TiO2 NPs (~150 nm) were employed for photorereduction of bacteria along with salt rejection (Figure 9B) (Karthik et al., 2017; Li et al., 2020a, and Li et al., 2020b). The strong interaction of nanomaterials with membrane is crucial for membrane stability and determines other physicochemical properties. Tannic acid with enediol groups displayed strong affinity toward trimesoyl chloride to form nano-filtration membrane (Zhang et al., 2013). Preparation of such nanocomposite membrane displayed substantial bacteriostatic activity (from 22.5% to 99.2%), while maintaining the outstanding pure water flux (7.5–28.8 L m$^{-2}$ h$^{-1}$) and salt rejection ($\text{NaCl/Na}_2\text{SO}_4; 57.9\%/94.6\%$), when coupled with UV irradiation. Our group also recently demonstrated modification of carbon-fiber-based membrane such as fabrics using ultra-small copper nanoclusters for antibacterial applications (Figure 9C) (Nain et al., 2020b). As-prepared nanoclusters exhibited hydroperoxyl and ascorbyl free radicals to induce the elevated oxidation-stress-assisted disintegration broad spectrum of bacteria. Not just metal but carbon-based nanomaterials including carbon dots, carbonized nanogels, g-C3N4, etc., with high hydrophilicity, chemical stability, antimicrobial activity, and nontoxicity have gained immense attention in recent years (Wu et al., 2020a, and Wu et al., 2020b). For example, Kouilvand et al. modified polyethersulfone membranes with nitrogen-doped carbon dots prepared from ammonium citrate, which provided higher water flux (~3-fold) and antifouling performance (~2-fold) in terms of flux recovery ratio when compared with bare PES membranes or the ones modified with un-doped carbon dots (Figure 9D) (Kouilvand et al., 2020).

SUSTAINABILITY AND COST VIABILITY OF MEMBRANES

Despite membrane technology’s overwhelming features and efficiency for removing various pollutants from water bodies, the impact on the environment and resource depletion due to inevitable pretreatments
and recovery of employed membranes are still controversial (Baten and Stummeyer, 2013; Miller et al., 2015). It is suggested that with optimal equipment design, operation, and maintenance, underlining issues can be alleviated; however, it is desired to further improve and strengthen the sustainability of membrane technology (Goh et al., 2016). In this regard, the paradigm shift made by incorporating state-of-the-art nanomaterials have led to the reduced membrane materials, reagents, and energy usage, which cut down the sources of environmental issues (Goh et al., 2016). Transport of water or salts across the membrane primarily depends on the physiochemical properties and structure (nano- to microscale) of the membranes; thus, it is anticipated to counter the limitations of existing materials and processes in the fabrication to optimize the membrane performance.

The unexpected quantum leaps confirm that these versatile nanomaterials and composites could open up an alternative route for sustainable development. The main reason for the stakeholders to be optimistic is the ability of these next-generation nanomaterial modified membranes to make a huge difference by introducing affordable, modern, and environmentally profound remedies for water scarcity (Bhadra and Mitra., 2014). Economic viability is a crucial parameter for realizing the potential of nanomaterials membranes (Bjorge et al., 2009). For example, the nanofiber membrane \( \frac{V}{m^2} \) is less expensive than commercial membranes \( \frac{50V}{m^2} \) (Ledakowicz et al., 1998). The manufacturing cost of nanofiber membranes is expected to be \( \frac{5V}{m^2} \), with the nonwoven support accounting for 75% of the total cost. Therefore, the adoption of less expensive supports can lower the overall cost. The cost of raw materials for the development of nanomaterials membranes, on the other hand, might be quite variable. According to reports, clay-based nanomaterials membranes improve the pollutants removal capacity from wastewater in a long-term manner; however, there is a significant price

![Figure 9. Removal of microbes by nanomaterial-functionalized membranes](image)

(A) (a) Graphical representation of the antibacterial AgNP@SiO₂-loaded PA thin-film composite (b) reverse osmosis (TFC RO) membrane. Bacterial viability of *E. coli*, *P. aeruginosa*, and *S. aureus* on the pristine TFC (black), TFC-SH (red), and TFC-AgNP@SiO₂ (green) membranes. Reproduced with permission from Park et al. (2016), Elsevier. (B) Representative colony formation assays of *E. coli* on luria bertani agar after contacting with (i and iii) thin-film composite (TFC, bare membrane) membrane without and with UV illumination and (ii and iv) TFN membrane without and with UV illumination. Reproduced with permission from Li et al. (2020a, 2020b), Copyright 2020, Elsevier. (C) Uniformly coated copper nanoclusters onto carbon-based fibers generate cytotoxic free radicals to destroy bacteria. Reproduced with permission from Nain et al. (2020a, 2020b), Copyright 2020, Elsevier. (D) Schematic representation of facile preparation of antifouling and antibacterial N-doped carbon dot immobilized PES membrane and their inhibitory effects against *E. coli* and *S. aureus*. Reproduced with permission from Koulivand et al. (2020), Copyright 2020, Elsevier.

![Figure 9. Removal of microbes by nanomaterial-functionalized membranes](image)
difference between clays and some polymers. Hence, for the future development of NMs-wastewater treatment systems, further in-depth cost-benefit assessments are required.

CONCLUSIONS AND FUTURE PROSPECTS
Membrane technology has been gradually advancing in the wastewater treatment industry, mainly due to its inexpensive capital cost, miniature equipment set-up, low power consumption, and high pollutant removal efficiency. Nanomaterial-functionalized membranes became an ideal solution to circumvent the limitation of conventional membranes. In order to achieve higher effluent rejections, membranes with hydrophilic nature, high water flux, fouling resistance, and surface roughness are crucial. Efficiency of membrane filtration processes largely depends on the surface modification strategy. Typically, nanomaterials can be incorporated either in the bulk/support layer and/or surface/active layer of the membrane. Various types of methods (e.g., electrospinning, interfacial polymerization, phase inversion, etching, layer by layer, and self-assembly method) have been used to fabricate nanomaterial modified membranes with improved properties. Introduction of nanomaterials in the polymeric matrix featured (photo) catalytic degradation, antifouling properties, and desired surface textures. Functional groups on the NPs surface allow selective removal of heavy metals or organic effluents. Moreover, additional feature including antimicrobial action, desalination, dairy demineralization, and dialysis separation etc. can also be obtained from membrane with proper modification with nanomaterials.

Despite the impressive progress, there are still many challenges that need to be addressed. First, it is still difficult to achieve uniform distribution of nanomaterial within membranes on a large scale. By choosing one or more suitable combinations of functionalization processes, preparation of large scales of high-quality and robust membranes shall be possible. Secondly, there is still great room for reducing the hydrophobicity of the membrane surface, especially for highly toxic aqueous dispersants. Hydrophilicity can be greatly enhanced by immobilizing with zwitterions or forming a hydration layer by exposing –NH₂, COO⁻, etc. groups on the membrane surface. Third, it is desirable to develop a re-usable membrane that can target different kinds of effluent and survive for a very long time, avoiding replacement cost. Some reports showed that modification of membranes with Ag NPs, TiO₂ NPs, etc. with intrinsic biocidal activity can promote antifouling performance of membranes, which undoubtedly improved the sustainability and antimicrobial resistance, but toxicity of released metal ions toward aquatic animals is a serious concern. Fourth, detection and subsequent elimination of waterborne pathogens, including bacteria and virus, are also a crucial part of wastewater purification. Till date, there are few papers on membrane technologies that target microbial eradication. Lastly, there is a possibility to integrate membrane technology with other conventional processes such as precipitation and coagulation to simultaneously employ more than one driving force for the removal of industrial effluents. For example, dissolved toxic products can be precipitated, whereas heavy metals or other effluents can be entrapped in the membrane. With the continuous efforts of scientists in nanotechnology and material science, we can foresee more progress in the future to achieve higher selectivity and efficiency for wastewater treatment. Thus, our strong belief that nanomaterial-modified membranes can become interesting modalities for the removal of various toxic effluents contributes significantly to the ongoing progress of clean water initiatives. Although this review mainly focusses on the role of nanomaterials in membranes technology for efficient removal of pollutants, it is important to note that progress of developing novel nanomaterials can also be beneficial for formulating membrane-based sensing and biosystems.

LIMITATION OF THE STUDY
A comparison of the limitations of different nanomaterial functionalized membranes can be further discussed.

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DECLARATION OF INTERESTS

The authors declare no competing interests.
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