Recent Developments in the Rational Fabrication of Thin Film Nanocomposite Membranes for Water Purification and Desalination

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ABSTRACT: Efforts have been rendered by researchers to address water purification and desalination challenges through membrane separation processes. However, the trade-off phenomenon in permeability and selectivity constrained the membranes' usage. Recent advances made in fabricating membranes, especially thin film nanocomposite (TFN) membranes using functionalized nano-fillers, have high performance in water purification and desalination. In this review, state-of-the-art thin film composite (TFC) membranes in water purification and desalination along with their drawbacks are discussed. The urgent demands as an alternative of TFC membranes are highlighted for high-performance membranes. Then, the fabrication and development of high permeability and selectivity of TFN membranes are discussed. Thin film nanocomposite membranes manufactured using rational nano-fillers are systematically summarized. Finally, the applications of TFN membranes in water purification and desalination are reported.

INTRODUCTION

Water scarcity and aquatic pollution are the most critical issues for modern societies. According to the World Health Organization (WHO), 1.1 billion people do not have a proper access to better quality drinking water. A 30% rise in fresh water demand is possible by 2030 if the current projection is well matched with population growth. Approximately 80% of wastewater without prior treatment is discharged into water resources such as groundwater and seawater. Thus, these water sources are being polluted and are deteriorating in parallel. To overcome these issues, water resources should be protected and seawater desalination or water purification must be continuously performed. Membrane separation processes have been adopted for water purification and desalination. A smaller amount of energy is consumed during membrane separation processes compared with thermal processes.

Thin film composite membranes are used in nanofiltration and reverse osmosis for water purification and desalination. The fabrication methodology and performance of TFC membranes in water desalination and purification have been reviewed. However, the separation performance of TFC membranes is limited due to the trade-off phenomenon in their permeability and selectivity. To address this issue, effort have been expended to design and manufacture thin film nanocomposite (TFN) membranes by integrating nano-fillers into their selective layers. The integration of the nano-fillers into the selective layer of the membranes provides extra pathways for high mass transfer via intrinsic nanosized pores of the nano-fillers and interface voids between polyamide (PA) chains and fillers, whereas the original molecular sieving capacity of the membranes is maintained.

Thus, high water flux TFN membranes without alteration in their selectivities are produced. The multifunctional polyelectrolyte nanoparticles (PNPs) have also been explored in constructing TFN membranes through interfacial polymerization. The progress made in different types of nano-filler-based hybrid or composite membranes has been addressed in several reviews on water treatment. However, it is noticed that recent developments in the fabrication of TFN membranes using nano-fillers and PNPs for water treatment applications have not been reviewed in a systematic way. Therefore, this review summarizes the recent progresses made in the fabrication of TFN membranes for water purification and desalination. Challenges encountered during the manufacturing of TFN membranes using the rationalized nano-fillers and improvement in separation performance are summarized, which would motivate more exciting developments in the future.

FABRICATION OF THIN FILM NANOCOMPOSITE MEMBRANES

Thin film nanocomposite membranes have been fabricated using the rationalized nano-fillers and multifunctional PNPs through interfacial polymerization. The recent trends in the development of the rational fabrication of TFN membranes...
Figure 1. (a) Recent trends in the development of the rational fabrication of TFN membranes (2011 to 2019), with data obtained from Scopus. (b) Schematic presentation for manufacturing TFN membranes through interfacial polymerization in the presence of the functionalized nanofillers. (c) CNTs-TFN membrane. (d) GO-TFN membrane. (e) CQDs-TFN membrane. (f) MOFs-TFN membrane. (g) PNPs-TFN membrane.

Figure 2. Fabrication of the PEI/PDA-MWCNTs TFN membrane from PDA-coated MWCNTs, PEI, and TMC via interfacial polymerization. (Reproduced with permission from ref 17. Copyright 2015, American Chemical Society.)
from 2011 to 2019 and the overall objectives of the review are presented in Figure 1. It can be seen that the number of publications on the fabrication of TFN membranes using the different nanofillers are increasing gradually.

**Carbon Nanotube-Derived TFN Membranes.** Carbon nanotubes (CNTs) have been applied in the fabrication of TFN membranes via interfacial polymerization (IP).\textsuperscript{12–15} The water permeability and the separation performance of the membranes were improved after incorporating the optimum amount of CNTs into their selective layers. High-water permeability was achieved due to the presence of hydrophobic channels in CNTs.\textsuperscript{12} The functionalized MWCNTs were utilized in fabricating TFN membranes. The surface morphology, thickness, and hydrophilicity of the membranes were altered after incorporating the functionalized MWCNTs. The nodular surface morphologies were observed for the membranes containing the functionalized MWCNTs. The membrane comprising hydroxylated MWCNTs (MWCNTs-OH) had the highest water flux.\textsuperscript{14} However, the rejection capabilities of CNT-loaded TFN membranes were reduced for a high amount of CNTs into the selective layers due to poor dispersion in the aqueous phase and defect creation through the agglomeration of CNTs.\textsuperscript{12} To overcome these difficulties, multifunctional polymer chains were grafted onto CNTs and then used as nanofillers in the fabrication of TFN membranes.\textsuperscript{15,16} Shen et al. performed a microemulsion polymerization of methyl methacrylate in the presence of acid-modified MWCNTs for grafting poly(methyl methacrylate) (PMMA) chains onto the MWCNTs. Thin film nanocomposite membranes with varied amount of PMMA–MWCNTs were prepared by IP using trimesoyl chloride (TMC) and piperaizine (PIP) monomers. The water permeability and salt removal efficiency were significantly improved after adding different amount of PMMA-MWCNTs to the selective layers.\textsuperscript{16} Polydopamine (PDA)-coated MWCNTs (PDA-MWCNTs) were inserted into the PA selective layer to fabricate positively charged TFN membranes via IP between polyethylenimine (PEI) and TMC. A schematic illustration of the fabrication of positively charged TFN membranes is presented in Figure 2.

A polysulfone (PSF) support membrane was immersed in an aqueous solution of PEI and PDA-MWCNTs for 2 min. Thereafter, the remaining aqueous solution was removed from the membrane surface. Furthermore, an organic solution of trimesoyl chloride (TMC) in hexane was poured onto the surface of the support membrane saturated with PEI/PDA-MWCNTs for a minute to form a PA-selective layer after IP. The extra TMC solution was then decanted, and the resulting TFN membrane was thermally treated at ambient temperature for 15 min. Polydopamine-coated MWCNTs were well dispersed in the selective layer of TFN membranes owing to the enhanced compatibility of PDA-MWCNTs with PA matrices through strong covalent interactions between PEI and PDA-MWCNTs. A similar protocol was explored in the fabrication of TFN membranes with different quantities of PDA-MWCNTs.\textsuperscript{17} Zwitterionic polymer chain-modified MWCNTs (ZPMWCNTs) were explored in the fabrication of TFN membranes. Zwitterionic polymer chain-modified MWCNTs facilitated the formation of the defect-free uniform selective layer on the TFN membranes as the dispersion of ZPMWCNTs in an aqueous solution of PIP was significantly upgraded. An almost 31% enhancement in water permeability was observed without sacrificing the selectivity of the TFN membrane containing 0.01% ZPMWCNTs.\textsuperscript{18} Thus, the fabrication of defect-free high-performance TFN membranes was achievable using the polymer-chain-grafted CNTs.

**Graphene Oxide and Its Nanocomposite-Assisted TFN Membranes.** Graphene oxide (GO) has received increasing attention with respect to the fabrication of TFN membranes because of its unique properties such as its atomic thickness and the existence of oxygen functional groups. The water permeability and rejection efficiency of TFN membranes are improved after the addition of GO to the PA selective layer. Graphene oxide nanosheets at high concentration cannot be dispersed homogeneously in the selective layer of TFN membranes; therefore, the performance of GO-enabled TFN membranes is ultimately hampered.\textsuperscript{19,20} To overcome these problems, the functionalized GO nanosheets have been prepared through chemical modifications and applied in the fabrication of TFN membranes.\textsuperscript{21–23} Kang et al. implanted sulfonated GO (SGO) nanosheets into the PA layer to make TFN membranes with different amounts of SGO. Membrane properties such as the hydrophilicity, surface roughness, charge density, pure water permeability, and antifouling capability were dependent on the concentration of SGO nanosheets. The surface roughness of the membranes was increased after the addition of a large quantity of SGO. At 0.3 wt % loading of SGO, the water permeability of the TFN-0.3 membrane improved to 87.3%, and this membrane was capable of removing more than 95% of MgSO\textsubscript{4} from its solution.\textsuperscript{24} Ma et al. synthesized zwitterionic poly(sulfobetaine methacrylate) (PSBMA) polymer chain-functionalized GO (PSBMA-GO) and incorporated it into the PA selective layer of the membranes to improve their water permeability, separation performance, and fouling resistance. The surface hydrophilicity significantly improved with the incorporation of PSBMA-GO. An approximately 2-fold increase in water permeability with no significant change in the salt rejection capacity was achieved after the incorporation of the 0.3 wt % PSBMA-GO nanohybrid. The incorporation of PSBMA-GO into the selective layer was efficient for improving the water permeability and fouling resistance of TFN membranes.\textsuperscript{21} Graphene oxide-derived nanocomposites such as reduced graphene oxide (rGO)@TiO\textsubscript{2}@Ag and GO-Ag-MOF have been applied in the fabrication of TFN membranes.\textsuperscript{25,26} rGO@TiO\textsubscript{2}@Ag was incorporated into the PA layer to fabricate multifunctional TFN membranes via IP on the robust hollow fiber substrate using an aqueous solution of phenylenediamine with rGO@TiO\textsubscript{2}@Ag and an organic solution of TMC in hexane. The rGO@TiO\textsubscript{2}@Ag nanocomposite was accountable in varying the surface texture and topography of the membranes. In addition, the water permeability was enhanced by incorporating a specific amount of the rGO@TiO\textsubscript{2}@Ag nanocomposite because water permeation was facilitated by the formation of additional water pathways at the interface of rGO@TiO\textsubscript{2}@Ag and the PA polymer matrix.\textsuperscript{25} Thus, the fabrication of antifouling and high-performance TFN membranes without sacrificing their rejection efficiencies is attainable using the functionalized GO and its nanocomposites.

**Carbon Quantum Dot TFN Membranes.** Carbon quantum dots (CQDs) have attracted a tremendous amount of attention in membrane technology for their applications in separation processes. Carbon quantum dots have been considered to be promising nanofillers for the fabrication of TFN membranes because of their ultrasmall size, high affinity for...
the PA matrix, superior hydrophilicity, and excellent dispersion in aqueous solutions of monomer used in IP. Carbon quantum dots disperse well in aqueous solutions and subsequently take part in IP to produce TFN membranes. Carbon quantum dot-derived TFN membranes are proficient at outperforming pristine membranes even at a small loading of CQDs. The hydrophilicity, water permeability, rejection rate, and antibiofouling properties depend on the loading amount of CQDs in TFN membranes.\(^{25}\) Li et al. reported that the surface morphology of TFN membranes was transformed from a leaflike structure to a ridge-and-valley structure with the incorporation of hydrophilic CQDs in the PA layer, and the resulting membranes became more hydrophilic.\(^{26}\) Carbon quantum dots with carboxyl, amine, and sulfonic acid groups were synthesized and used in the production of new types of TFN membranes through IP using an aqueous solution of PIP, functionalized CQDs, and an organic solution of TMC. The chemical structure of the PA layer was influenced by the functional moieties (\(-\text{COOH}, \, \text{−NH}_2, \, \text{−SO}_3\text{H}\)) presented in CQDs. The sulfonic acid group-functionalized CQDs (SCQDs) and PA macromolecular chains in the selective layers of the membranes were arranged in a systematic mode. As a result, the negatively charged and loose PA layer was formed due to the presence of sulfonic acid (\(\text{−SO}_3\text{H}\)) groups in SCQDs. More transport pathways for water molecule permeation were formed in TFN membranes comprising SCQD. The water permeability and separation performance were tunable with the number of functionalized CQDs.\(^{27}\) Graphene oxide quantum dots (GOQDs) (a new type of CQDs) containing TFN membranes were fabricated via in situ polymerization using an aqueous solution of tannic acid–GOQDs–TMC and an organic solution of isophorone diisocyanate in hexane. The water permeability was increased with the loading amount of GOQDs in the PA layer of the membranes. The short flow paths in GOQDs played a significant role in improving the water permeation of the membranes.\(^{28}\) Yu et al., embedded a Ag-GOQDs nanohybrid into the PA-selective layer to manufacture antibacterial TFN membranes. The water permeability was highly dependent on the loading concentration of Ag-GOQDs into the selective layer of the membranes. An approximately 44.3% improvement in water permeability was observed, whereas the salt removal efficiency did not deteriorate with the incorporation of Ag-GOQDs. Ag-GOQD-based TFN membranes had bacterial resistance against \textit{E. coli} and \textit{S. aureus}. The incorporation of Ag-GOQD into the TFN membranes provided an efficient approach in controlling the organic fouling and biofouling during filtration at high feed pressure in nanofiltration (NF) and reverse osmosis (RO) processes. Subsequently, the sustainability of water reclamation and the desalination performance of the membranes were improved.\(^{29}\) The utmost performance of TFN membranes can be alleviated through a suitable functionalization of CQDs and loading concentration optimization into the PA layer.

**Metal–Organic Framework-Mediated TFN Membranes.** Metal–organic frameworks (MOFs) have received substantial attention in membrane separation technology. The highly porous structure and tunable chemical functionality of MOFs make them promising candidates for use in fabricating different types of membranes for water treatment. To be specific, MOFs have been incorporated into the PA-selective layer of TFN membranes to improve the water permeability and high-salt removal efficiency.\(^{30,31}\) However, the separation performance of TFN membranes manufactured from MOFs is hampered by the agglomeration of MOF nanoparticles and the formation of nonselective defects in the interphase boundaries of PA-selective layers. In addition, expensive MOFs are unavoidably wasted during IP. Therefore, these major issues (an agglomeration of MOF nanoparticles, interphasial defects, and the wasting of MOFs) should be resolved to develop high-performance TFN membranes using MOFs. To overcome the major issues encountered in the fabrication of MOF-enabled TFN membranes, an ultrathin layer of MOF nanoparticles was predeposited on the top surface of the membrane support with the help of a spray-assisted deposition method, a PDA buffering layer with controlled loading of UiO-66-NH\(_2\) and evaporation-controlled nanofiller positioning. Thereafter, IP was performed to fabricate defect-free high-performance TFN membranes. It should be noted that
a minute quantity of MOFs was required to develop TFN membranes using the above-mentioned approaches compared to conventional IP in the presence of MOF nanoparticles.\(^{32-34}\) Zhang et al. first deposited PDA on the surface of a membrane support as a buffering layer to fabricate continuous, well-intergrown, and stable MOF/UiO-66-NH\(_2\) nanoparticle-integrated TFN membranes. A polydopamine layer facilitated in the close fixing of the MOF particle positions on the surface of the membrane support and UiO-66-NH\(_2\) nanoparticles were fixed covalently onto the surface of a membrane support through Michael addition or Schiff base reaction. The chances of leaching UiO-66-NH\(_2\) nanoparticles during the draining of a PIP aqueous solution were significantly reduced. Only 0.01 wt % UiO-66-NH\(_2\) nanoparticles with respect to the v % of the PIP aqueous solution was adequate to acquire defect-free TFN membranes with dense PA-selective layers. UiO-66-NH\(_2\) nanoparticle-integrated TFN membranes displayed extremely high water permeability and very competitive salt rejection efficiency.\(^{33}\) The ZIF-8 nano filler was implanted into PA layers by an evaporation-controlled filler positioning (EFP) method and IP using an aqueous solution of \(m\)-phenylenediamine (MPD), a suspension of ZIF-8 in hexane, and an organic solution of TMC in hexane. The controlled position of ZIF-8 in PA layers increased the water permeability of the resulting membranes to 220% without a loss of rejection efficiency.\(^{34}\) The ZIF-8 nanofiller was implanted into PA layers by an evaporation-controlled filler positioning (EFP) method and IP using an aqueous solution of \(m\)-phenylenediamine (MPD), a suspension of ZIF-8 in hexane, and an organic solution of TMC in hexane. The controlled position of ZIF-8 in PA layers increased the water permeability of the resulting membranes to 220% without a loss of rejection efficiency.\(^{34}\) The ZIF-8 nanofiller was implanted into PA layers by an evaporation-controlled filler positioning (EFP) method and IP using an aqueous solution of \(m\)-phenylenediamine (MPD), a suspension of ZIF-8 in hexane, and an organic solution of TMC in hexane. The controlled position of ZIF-8 in PA layers increased the water permeability of the resulting membranes to 220% without a loss of rejection efficiency.\(^{34}\)

Ji et al. reported self-sealed PA-zinc imidazole framework (ZIF) TFN membranes with nanoscale turing-type surface morphology. The fabrication protocol for the new type of TFN membrane is presented in Figure 3. Initially, the PSF membrane support was saturated with a zinc nitrate solution of a defined concentration to form a PSF-Zn membrane. A polysulfone-Zn membrane was then exposed to PIP solution to produce the PSF-Zn(II)-PIP membrane. An organic solution of TMC in hexane further poured onto the surface of the PSF-Zn(II)-PIP membrane and left for some time interval. The fabricated membrane was heated at ambient temperature to produce the TFC-Zn(II) membrane, which was immersed in a mixture of 2-imidazole and methanol for the self-sealing of the selective layer. Finally, ZIF-8 incorporated TFN membrane with turing type morphology was formed. A similar protocol was explored in fabricating other membranes comprising different amount of ZIF-8. Compared with pristine TFC membrane, the water permeability of TFN membrane containing minute amount of ZIF-8 (2 mmol m\(^{-2}\)) was almost 400% higher. This could be attributed to the existence of high water permeating turing-type PA networks on the membrane surface and the existence of multiple internal water-permeating channels inside the ZIF-8 nanoparticles.\(^{35}\) Thus, the high-performance TFN membranes for water desalination and purification can be built using a different metal salt solution by following the above-mentioned protocol.

**Multifunctional Polyelectrolyte Nanoparticle-Mediated TFN Membranes.** Recently, polyelectrolyte nanoparticles (PNPs) as organic fillers have been incorporated in the construction of water channels in PA-selective layers of TFN membranes. It is reported that the separation performance and the fouling resistance of the membranes were greatly improved after introducing PNPs.\(^{36-38}\) PNPs are well-dispersed without agglomeration into the matrix of the PA-selective layer of the membranes owing to their superior compatibility with the PA layer. Moreover, the water channels throughout the matrix of PA layers are constructed through the precise control of the functional groups’ content and degree of ionic cross-linking of PNPs. The interfacial channels between PNPs and the PA layer matrix assist in water molecule transport at a high rate whereas the highly efficient separation of various ions is maintained.\(^{36,37}\) Ji et al. synthesized zwitterionic nanogel (ZNG) particles through a surfactant-free emulsion polymerization using DMAPS and 2-hydroxyethyl acrylate. The synthesized ZNG particles were used as an organic filler in making TFN membranes with controlled water channels. ZNGs-integrated TFN membranes were fabricated on the PSF membrane support.
via IP using an aqueous solution of PIP with ZNGs particles and an organic solution of TMC in hexane (Figure 4).

The membrane support fixed on a glass plate was initially immersed in an aqueous solution of PIP (0.35%, w/v) with a certain quantity of ZNG particles and left for a specific time. Then, the superflocculent aqueous solution was decanted from the surface of the membrane support. Thereafter, the aqueous solution-saturated membrane support was kept in an organic solution of TMC (0.20% w/v) in hexane. The excess organic solution was discarded, and the resulting membrane was dried in an oven at ambient temperature to complete the polymerization and acquire a TFN membrane with a ZNG particle-loaded PA-selective layer. The produced membrane was washed thoroughly with deionized water to remove chemical residues and solvents.

The best separation performance was attained for TFN membranes comprising 0.035% (w/v) ZNGs particles as the preferential flow pathways for water molecule transport were provided by the existing nanoscale pores in the PA-selective layer. Thus, the development of a new type of TFN membrane with fine permselective microstructures without phase separation was possible using ZNGs particles as organic fillers during IP.36 A facile and versatile strategy was proposed for fabricating TFN membranes with in situ polydopamine-piperazinone (PDP) nanoparticles. Dopamine was added to an aqueous solution of PIP to form PDP nanoparticles that were dispersed homogeneously in an aqueous solution. The well-dispersed PDP nanoparticles were reacted promptly with organic solution containing TMC. As a result, PDP nanoparticles were reinforced in the selective PA layer and the porous support. The fouling resistance of the membranes against bovine serum albumin was improved by incorporating hydrophilic bioinspired PDP nanoparticles.37 Zhang et al. prepared TFN membranes from IP using an aqueous solution of PIP with ZNGs particles and left for a specific time. The well-dispersed PDP nanoparticles were reacted promptly with organic solution containing TMC. As a result, PDP nanoparticles were reinforced in the selective PA layer and the porous support. The fouling resistance of the membranes against bovine serum albumin was improved by incorporating hydrophilic bioinspired PDP nanoparticles.37 Zhang et al. prepared TFN membranes from PIP with TMC in the presence of PDA-poly(ethylene glycol) (PDA-PEG) nanocapsules. A defect-free PA separation layer was obtained for the membranes due to better miscibility of PDA-PEG nanoparticles with the matrix of the PA layer. The inner cavities of the nanocapsules played a significant role in additional water permeation through the membranes.38 Thin film nanocomposite membranes with controlled nanovoids in the PA layers were fabricated using hollow zwitterionic nanocapsules (HZNCs) by performing IP. The internal free volume, the water permeability, and the fouling resistance capacity of the membranes were enlarged after embedding HZNCs into PA-selective layers. The water permeability of the membrane comprising 19 wt % HZNCs was found to be 70% greater with reference to the control TFC membrane. The rejection efficiency of the resulting membrane was not altered for multivalent ions. The separation performance of HZNC-mediated TFN membranes can be tuned by regulating the size and amount of the nanovoid free volume and the shell structure of HZNCs for practical applications.39

**Water Purification and Desalination Applications.**

The nanofiller-assisted TFN membranes have been applied in water desalination and the removal of metal ions or dyes from a contaminated aqueous solution for water purification. (Figure 5). The water permeability and salt rejection efficiency of the TFN membranes are highly dependent on the types of nanofillers and polyelectrolyte-based PNP fillers. TFN membranes derived from functionalized CNTs and organic PNP fillers have the highest permeability without sacrificing their salt rejection efficiencies.

The membranes fabricated from zwitterionic polymer chain-grafted MWCNT (ZPCNT) via interfacial polymerization were applied in the separation of a solution of two typical inorganic salts (MgSO4 and NaCl) with the help of two-stage NF. The selectivity of the membranes for MgSO4 and NaCl depends on the feed concentration of salts in their solution. The MgSO4/NaCl selectivities for ZPCNT-embedded TFN membranes were 2 to 3 times higher than for pristine TFC membranes at all feed concentrations in the range from 1 to 10 g L−1. The ZPCNT-TFN membranes were suitable for the practical fractionation of salts from simulated brackish water.18 The separation performance of GO nanosheet-incorporated TFN (SGO-TFN) membranes was tested in the desalination of a single salt (NaCl, Na2SO4 or MgSO4) solution of 2500 mg L−1 concentration through NF at 6 bar feed pressure. Sulfonated GO nanosheet-incorporated TFN membranes were efficient in the removal of Na2SO4 and MgSO4 (more than 95% from aqueous salt solutions) under the optimized experimental parameters. The fabricated membrane had a moderate NaCl removal efficiency (75.3%) from aqueous solution.22 The functionalized CQD-assisted TFN membranes were utilized in the NF of Na2SO4, MgSO4, MgCl2, and NaCl distinct solutions to evaluate their separation performance. The size sieving and Donnan exclusion were accountable for salt removal from aqueous solution. The maximum retention by the membranes was attained for Na2SO4 and MgSO4. Moreover, the salt retention capability of the membranes depended on the functional moieties presented in CQDs. The membrane containing aminated CQDs (CQDs-NH2) displayed an improvement in the retention of MgCl2 or NaCl.27 The GOQD-loaded TFN membranes were explored for water desalination of 2 g L−1 NaCl solution at 16 bar feed pressure. The membrane with a minute quantity of GOQDs (<5 mg) was competent in the removal of >98% NaCl from the aqueous solution.40 The separation performance of self-sealed ZIF-8-TFN membranes was tested in the desalination of a 1 g L−1 Na2SO4 solution. More than 90% of Na2SO4 was rejected by the selective layers of membranes comprising different quantities of ZIF-8. The high rejection for Na2SO4 was achieved due to the self-sealing of almost all larger nanopenes without creating extra interphasal defects after the completion of the counterdiffusion self-sealing reaction process.45 The water desalination performance of HZNCs containing TFN membranes was assessed by filtering an individual salt (NaCl, Na2SO4, or MgSO4) solution. The
water desalination performance of the respective membranes was tunable with the loading amount of HZNCs in the PA-selective layer. The rejection of Na2SO4 was increased with the loading amount of HZNCs, and the maximum rejection (94.5% of Na2SO4) was obtained for the membrane containing 19.1 wt % HZNCs. The separation performance of ZNG particle-mediated TFN (ZNG-TFN) membranes was investigated using 1 g L−1 aqueous solution of salts (NaCl, MgCl2, Na2SO4, and MgSO4). The rejection efficiency of the membranes was found to be high for sulfate salts (Na2SO4 and MgSO4) compared to that for chloride salts (MgCl2 and NaCl) under similar experimental conditions owing to the weak electrostatic attraction of sodium ions with membranes other than that of magnesium ions, which resulted in the highest rejection capability of the membranes for Na2SO4. The rejection efficiency was maintained during the long-term filtration of Na2SO4 solution using the manufactured TFN membranes. The rejection efficiency was varied with the feed concentration of Na2SO4 solution. A slight decline in salt rejection was observed with the increasing concentration of Na2SO4 solution. Overall, the fabricated membranes had superior separation performance during the NF of salt solutions at constant feed pressure and different feed concentrations. Multifunctional TFN membranes (MTFN) membrane-incorporated rGO@TiO2@Ag nanocomposites were used in high-pressure crossflow filtration for the decontamination of rose Bengal (RB) and bromothymol blue (BTB) from synthesis solutions. Approximately 98% of RB and 95% of BTB were rejected by the MTFN enriched with 0.2 wt % rGO@TiO2@Ag. Thus, the fabricated membranes can be utilized in the separation and removal of other types of water-soluble dyes from solutions and contaminated wastewater. The NF performance of TA–GOQD–TFN membranes was systematically inspected by passing an aqueous solution of negatively charged dyes (Congo red (CR), methyl orange (MO), and methyl blue (MB)) and a positively charged dye (methylene blue (MEB) dye) at 2 bar feed pressure. The rejection efficiency of the TA–GOQD–TFN membrane depended on the molecular weights of dyes and their characteristics. The membranes had a higher rejection for MB than for MO due to the high molecular weight of MB. In addition, the rejection rate of the membrane for CR (99.8%) was greater than that of MB (98.1%). Thus, the efficient removal of negatively charged dyes from the contaminated aqueous solution was possible using the TA–GOQD–TFN membranes at low feed pressure.

CONCLUSIONS AND FUTURE PERSPECTIVES

In recent years, progress has been made in the fabrication and development of high-performance TFN membranes using the functionalized fillers derived from GO, CNT, TiO2, Ag–TiO2, MOFs, and organic fillers for water purification and desalination applications through the exploitation of membrane separation process such as NF, UF, and RO. Several functionalized nanofillers with different functional moieties (−NH2, COOH, and zwitterionic) are synthesized first via chemical modifications and controlled polymerization reactions. The synthesized nanofillers are then utilized in the fabrication of TFN membranes through performing IP between aqueous-solution-confined nanofillers and an organic solution of the monomers in nonpolar solvents. The water purification and desalination performance depend on the types of functionalized nanofillers and the loading quantity into the PA-selective layers of the TFN membranes. The water permeabilities are improved without an alternation in selectivity after implanting a small amount of the functionalized nanofillers. However, an agglomeration of the nanofillers in the selective layers matrix of the membranes at high loading concentration is one of the main hurdles in manufacturing TFN membranes on a large scale and their applications in water desalination and purification. Therefore, effort should be rendered in avoiding the agglomeration of the functionalized nanofillers in the selective layers at high loading amounts by designing new types of functionalized nanofillers that are more compatible with the selective layers of the membranes. In some cases, the functionalized nanofillers are initially positioned on the top surface of the membrane supports with help of an intermediate layer of bioinspired polymers such as PDA through vacuum filtration and evaporation-controlled nanofiller positioning (EFP) methodology. In the above-mentioned methods, a minute quantity of the functionalized nanofillers is sufficient for constructing the defect-free high-performance TFN membranes with efficient salt removal capability. In addition, the chance of leaching of expensive nanofillers during the decantation of a monomer aqueous solution is neglected. Moreover, the fabrication of TFN membranes of high-water permeability and selectivity is achievable using rationally designed organic fillers because the inner cavities of the incorporated organic fillers act as additional water transport pathways. In the future, more efforts should be focused on the fabrication of high-performance TFN membranes by either the predisposition of new types of functionalized nanofillers with the help of bioinspired polymers or the functionalized organic fillers compatible with selective layers of the respective membranes. The design and development of TFN membranes from the functionalized nanofillers or organic fillers can be an interesting area of scientific or industrial research for those researchers working in the separation and removal of personal care products from wastewater and aqueous solutions at low operation costs.

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