Carbon-based nanocomposite membranes for water and wastewater purification

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2.1 INTRODUCTION

The technology for the production of clean and safe water is essential to the world. In recent times, the scarcity of clean water has been a major concern (Shannon et al., 2008; Werber et al., 2016), as the sudden increases in population growth and industrialization have befouled the world's water to a greater extent. Anthropogenic emissions and industrial wastewater are making the situation worse. New technology is needed for the production of fresh water and treatment of wastewater, to mitigate the growing scarcity of clean, safe water.

Membrane technology plays a vital role in water and wastewater purification. It produces water of superior quality with a smaller carbon footprint as compared to the conventional "Victorian" water treatment technologies (Shannon et al., 2008; Shenvi et al., 2014; Hebbar et al., 2016; Yin and Deng, 2015). Further, usage of polymeric membranes for wastewater and water purification is a more energy efficient, easily scaled, and time-saving process than other processes such as distillation, adsorption, electrolysis, chemical oxidation, electrodialysis, ion exchange, and bioremediation (Ali and Gupta, 2006; Andreozzi et al., 1999; Rautenbach et al., 1989; Malik et al., 2001; Wang et al., 2008; Keharia and Madamwar, 2003; Rengaraj et al., 2001). Membrane-based purification technologies such as ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and the recently emerging osmotically driven forward osmosis (FO) are serving as alternatives for providing clean and safe drinking water to mankind. Generally, an ideal membrane should have the following characteristics: high water permeability and solute rejection, antifouling and antibiofouling nature, and greater chemical and thermal stability.

The commercially available materials for the fabrication of polymeric membranes are polysulfone (PSF), polyvinylidene fluoride (PVDF), polyethersulfone (PES), and so on. In general, the polymeric material should have good film-forming ability, hydrophilicity, and mechanical, chemical, and thermal stability. The polymers PSF, PVDF, and PES have all these properties except for hydrophilicity, as these polymers are less hydrophilic in nature. Consequently, the membranes prepared using these polymers suffer severely from fouling and reduced water permeability. The fouling can be caused by adsorption, accumulation, or precipitation of organic and inorganic foulants on the membrane surface (Saqib and Aljundi, 2016; Ibrahim et al., 2017b; Rana and Matsuura, 2010). Accordingly, the membrane performance is affected, which results in an increase in operational costs and reduced membrane lifespan (Sun et al., 2013; Ibrahim et al., 2017a). To mitigate the fouling and enhance water permeability, tremendous efforts have been made.

In the last few decades, outstanding membrane performance improvement has been achieved by incorporating nanomaterials such as TiO_2, SiO_2, ZnO, Fe_3O_4, halloysite nano clay and so on. Among the nanomaterials reported, the carbon-based nanomaterials, for instance, carbon nanotubes (CNTs) and graphene oxide (GO), are well studied as additives in the fabrication of polymeric nanocomposite membranes (Liu et al., 2015; Yin et al., 2013; Ong et al., 2016; Hebbar et al., 2017; Ganesh et al., 2013). The CNTs are predominantly used because of the one-dimensional nanochannel tubular structure, which facilitates the passage of water molecules, and also they have very high mechanical strength. Similarly, the two-dimensional graphene and its derivatives such as GO open up a new way of improving separation properties (Mi, 2014; Geim and Novoselov, 2007). The ultrafast water transport across the GO nanocomposite membrane is attributed to the one-atom thickness of GO. The improved chemical and mechanical properties and more cost-effective production make the carbon-based nanomaterials an efficient candidate for water and wastewater purification applications. In this chapter, more details are presented about the usage of carbon-based, particularly carbon nanotubes and graphene oxide nanocomposite, membranes for desalination, dye removal, oil/water separation, and natural organic matter removal.

2.2 CARBON NANOTUBES AND GRAPHENE OXIDE

CNTs were first discovered by the Japanese physicist Sumio Iijima in 1991 (Iijima, 1991). They have been developed as an efficient nanomaterial for water and wastewater purification. The improved performance of CNTs is attributed to the ultrafast water flow through nanochannels without losing rejection ability, very high surface area, and easy functionalization (Majumder et al., 2005; Hummer et al., 2001; Holt et al., 2006; Hinds et al., 2004; Corry, 2008). Fig. 2.1A indicates the increased attention paid toward the use of CNTs as a nanomaterial for the preparation of nanocomposite membranes, and application of CNTs in the various fields is described in Fig. 2.2A. Further, CNTs have high thermal, electrical, and mechanical and partial
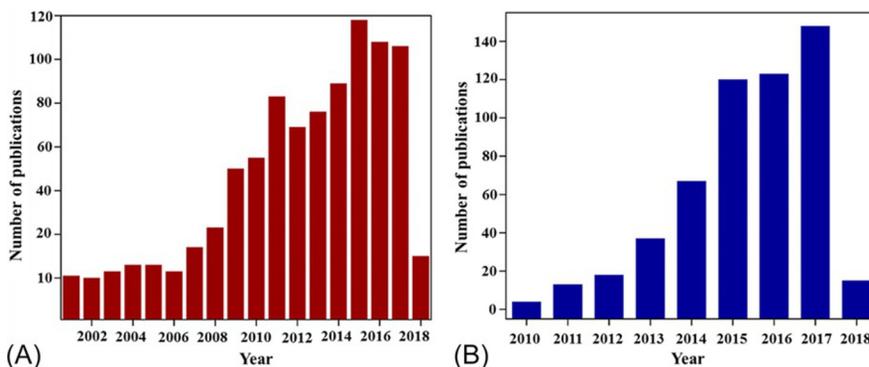
FIG. 2.1

The number of publications based on the keyword (A) "carbon nanotubes nanocomposite membranes" and (B) "graphene oxide nanocomposite membranes" in Scopus database (data collected on 01.01.2018).

antibacterial properties (Wu et al., 2010; Kang et al., 2008) and also improve the physicochemical properties of the nanocomposite membrane. The schematic representation of water transport across CNTs is given in Fig. 2.3.

GO extends tremendous advantages as a nanomaterial for the preparation of both TFN and MMM, as it has functional groups, for instance —OH, —COOH, epoxide, and C=C, on the surface, which provide lots of opportunities to use this material and for further modifications. The added GO forms interconnected nanochannels, through which water molecules can be transported (Mi, 2014). The presence of hydrophilic groups makes the GO hydrophilic in nature. It offers excellent antifouling, antibiofouling, and antibacterial properties (Liu et al., 2012; Lee et al., 2013; Chae et al., 2015). Fig. 2.1B shows the attention paid to this nanomaterial. GO is undoubtedly the most intensely used nanomaterial, with applications in a variety of fields (Fig. 2.2B). The transport phenomenon of water molecules in a GO nanocomposite membrane is represented in Fig. 2.4.

2.2.1 APPLICATIONS OF CNTs AND GO IN WATER AND WASTEWATER PURIFICATION

2.2.1.1 Desalination

In spite of the many advantages exhibited by CNT and GO membranes, their practical applicability is hampered by some of their disadvantages, such as the excessive cost of membrane fabrication and the lack of technology to fabricate defect-free and continuous membranes. Thus, this kind of inorganic membrane can be replaced with polymeric nanocomposite membranes, which can relatively counterbalance the drawbacks (Ciobanu et al., 2008; Ismail et al., 2009). The conventional methods for the desalination of seawater consist of distillation, NF, and RO. The distillation

(A)

(B)
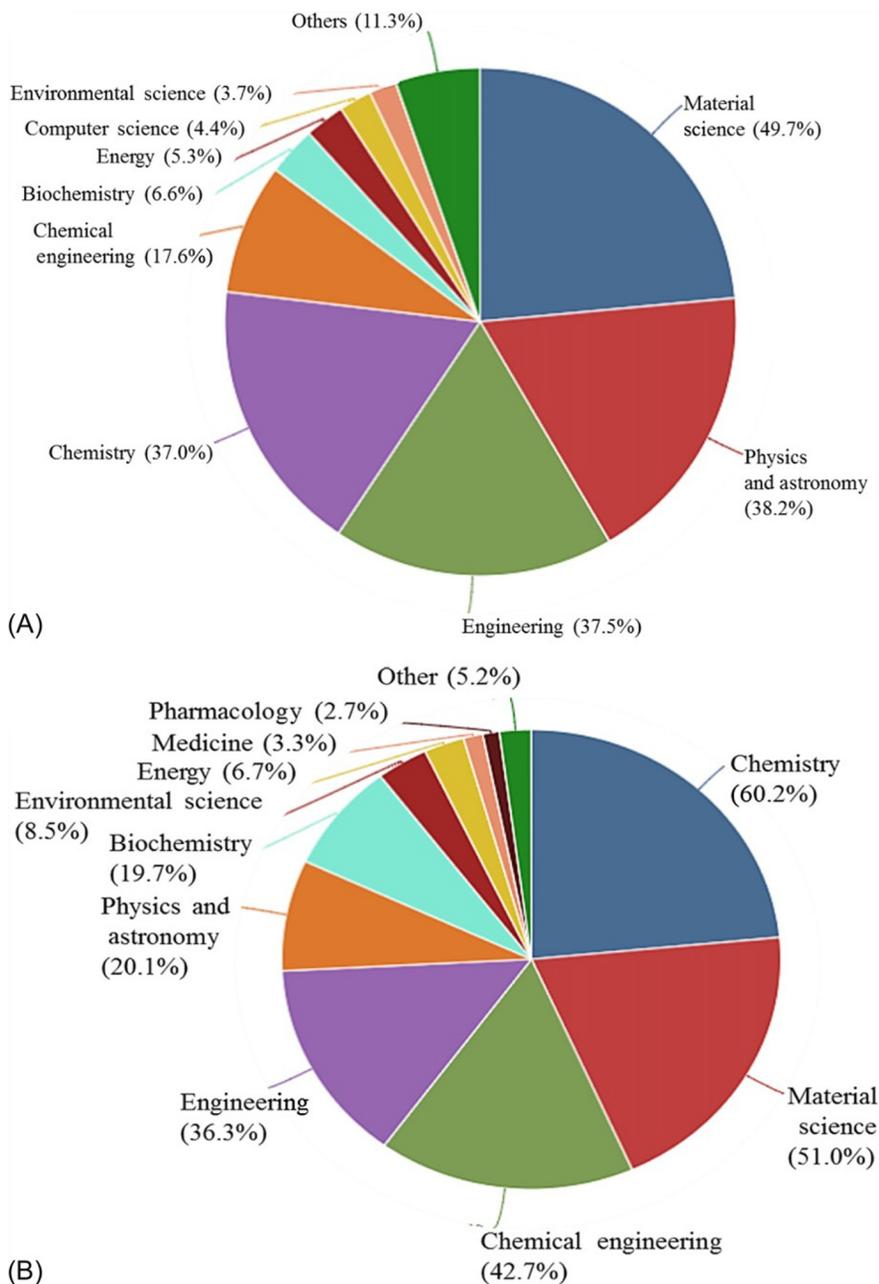
FIG. 2.2

Application of (A) CNTs and (B) GO in various fields (Scopus, data collected on 01.01.2018).
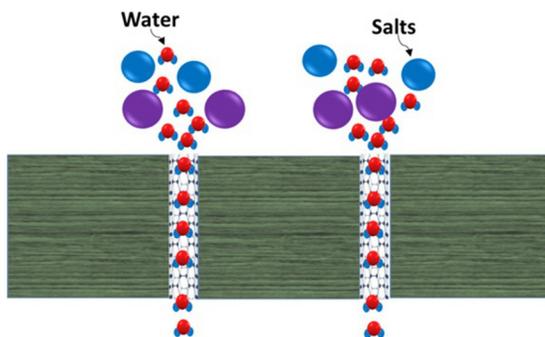
FIG. 2.3

Transportation of water molecules across CNTs.
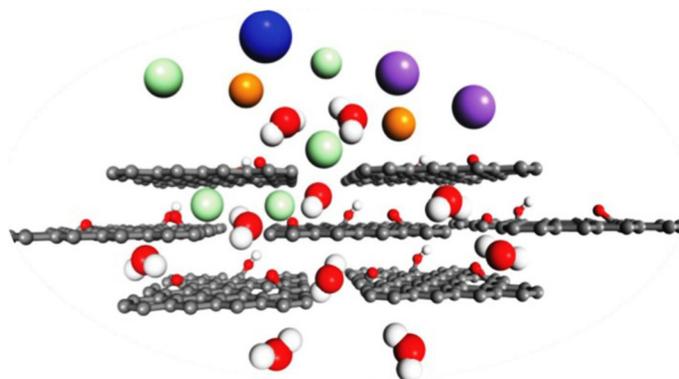
FIG. 2.4

Transportation of water molecules across GO (You et al., 2016).

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method is inevitably energy intensive, as the heat of vaporization of water is high. Therefore, NF and RO polymeric nanocomposite membranes are an effective method for desalination. However, the water permeability of RO membranes is less. Thus, there is a requirement for an improvement in water permeability without compromise in the solute rejection (Chan et al., 2013). Similarly, solute rejection in the NF membrane is less compared to RO membranes. CNTs and GO can be used as nanofillers to improve the NF and RO membrane performances, as they exhibit ultra-fast water transport. Although CNTs facilitate ultrahigh water flow, they are relatively hydrophobic in nature (Hummer et al., 2001), which limits the effective dispersion in the polymer matrix and surface hydrophilicity. Accordingly, modification of CNTs becomes inevitable for the improvement of polymeric nanocomposite membrane performance. The hydrophilic functional groups such as —OH

and —COOH present in GO make it more hydrophilic and also bestow a negative charge. Further, appropriate functionalization of GO will improve the nanocomposite membrane performances.

As far as NF and RO membranes are concerned, there are two types of membranes available for the effective removal of inorganic salts: a thinfilm nanocomposite membrane (TFN), which consists of a thinfilm polyamide layer and nanofiller; and a mixed matrix membrane (MMM), which is formed by the uniform dispersion of organic/inorganic nanofiller in the polymer matrix. Farahbakhsh et al. (2017) prepared a TFN membrane with raw and oxidized multiwalled carbon nanotubes (MWCNTs) (Fig. 2.5). It is implied that with raw MWCNTs the TFN membrane hydrophobicity was improved and the maximum water flux of $25.9 \, L/m^2 \, h$ was observed. However, with oxidized MWCNTs, the lowest contact angle of 59.6 degrees was observed with a water flux of $28.9 \, L/m^2 \, h$. The increase of contact angle with raw MWCNT TFN membrane was ascribed to the nonwetting behavior of MWCNTs. Nevertheless, after oxidation, the presence of hydrophilic functional groups such as —COOH and —OH increased the surface hydrophilicity, which also improved the water flux compared to unoxidized MWCNTs. The prepared TFN membrane exhibited a NaCl rejection of 98.1% with 0.002 wt% of raw MWCNTs and 97.8% with 0.002 wt% of oxidized MWCNTs. Still, with increased concentration of both raw and oxidized MWCNTs, the flux and salt rejection was decreased. The reason for the decrement was reported as agglomeration of the MWCNTs.

Aani et al. (2018) demonstrated the preparation of TFN membranes incorporated with polydopamine/metal/metal oxide/MWCNTs. The as-prepared membranes exhibited improved water flux, surface roughness, hydrophilicity, and above 94% of divalent and 90% of monovalent salts rejection. Polypyrrole (PPy) coated MWCNTs were prepared and integrated into a TFN membrane for improved salt
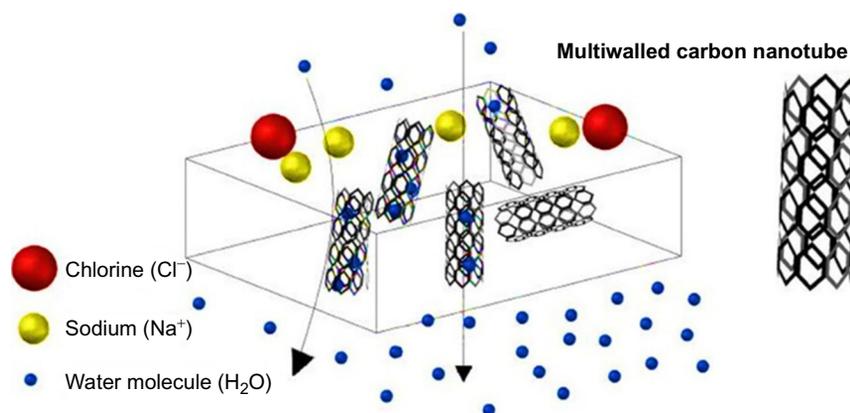
FIG. 2.5

Schematic representation of MWCNT TFN membrane (Farahbakhsh et al., 2017).
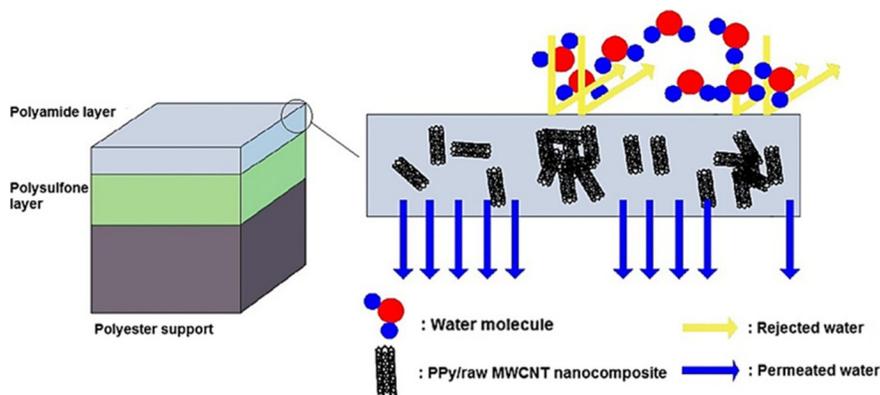
FIG. 2.6

Graphic illustration of agglomeration of PPy coated raw MWCNTs in TFN membrane (Mahdavi et al., 2017b).

rejection and antifouling properties by Mahdavi et al. (2017b). As described, the TFN membranes were prepared with PPy coated both raw and oxidized MWCNTs. The TFN membrane with 0.001 wt% of modified MWCNTs exhibited a Na_2SO_4 rejection of 97.9%. It is also stated that, while increasing the PPy coated raw MWCNT concentration, there was a reduction in the water flux due to agglomeration (Fig. 2.6). In contrast, a continuous improvement in the water flux was obtained with PPy coated oxidized MWCNTs. The continuous increment of water flux was due to the increased hydrophilicity. Carboxylated CNTs/polyethersulfone (PES) MMM was reported by Wang et al. (2015b). The effect of nanomaterial size and concentration on surface hydrophilicity, water flux, and salt rejection were studied. The lowest contact angle of 54.95 degrees was observed for MWCNTs having a diameter of 20 nm. A few recent studies on desalination using CNTs and GO nanocomposite membranes are presented in Table 2.1.

The superior properties, such as hydrophilicity and nanochannel formation, of GO make it a promising material for desalination. Wen et al. (2017) performed studies on desalination applications through an acyl chlorided-GO inserted thin film composite NF membrane (Fig. 2.7). The nanohybrid membrane showed a water flux of $22.6 L/m^2$ h and Na_2SO_4 rejection of 97.1%. It was specified that the added modified GO reduced the active layer thickness without any defects, which improved the rejection without compromise in the rejection.

Another study with a polyvinylpyrrolidone (PVP) modified GO incorporated TFN forward osmosis (FO) membrane was reported (Wu et al., 2017b). The PVP improved the dispersability and hydrophilicity of GO in the polyamide matrix; consequently, the highest FO membrane water flux of $33.2 L/m^2$ h with lower reverse solute flux was observed.

Table 2.1 Recent Literature on CNTs and GO Nanocomposite Membranes for Desalination

Type of Modification/ Membrane	Nanomaterial Loading (wt%)	PWP[a] (L/m^2 h bar)	Rejection (%)	Reference
Sulfonated MWCNTs/NF	0.01	13.2	Na$_2$SO$_4$—96.8	Zheng et al. (2017b)
Tannic acid-Fe^{III}-MWCNTs/NF	0.03	5.23	Na$_2$SO$_4$—75.0	Wu et al. (2017a)
Carboxylated MWCNTs/NF	0.005	8.87	Na$_2$SO$_4$—98.5	Li et al. (2017)
NH$_2$-MWCNTs/RO	0.002	~3.86	NaCl—96.16	Vatanpour et al. (2017)
Acid treated MWCNTs-TNT/RO	0.05	0.74	NaCl—97.97 Na$_2$SO$_4$—98.07	Azelee et al. (2017)
Oxidized MWCNTs/NF	0.005	6.57	Na$_2$SO$_4$—97.9	Mahdavi et al. (2017a)
Zwitterionic MWCNTs/NF	0.01	14.9	NaCl—20.0 Na$_2$SO$_4$—99.0	Zheng et al. (2017a)
rGO-TiO$_2$/RO	0.02	3.42	NaCl—99.45	Safarpour et al. (2015)
GO/RO	0.015	2.87	NaCl—93.8	Yin et al. (2016)
GO/NF	0.2	1.46	NaCl—89 MgSO$_4$—98	Bano et al. (2015)

[a]Pure water permeability.
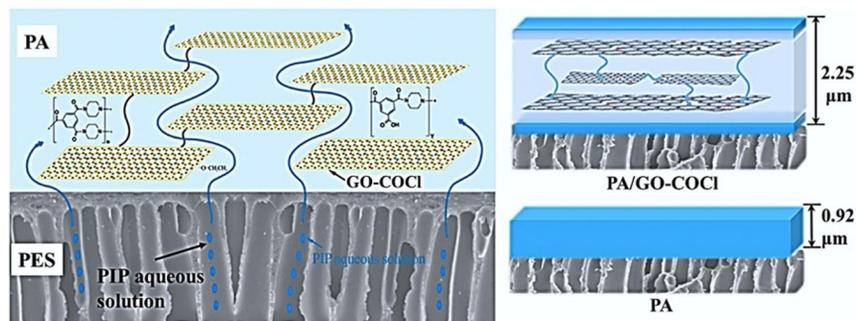
FIG. 2.7

Water transport in GO-COCl/PES membrane (Wen et al., 2017).

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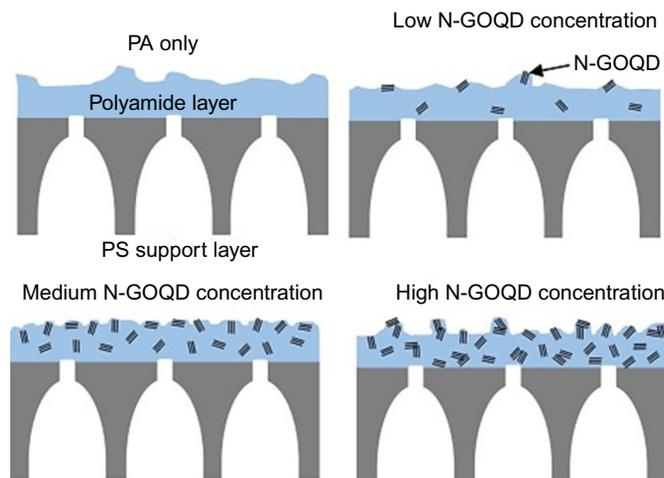
FIG. 2.8

Schematic representation of TFN membrane with different concentration of N-GOQD (Fathizadeh et al., 2017).

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Novel nitrogen-doped GO quantum dots (N-GOQD) were used for the preparation of a TFN membrane (Fathizadeh et al., 2017). With only 0.02 wt% of N-GOQD, there was a drastic change in the water flux while preserving the high salt rejection. The improved performance was attributed to the superior surface hydrophilicity, higher surface area, and the cavity created between the quantum dot and polyamide matrix. The effect of the concentration of N-GOQD was also studied (Fig. 2.8). It was concluded that, with a lower concentration, a leaf-like hill and valley formation was observed in the polyamide layer. On the other hand, with higher concentration, a severe agglomeration was attained, which led to the formation of a fully hill and valley-like morphology on the polyamide selective layer.

A novel TFN membrane preparation was proposed in which the polyamide layer was modified with octadecylamine-modified GO and fluorine-containing monomer (Xue et al., 2018). The incorporation of a fluorine-containing moiety in the TFN membrane was to increase the chlorine resistance. The TFN membrane exhibited a pure water flux of 49.9 L/m^2 h with a Na$_2$SO$_4$ rejection of 98.4%. Nonetheless, a higher percentage of nanofiller increased the hydrophobicity and particle aggregation, which resulted in a reduced water flux. Based on the sieving mechanism, the TFN membrane follows the subsequent order of salt rejection Na$_2$SO$_4$ > MgSO$_4$ > NaCl. The MMM performance at a higher salt concentration was evaluated using GO/polyimide MMM (Zaman et al., 2018). At a higher concentration of the salt solution, the MMM exhibited only 4% of the reduction in rejection, whereas the pristine polyimide membrane revealed a reduction of 16%. The decreased reduction in rejection in the case of MMM was ascribed to the increase of amorphous structure, which ultimately increases the thickness of the membrane.

2.2.1.2 Dye removal

Rapid industrialization and population growth have increased the demand for dye wastewater purification. The direct discharge of dye wastewater into the main water stream can affect both humans and animals, as the dye molecules are toxic in nature (Miksch et al., 2015). In that respect, carbon-based nanomaterials such as CNTs and GO can be used as a nanofiller to improve membrane performance for dye removal. These nanomaterials have very high surface area and good adsorption capability (Yu et al., 2012). It is reported that the dye removal efficiency can be tuned by altering the surface properties of the MWCNTs. The negatively charged dye molecules are efficiently rejected by the negatively charged membrane surface via electrostatic repulsion, and vice versa. The zeta potential of GO was observed as $-30\,mV$ at pH 6.1 (Li et al., 2008). However, the zeta potential of MWCNTs is $3.2\,mV$ at pH 7 (Kim and Sigmund, 2004). Therefore, it is necessary to improve the surface charge of the MWCNTs, so the dye rejection efficiency can be improved. Further, when the rejection mechanism is via electrostatic repulsion, a layer will not be formed on the membrane surface. Nevertheless, in the case of electrostatic attraction, there will be a formation of a thin layer, which consists of dye molecules. Consequently, it is difficult to clean the membrane and this also affects the membrane permeability. Still, there are some reports in which the dye rejection mechanism was based on the electrostatic attraction. In addition, the tendency toward aggregation and poor interaction between the nanomaterial and polymer matrix (Sahoo et al., 2010; Celik et al., 2011) can also be improved with suitable functionalization. In the recent literature, a considerable number of modifications have been reported toward the functionalization of MWCNTs and GO for preparing nanocomposite membranes, to increase the membrane performance.

Ghaemi et al. (2015) demonstrated the preparation of poly(4-styrenesulfonic acid) sodium salt functionalized MWCNTs and employed them for the preparation of a PES mixed matrix NF membrane, which improved the water flux and acid orange 7 removal. The positively charged mixed matrix NF membrane was prepared by the inclusion of triethylenetetramine-coated MWCNTs (Peydayesh et al., 2018). The prepared NF membranes were able to reject cationic dyes of rhodamine B (99.23%), crystal violet (98.43%), and anionic dyes such as indigo carmine (87.12%) and orange G (82.13%). The higher rejection was observed for cationic dyes, owing to electrostatic repulsion, compared to the anionic dye removal, which was due to electrostatic attraction. The dye solution flux was higher for the cationic dyes. However, for anionic dyes, the dye solution flux was reduced, as the anionic dye molecules are adsorbed on the positively charged membrane pore walls and surface via electrostatic attraction. Hence, the mass transfer resistance was increased significantly. Moreover, the permeate flux and dye rejection with increasing concentration of salt were also studied, as the salts are inevitable in real-time samples. The flux and rejection of the mixed matrix NF membrane were decreased owing to the shielding effect of counter ions, which reduces the surface charge of the nanocomposite membrane.

Wasim et al. (2017) revealed the usage of a biopolymer chitosan coated PVDF/ MWCNT TFC membrane. The presence of hydrophilic functional groups such as

—OH, —NH$_2$ in chitosan upgraded the TFC membrane performance. Nonetheless, the TFC membranes exhibited reduced pure water flux compared to pristine PVDF membrane. The reduction in flux was accredited to the pore blockage of the MWCNTs. The results suggested that the anionic dye (reactive orange 16) removal was high at pH 4. At pH 4 chitosan and dye molecules are protonated; as a result, there was an electrostatic attraction between the chitosan and dye molecules, which improved the dye removal efficiency of the TFC membranes.

In another study, PES blend membranes were prepared with ZnO-coated MWCNTs (Zinadini et al., 2017). The blend membrane exhibited improved water flux and dye removal. The nanocomposite membrane with 0.1 wt% of nanofiller showed the highest Direct Red 16 dye removal. Still, with 0.5% of nanofiller, the dye removal efficiency was reduced owing to enlargement of the pore radius. Since the dye removal followed the electrostatic repulsion mechanism, there was no sudden drop in the dye solution permeability compared to the neat PES membrane. The enriched dye removal was also ascribed to the photocatalytic nature of ZnO, where the dye molecules were degraded under UV irradiation. Thereby, the membrane could perform with low fouling. The flux recovery ratio (FRR) for the nanocomposite membrane with 0.5 wt% of nanofiller was 90.5%.

The water flux of the GO integrated nanocomposite membrane was improved via adjusting the layer spacing of GO by adding dopamine modified halloysite nanotubes (D-HNTs) (Zeng et al., 2017). The hybrid membranes were prepared by vacuum filtration. The nanocomposite membrane presented high flux and extraordinary removal of cation dye methylene blue (MB). The negative charge exhibited by both GO and D-HNTs afforded easy removal via electrostatic attraction. The increased layer spacing accounted for the high flux. In another report, Zhang et al. adjusted the GO nanochannel by cross-linking with isophorone diisocyanate (Zhang et al., 2017c), which resulted in improved flux and above 96% rejection of dye molecules, for instance, methylene blue, methylene orange, rhodamine B, and Congo red.

Use of a partially reduced GO (rGO)/TiO$_2$ nanocomposite for preparing a PES mixed matrix NF membrane was suggested (Safarpour et al., 2016). Introduction of 0.15 wt% of rGO/TiO$_2$ brought a higher water flux of 45 kg/m^2 h, which was near twice that of the pristine PES membrane. The antifouling ability of the nanocomposite membrane was studied using BSA as model foulant and the results showed an enhanced antifouling property with 0.1 wt% of nanofiller. The role of TiO$_2$ was to improve the dispersion and hydrophilicity and reduce the agglomeration. It was observed that the NF membrane had a higher capacity to reject reactive green 19, direct yellow 12, and reactive blue 21 at pH 7 via electrostatic repulsion.

The low-pressure NF membrane was fabricated by dispersing GO quantum dots (GOQD) within a tannic acid (TA) film by interfacial polymerization (Zhang et al., 2017a). The TFN membrane presented a Congo red and methylene blue rejection of 99.8% and 97.6% with water flux of 23.33 L/m^2 h, higher than the TA TFC membrane. It was suggested that the upgraded performance was due to the improved hydrophilicity, smooth, and negatively charged surface (Fig. 2.9).
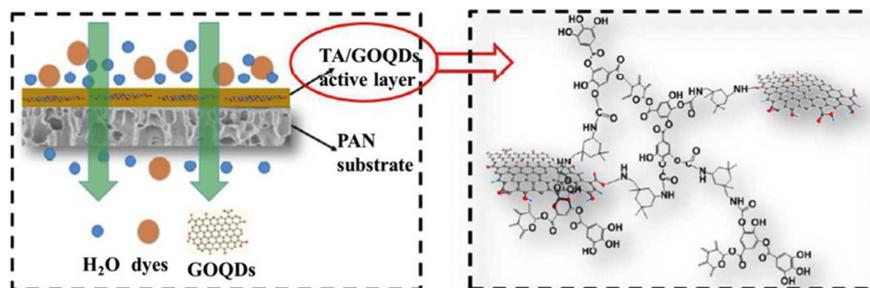
FIG. 2.9

Dye rejection of TA/GOQD TFN membrane (Zhang et al., 2017a).

2.2.1.3 Oil/water separation

Among the methods available for the separation of oil/water, polymeric membrane separation plays an important role. The commercially available UF membranes are less hydrophilic in nature. As a result, they foul at a faster rate than the nanocomposite membrane. Thus, use of hydrophilic nanomaterials will mitigate the fouling issues. The functionalized MWCNTs and GO are more appropriate hydrophilic nanofillers, as these are one atom thick, and have a high surface area, tubular structure, and flexibility. In the modern literature, many types of functionalized MWCNTs and GO-incorporated nanocomposite membranes have been reported to improve oil/water separation.

Santosh et al. (2018) reported on acetyl-D-glucopyranoside modified MWCNT nanocomposite membranes for oil/water separation. The acetyl modified MWCNTs membrane showed the lowest contact angle of 69 degrees. Conversely, after deacetylation, there was no decrease in the contact angle, owing to the presence of the functional group in lower concentration. Still, the surface roughness was decreased after deacetylation. The nanocomposite membrane with 0.2 wt% of modified MWCNTs exhibited oil rejection of 100% with a flux of 112 L/m^2 h.

Fabrication of superhydrophilic PVDF membranes by the inclusion of 3-aminopropyltrimethoxysilane and dopamine functionalized MWCNTs was recently reported (Yang et al., 2017). The contact angle was reduced with increasing loading of nanofiller and the lowest contact angle of 26.77 degrees was observed with 30 mg of functionalized MWCNTs. The obtained result was in parallel with surface roughness analysis. While increasing the concentration of nanofiller, the surface roughness was also reduced. It is preferable to prepare hydrophilic nanocomposite membranes rather than hydrophobic ones, since in general water is denser than oils. Therefore, the hydrophilic membrane forms a hydration layer on the membrane surface, which promotes water permeation across the nanocomposite membranes (Fig. 2.10). It was also described that the prepared membrane exhibited oil rejection of around 99% in acidic, neutral, and basic environments. Yet at pH 12, the
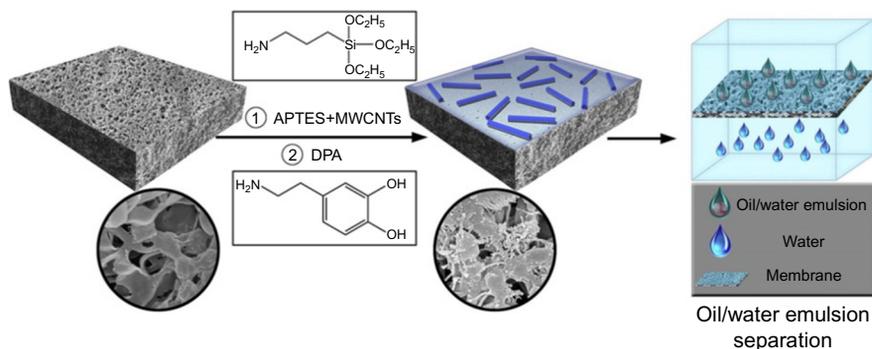
FIG. 2.10

Oil/water separation of functionalized MWCNT nanocomposite membrane (Yang et al., 2017).

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performance was not stable due to the instability of dopamine at the higher basic condition. The enhanced FRR and oil rejection were attributed to the presence of hydrophilic functional groups such as —OH and —NH$_2$.

The performance of Pebax/MWCNT coated PSF membranes for oil/water emulsion separation was studied (Saadati and Pakizeh, 2017). It was noted that the superior oil/water separation was due to the improved hydrophilicity afforded by the additives. A polyvinyl alcohol (PVA) coated CNTs/PSF nanocomposite membrane was fabricated (Maphutha et al., 2013). It was shown that the nanocomposite membrane revealed better mechanical strength and oil rejection of 98.61% with 5% of CNTs at 4 bar and rejection was decreased with 10% of CNTs loading. A nanohybrid membrane prepared with PEI@CNT/TMC for oil/water emulsion separation has also been suggested (Liu et al., 2017). The role of PEI was to endow a reactive amine functional group for crosslinking with TMC. The TMC was able to afford mechanical strength and hydrophilicity and a negative charge to the nanohybrid membrane after hydrolysis of unreacted acyl chloride. The nanohybrid membrane was able to exhibit an FRR of 81.7% against soybean oil/water emulsion and the rejection was above 99.9% with high flux.

Adding GO in a polyamide membrane by vacuum filtration is one of the ways to obtain active separation of oil/water emulsion (Huang et al., 2015b). The ultrathin and "water locking" coating of GO with optimized surface roughness contributed to the reduced oil adhesion over the membrane surface. The nanocomposite membrane achieved 100% recovery, simply by water flushing. Oil/water emulsion separation using GO-modified Al_2O_3 ceramic microfiltration (MF) was proposed (Hu et al., 2015). It was put forward that the –COOH group in GO interacted with the —OH group present in Al_2O_3 to make the GO coating. The modified membrane flux was improved to 27.8% and enhanced oil rejection compared to the unmodified membrane.
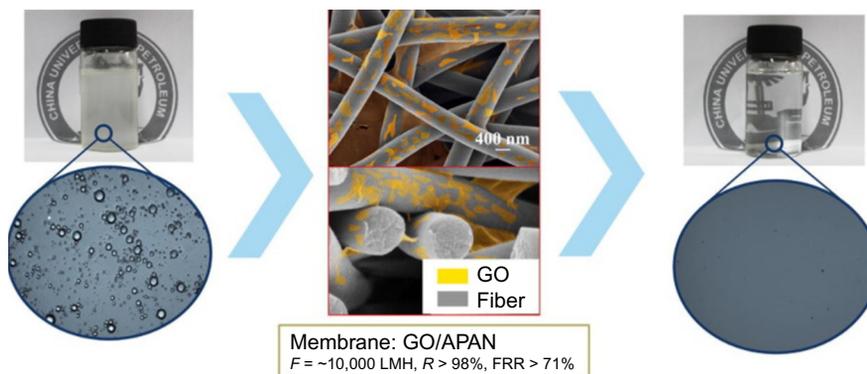
FIG. 2.11

Oil/water emulsion separation of GO-APAN membrane (Zhang et al., 2017b).

The performances of polyacrylonitrile (PAN), aminated PAN (APAN), and GO-coated APAN (GO-APAN) for oil rejection have been studied (Fig. 2.11) (Zhang et al., 2017b). A considerable improvement was found in the oil rejection of the GO-APAN membrane compared to the APAN and PAN membranes. The nanohybrid membrane revealed an oil rejection of above 98% with FRR of 71%. The enhanced oil rejection and flux was accounted for by the improved surface hydrophilicity and porosity of the GO-APAN membrane.

PES HF membranes modified with functionalized graphene oxide have also been suggested (Prince et al., 2016). The lower water contact angle of 22.6 degrees and highest oil contact angle of 112.5 degrees were observed for the nanocomposite PES HF membrane, which is 64.5% reduction and 158% higher than the pristine PES HF membrane, respectively. The oil removal efficiency of the nanocomposite membrane was studied for 8 h. During the analysis, a slight drop in the oil removal efficiency was observed for the nanocomposite membrane. However, for the unmodified PES membrane, a sudden drop was observed. The increased surface hydrophilicity was attributed to the improved oil/water emulsion separation. Recently, fabrication of a high flux nonlaminated GO membrane crosslinked by polyethyleneimine (PEI) was reported (Huang et al., 2015a). The superhydrophilic nature of the nanocomposite membrane was confirmed by the water contact angle of 0 degree. The improved flux was due to the disordered GO nanosheets, which assist in the transport of water molecules. Further, the slight decrease in the oil rejection of a toluene/water emulsion was observed. The decrement was due to the slight solubility of toluene in water. Likewise, a palygorskite nanorod intercalated GO nanohybrid membrane was also demonstrated for oil rejection (Zhao et al., 2016). The flux was increased and then began to decrease with a higher concentration of nanomaterial. The higher flux of the nanohybrid membrane was justified by the increase of nanochannels from the intercalation of nanorods in the GO nanosheet interlayers. The superior wetting

behavior of the nanohybrid membrane eliminated oil adhesion by forming a hydration layer on the membrane surface by which the modified membrane could improve the oil/water emulsion separation and antioil fouling properties.

2.2.1.4 Natural organic matter removal

Nowadays, UF membranes are used for the effective removal of natural organic matter (NOM), as these membranes are capable of demonstrating high flux with less energy consumption (Lowe and Hossain, 2008; Fu et al., 2008; Hebbar et al., 2015). NOM such as humic acid (HA) and fulvic acid are naturally abundant in ground/surface water. These are produced during the chemical and biological degradation of animal and plant residues. This gives color and odor to the drinking water and also produces some carcinogenic substances when it reacts with chlorine.

Hudaib et al. (2018) reported the removal of HA using polyaniline-coated MWCNTs/PVDF UF membranes. It was understood that the added polyaniline improved the surface positive charge of the PVDF membrane. Thus, the HA rejection was based on the mechanism of electrostatic attraction and an HA rejection of 81% was achieved. In addition, MWCNTs have high surface area and through π-π interaction with HA, the rejection was also improved compared with a pristine PVDF membrane. In another report, a polyaniline-coated MWCNTs/PES membrane was also studied for NOM removal (Fig. 2.12) (Lee et al., 2016). A TiO$_2$/MWCNT/PSF MMM was fabricated. The synergistic effect of 0.5/0.5 wt% of TiO$_2$/MWCNTs assisted in improving the MMM surface hydrophilicity. The MMM permeability was characterized by 2 and 700 ppm of HA concentration. At low concentrations, there was no significant reduction in permeability due to the insignificant effect of
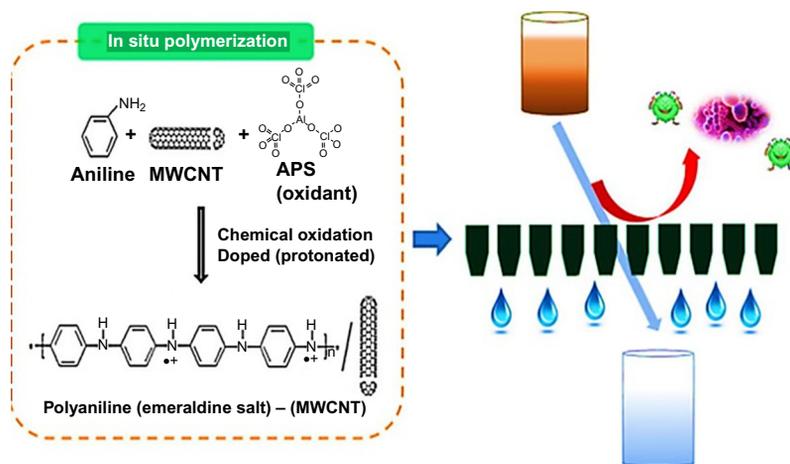
FIG. 2.12

HA removal using polyaniline-coated MWCNT/PES membrane (Lee et al., 2016).

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concentration polarization. However, with higher concentrations, there was a substantial decrease in the permeability. As a whole, the MMM exhibited improved HA rejection with greater FRR.

Modification of MWCNTs with a hydrophilic polymer is one of the simple techniques to improve membrane performance. UF membranes with polyethylene glycol (PEG) coated MWCNTs were studied and their physicochemical behavior was also compared with unmodified and carboxylated MWCNTs (Bai et al., 2015). The superior dispersion of modified MWCNTs is ascribed to the presence of a hydrophilic functional group such as ─COOH and ─OH. The PEG-MWCNT membrane demonstrated superior antifouling performance, which was attributed to the stronger negative charge and lower surface roughness. In another report, an oxidized MWCNTs modified poly(vinyl butyral) hollow fiber membrane for the UF removal of bovine serum albumin (BSA) and HA was studied. The larger nanocomposite membrane permeability and FRR were due to the enriched surface hydrophilicity and low protein adsorption (Wang et al., 2015a).

Fabrication of a reduced GO/TiO_2 modified PVDF mixed-matrix UF membrane was proposed (Safarpour et al., 2014). When compared with a pristine PVDF membrane, the pure water flux of the modified PVDF membrane was increased by 54.9% using 0.05 wt% of nanofiller concentration. Nevertheless, a high concentration of nanofiller reduced the water flux, as there was a pore blockage by the nanofiller. Also, the $GO/TiO_2/PVDF$ membrane exhibited a high rejection to BSA with an FRR of 88.1%. Correspondingly, a novel nanocomposite membrane was prepared by vacuum filtration of $TiO_2/Fe_2O_3/GO$ on glass-fiber filter paper (Rao et al., 2016). The results established that the nanocomposite membrane prepared with $TiO_2/Fe_2O_3/GO$ nanomaterials increased humic acid removal compared to the nanocomposite membrane fabricated with TiO_2/Fe_2O_3 nanomaterials. The membrane performance was higher in the presence of sunlight than in dark. The added Fe_2O_3 nanoparticles improved the adsorption of HA and GO increased the charge transfer from TiO_2, which resulted in the enhancement of photocatalytic activity of TiO_2 to photodegrade HA. Thus, the nanocomposite membrane exhibited a superior HA removal of 93%.

In another report, a commercially available PES UF membrane was coated with multilayers of GO by vacuum filtration (Song et al., 2015). A maximum HA removal of 67% was achieved for 30 nm of GO coating. The enriched surface hydrophilicity resulted in the improvement of flux and antifouling properties. Similarly, GO-incorporated PVDF membranes were prepared by a phase inversion method for NOM removal (Xia and Ni, 2015).

The polyamide layer of composite membrane was fabricated with different concentrations of GO to eliminate the NOM present in natural river water (Xia et al., 2015b). The TFN membrane had outstanding water flux and NOM removal capacity. It was found that the improvement was ascribed to the reduced contact angle, enhanced negative charge, denser structure, and adsorption ability of GO.

Use of diamine for crosslinking the GO on a PES membrane by vacuum filtration was reported by Xia et al. (2015a). The added diamine effectively increased the

interlayer spacing and stretching by forming a C—N covalent bond with GO, which reduced the mass transport resistance. Moreover, the interlayer spacing was smaller than the size of the NOM and, as a result, the nanocomposite membrane could achieve high flux without compromising the NOM removal.

2.3 CONCLUSION AND FUTURE POTENTIAL

In recent scenarios, considerable attention has been paid to carbon-based nano-materials as a nanofiller to fabricate nanocomposite membranes for water and wastewater purification. In particular, these nanomaterials have potentially wide-ranging applications in the fields of desalination, dye removal, oil/water emulsion separation, and NOM removal. Even though most of the CNTs and GO-based nanocomposite membranes are still in the R&D stage, it is anticipated that the commercial market will rise relatively quickly with continuous improve-ments in membrane performance, especially with the ease of preparation and functionalization of CNTs and GO. However, to estimate the cost-effectiveness of commercial production and the long-term stability of the membranes, more research is needed into more efficient production of carbon-based nanocompo-site membranes.

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