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Nanocomposite membranes

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ABSTRACT

Nanocomposites find their application in membrane technology to improve the performance of membrane material and enhance the membrane life. Membrane technology involves processes like microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pervaporation, membrane distillation, dialysis, electrodialysis, gas separation, etc. The advantages of this technology over conventional separation methods are high removal capacity, flexibility of operation, and cost effectiveness. Since the past two decades, synthetic membranes are being researched and commercialized for industrial and domestic use. The membranes may be composed of organic substances (polymers) and inorganic substances (ceramics), though polymeric materials are widely studied due to mechanical strength, flexibility, and chemical stability. However, the main limitation to the greater use of membrane technology is membrane fouling. Fouling is the process of deposition or adsorption of colloids, particles, macromolecules (e.g. proteins, polysaccharides), salts, etc. on the membrane surface and/or inside pores and pore walls. This leads to decline in permeation flux, change in selectivity, and separability during filtration operation and reduces membrane life. When the fouling of membrane is caused by formation of biofilms of extracellular polymeric substances and microbial cells matrix, then it is called biofouling. It is concluded from various studies that intrinsic hydrophobicity of membrane materials is one of the main reasons for fouling. To overcome this drawback, various nanocomposite membranes are being tailored to impart properties such as hydrophilicity, anti-fouling, self-cleaning, photocatalytic, and photodegradation. Nanocomposite membranes are made by incorporating inorganic or organic nanoparticles (NPs) into polymeric membrane matrix. Some of the nanocomposite membranes reported include inorganic NPs viz. TiO_2, SiO_2, Al_2O_3, Si, Ag, ZnO, ZrO_2, $Mg(OH)_2$, $CaCO_3$, $TiSiO_4$, etc., organic NPs viz. graphene oxide (GO), carbon nanotubes, etc., and NP composites viz. GO-SiO_2, GO-TiO_2, SiO_2-TiO_2, Ag-SiO_2, etc. Detailed study is necessary in this area because improper selection of NPs and their composition might deteriorate the performances.

Keywords: Nanofiltration; Nanocomposites; Anti-fouling; Hydrophilicity; Membrane

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1. Introduction

1.1. Membrane technology

Membrane technology is gaining great importance in many of the industrial sectors like food, medicine, pharmacy, biotechnology, water and wastewater treatment, and chemicals. The advantages of this technology over conventional separation methods are high removal capacity, flexibility of operation, and cost effectiveness. Besides these, less energy requirement and easy availability of membrane materials make them more demanding. The technology includes pressure-driven processes like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), and other processes (here we categorize as non-pressure-driven processes) like gas permeation (GP), pervaporation (PV), dialysis, electrodialysis (ED), and liquid membranes. All of these are non-equilibrium-based separations, i.e. they are based on the rate at which solutes transfer though a semipermeable membrane. Forward osmosis (FO) is also included in membrane processes, however, unlike others, this is considered as equilibrium-based process [1].

The origin of the motivation of membrane separation processes lies in the natural biological systems. Most of the chemical engineering processes takes place in the biological systems. Let us take the example of human body. Heart acts as pump to pump the blood into and out of the organs and lung acts as blower to blow the gas in and out of the body. Biological cells are encapsulated within semi-permeable membrane, called cell membrane. The largest organ, skin, acts as barrier to protect us from harmful environment while throwing out sweat, analogous to RO. Stomach absorbs the vital chemicals from food we eat and convert it to vital products by metabolism. The exchange inside tissues of stomach and liver is analogous with MF or UF. Red blood cells (RBCs) act as exchange medium for gasses from cells to alveoli of lungs, and vice versa, analogous to liquid membranes. Alveoli, in turn, exchange air components with inhaled air, analogous to GP. Kidney purifies blood by the process analogous to dialysis. In fact, artificial kidney, commonly known as hemodialysis in medical terms, is the same as dialysis. Exchange of Na^+ and K^+ ions among the neurons for exchange of information can be compared to NF and ED processes.

Since past two decades, synthetic membranes are being researched and commercialized for industrial and domestic use. The membranes may be composed of organic substances (polymers) and inorganic substances (ceramics), though polymeric materials are widely studied due to mechanical strength, flexibility, and chemical stability. Polysulfone (PSf) is most widely used membrane material due to excellent chemical as well as thermal stability [1]. Polymers like Polyvinylidene fluoride (PVDF), Polyether sulfone (PES), Polyacrylonitrile (PAN), Poly(vinyl alcohol) (PVA), Polyvinyl chloride (PVC), Polyethyene (PE), Polypropylene (PP), Polyamide (PA), etc. are also being studied and used.

1.2. Membrane fouling

The major factor that limits the commercialization of most of the membranes is membrane fouling. Fouling is the process of deposition or adsorption of colloids, particles, macromolecules (e.g. proteins, polysaccharides), salts, etc. on the membrane surface and/or inside pores and pore walls. This leads to decline in permeation flux, change in selectivity, and separability during filtration operation and reduces membrane life. Fouling can be categorized based on the type of foulants present in the feed solution. When the fouling of membrane is caused by formation of biofilms of extracellular polymeric substances (EPS) and microbial cells matrix, then it is called biofouling [2]. Colloidal fouling is caused by the inorganic/organic particles or colloids that block the pores of membrane and enhance the cake formation, termed as concentration polarization. Precipitation of salt crystals onto membrane surface due to supersaturation during filtration causes inorganic fouling, usually termed as mineral scaling. Usually, calcium and magnesium salts are responsible for this type of fouling. Organic fouling is caused by dissolved organic matter (DOM) in the form of natural organic matter (NOM), synthetic organic compound (SOC) or soluble microbial products (SMP) [3]. However, there is no such distinct classification of foulants because organic foulants like humic substances are usually derived from biological origin like EPS and are in colloidal form.

Reversible or temporary fouling, also known as concentration polarization, can be removed by backwashing, hydraulic cleaning, chemical cleaning, or even by adjusting/manipulating the flow velocity because foulants are loosely adhered or physically adsorbed on the surface or in the pores. While irreversible or permanent fouling cannot be removed as foulants chemisorbs on to the surface and plug the membrane pores. This leads to flux decline and reduced membrane life. However, cleaning and backwashing steps lead to discontinuity in operation due to maintenance shut-down and creates waste-disposal problems [3–5]. It is concluded from various studies that intrinsic hydrophobicity of membrane materials is one of the main reasons for fouling. Most of the foulants are of biological origin and hence, organic in nature. These organic foulants are usually attracted to hydrophobic membrane surfaces and pores, and adsorbs onto them. The above prevention methods like cleaning or back-washing can only remove reversible fouling. But irreversible fouling that lead to permanent decline in flux can only be reduced by modification in membrane preparing techniques. In next section, some of the membrane preparation and modification techniques will be discussed in brief.

2. Membrane modification techniques

Before starting with modification techniques, some overview about basic preparation methods is discussed in this section. Usually, polymeric membranes are made by casting method, for which polymer dope solution is prepared. Polymer dope solution is the dispersion of polymer in given solvent. Sometimes, additives are also added to the dispersion. Common solvent used to dissolve membrane polymers and some additives are listed in Table 1.

Various preparation methods include non-solvent-induced phase separation (NIPS), thermally induced phase separation (TIPS), evaporation-induced phase separation, track-etching, etc. However, NIPS method, also known as phase inversion via immersion precipitation, is the most widely used preparation technique reported in literature. The procedure is discussed briefly in the next section. To combat the fouling issues, many research studies are going on in the direction of making anti-fouling or low fouling and self-cleaning membrane since a decade and a half. Some of the modification techniques reported in literature are listed briefly in Table 2.

The research on modification of polymeric membranes have been done since past few decades not only for preparing anti-fouling or low fouling membranes but also for improving the desalination of sea water and enhancing the removal of trace metals [31,32]. Shenvi et al. [33] have given a review on RO technology, classifying the membrane materials, membrane modules and associated problems as well as future opportunities. However, major economic development depends on the how much environmental-friendly the chemical/petrochemical processes are, and hence depends on the wastewater and industrial effluent management that requires additional processes to achieve "zero discharge" with minimum "carbon footprints". Hence, separation processes employing membranes always expect membranes to have consistent flux, higher rejection and maximum durability which require developing the anti-fouling or self-cleaning high-performance nanocomposite membranes.

3. Nanocomposite membranes

To mitigate the fouling and to make the membrane anti-fouling or fouling resistant, various inorganic metal/metal oxide or carbon-based nanoparticles have been used in polymeric membranes because of the properties such as hydrophilicity, anti-fouling, self-cleaning, photocatalytic, photodegradation, etc. Different membranes can be tailored with some or all of these properties but the overall effect should be prevention in fouling. Inorganic materials like alumina, zirconia, silica, etc. mostly used as fillers, improved the performance of membrane process by enhancing the permeate flux, increasing the salt rejection and improving the thermal, chemical and mechanical stability [34–37]. However, due to large size of these particles, their use was limited to MF and UF, which requires membranes of pore size ca. 0.1 micron and ca. 0.01 micron, respectively. With the development in the field of novel materials with at least one dimension in nano-range, the scope of application of inorganic materials was extended to NF as well as RO. In the present context, nanocomposite membranes

Table 1
Solvents and types of additives

Solvents	
Water, N,N´-dimethyl acetamide (DMAc), N,N´-dimethyl formamide (DMF), N-methyl-2-pyrrolidone (NMP), Tetrahydrofuran (THF), etc.	
Additives	
Pore-forming agent	Poly vinyl pyrrolidone (PVP), Polyethylene glycols (PEG) - PEG400, PEG600, PEG2000, etc.
Cross-linking agent	Glutaraldehyde, Tetra ethoxy silane, Borax, etc.
Surface modifier	Metal/Metal oxide nanoparticles, Amphiphilic block co-polymers—e.g. Pluronic F127, PEO, PPO, etc. Zwitterionic co-polymers as studied in various literature.
Fillers	Silica, Alumina, Titania, Zirconia, Zeolites, etc.

Table 2
Membrane modification techniques

Membrane material	Modification	Refs.
Surface modification		
Polypropylene (PP)	Grafting of ozone-treated PP membrane by 2-hydroxyethyl methacrylate (HEMA)	[6]
Cardo-polyetherketone (PEK-C)	UV-induced grafting with acrylic acid monomer	[7]
Polypropylene (PP)	Plasma treatment in CO_2, NH_3 atmosphere	[8,9]
Polyether sulfone (PES)	Adsorption of PVA and crosslinking with Borax solution	[10]
Polysulfone (PSf)	UV-initiated grafting polymerization with [3-(Methacryloylamino)propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide inner salt (MPDSAH) using benzophenone as photo- initiator.	[11]
PVDF- and PSf-based amphiphilic PSf-/PVDF-graft-PDMAEMA; PDMAEMA = poly(N,N-dimethylamino-2-ethylmethacrylate)	Different concentration of PSf-/PVDF-g-PDMAEMA in PSf/PVDF base—treating with two quaternizing agents (viz. 3-bromopropionic acid (3-BPA) and 1,3-propane sultone)	[12,13]
PES	PVA coating and immersion into cross-linking bath of 5 wt% Glutaraldehyde and 0.5 wt% H_2SO_4	[14]
PES	N,O-carboxy methyl chitosan (NOCC) coating over PES membrane and then, cross-linking using glutaraldehyde.	[15]
PES	Acrylonitrile butadiene styrene (ABS)/chitosan (CS) polymer blend casted over PES substrate	[16]
PAN	Sulfated chitosan coating over PES and then crosslinking using epichloro hydrine (ECH)	[17,18]
Polymer blend modification		
PAN-DMAEMA based zwitterionic copolymer in PAN	Reaction of DMAEMA radical with 1,3-propane sultone to form zwitterionic copolymer with PAN	[19]
PAN-MPDSAH in PAN; MPDSAH = ([3-(Methacryloylamino)propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide)	Acrylonitrile and MPDSAH randomly co-polymerized using azobis-isobutyro-nitrile (AIBN) as initiator to form PAN-MPDSAH	[20]
P(HFBM-SPP) in PVDF; HFBM = hexafluorobutyl methacrylate; SPP = [3-(methacryloylamino)propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide	Different concentrations of HFBM in amphiphilic co-polymer P(HFBM-SPP)	[21]
PVC/Polyvinyl formal (PVF)	Different concentrations of PVF with PVC dissolved in DMAc	[22]
Cellulose acetate (CA)	Casting solution prepared from different blends of NOCC/CA	[23]
Reactive modification		
Acetalized PVA	Reacting concentrated aqueous PVA solution with acetaldehyde in the presence of HCl—different degree of acetalized PVA/PEG600—DMAc casting solution prepared	[24]
Tertiary amine grafted PES (TA-PES)	Chloro-sulfonation of PES to S-PES and then amination of S-PES to TA-PES, then solution prepared by adding with PEG2000 into DMF	[25]
PES-TA, PES-CB, PES-SB; PES-TA = Poly(arylene ether sulfone) bearing pendant tertiary amine groups; PES-CB = carboxybetaine poly(arylene ether sulfone); PES-SB = Sulfobetaine poly(arylene ether sulfone)	Monomer obtained from Phenolphthalein and N,N,-Dimethyl-1,3-propanediamine (DMAPA), reacted with 4,4-Difluorodiphenyl sulfone (DFDPS) to get PES-TA, which is zwitterionicalized with sodium bromoacetate and sodium-2-bromoethanesulfonate to yield PES-CB and PES-SB, respectively	[26]

(*Continued*)

Table 2 (*Continued*)

Membrane material	Modification	Refs.
Sol–gel method		
PES	Tetraethyltitanate (TET) added to DMAc with appropriate amount of HCl and Deionized (DI) water to yield TET sol—then added to PES-DMAc solution	[27]
PSf	Tetrabutyltitanate (TBT) added to NMP with appropriate amount of HCl and DI water to yield TiO_2 sol—then added to PSf/PVP-DMAc/NMP solution	[28]
PVDF	Tetraethoxysilane (TEOS) and DI water added DMF and pH adjusted by HCl to yield SiO_2—then different concentrations of sol doped into PVDF-DMAc solution	[29]
PVA	TEOS added to HCl and DI water to get SiO_2 sol—then different concentrations of sol added to PVA/PEG aqueous solution	[30]

mean modification of polymeric membranes (usually, MF, UF, NF, and RO membranes) using nanoparticles (NPs) or the composite of nanoparticles (here we refer to as nanoparticles composite). NPs used for membrane modification are mostly metal, metal oxide, or carbon nanotechnology-based NPs.

3.1. Metal and metal oxide nanocomposite membranes

Organic–inorganic membranes are classified as mixed-matrix nanocomposite membranes and thin-film nanocomposite membranes. In former type, nanoparticles are dispersed into polymer casting solution before membrane casting, hence also called as nanoparticles-blend membranes or nanoparticles-entrapped membranes. In latter type, nanoparticles are allowed to self-assemble onto membrane surface and pores by dip-coating or pressurized deposition on the prepared membrane. For example, thin-film nanocomposite membranes were prepared by Pourjafar et al. [14] in which PVA was coated and cross-linked onto PES membrane and then, self-assembled with TiO_2 nanoparticles.

Most of the inorganic nanoparticles (NPs) used in membrane modification are either metal or metal oxide, with some exceptions like $Mg(OH)_2$ [38], $CaCO_3$ [39], hydrous manganese dioxide NPs [40], etc. reported in recent years. The advantage of using metal oxide NPs is their easy and well-developed synthesis method, cost effectiveness, and improvement in hydrophilicity of membrane. There have been bountiful of literature published on application of TiO_2 NPs in polymer membranes since past decade because of their excellent photocatalytic effect in decomposing organic foulants and microbes. This effect is explained well by Miyauchi et al. [41] as well as Madaeni and Ghaemi [5], independently in their works. Briefly, on illuminating TiO_2 NPs with ultraviolet (UV) light, two phenomena are observed: (1) electron–hole pairs are generated that reacts with oxygen producing superoxide radical, which decomposes the foulants on the membrane surface, and (2) the empty sites of O_2^- radical adsorbs OH^- groups from water molecules, thereby inducing ultra-hydrophilicity. In recent years, several papers were published in literature describing studies on membranes modified with NPs by self-assembly, entrapment (i.e. impregnated or embedded or blended), pressurized deposition, dip-coating, sol–gel method, etc. for analyzing fouling performance, and some of these methods have been reviewed in the literature [2,42,43]. Table 3 lists out some of the examples of works done in this area.

Self-cleaning property of TiO_2/polymer nanocomposite membrane was studied by Madaeni and Ghaemi [5] and Damodar et al. [51], independently. Both the works represent the example of thin-film nanocomposite membranes and mixed-matrix nanocomposite membranes, respectively. The affinity of metal oxide toward water keeps the membrane surface hydrated by hydrogen bonding while removing the contaminants. This phenomenon happens by exposing membrane surface to UV light so as to induce photocatalysis. Kim et al. [45] prepared PA thin film composite (TFC) membrane by interfacial polymerization of m-phenylene diamine (MPD) and trimesoyl chloride (TMC) on the PSf support. TFC is then dipped in the TiO_2 colloidal solution that was prepared from titanium tri isopropoxide. The self-assembly of TiO_2 on the PA TFC is described in the Fig. 1. The photocatalytic effect of TiO_2 self-assembled membrane was studied using *Escherichia coliform* (*E. Coli*) cells [45,51,60].

Yang and Wang [28] used metal oxide nanocomposite membrane of PSf/TiO_2 prepared by sol–gel

(a) Bidendate coordination with Ti^{4+} group (b) Hydrogen bonding with OH^- group

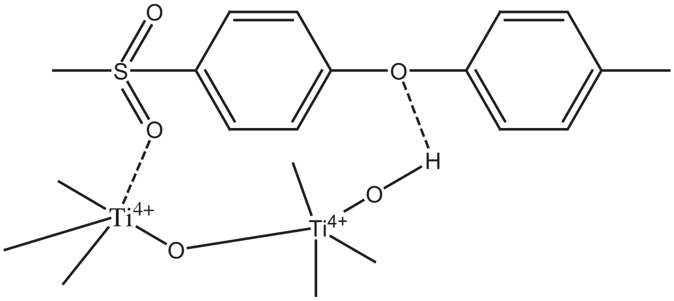

Fig. 1. Self-assembly mechanisms of TiO_2 NPs on carboxyl group of polyamide (Adapted from [45]): (a) bidendate coordination with Ti^{4+} group and (b) hydrogen bonding with OH^- group.

technique to study the UF performance. The precursor used for TiO_2 sol was tetrabutyl titanate (TBT). The different amount of sol was added to casting solution of PSf in DMAc and NMP as solvent, and PVP as pore-forming agent. After casting, glass piece was immersed in coagulation bath of ethanol/water mixture. Since PSf is hydrophobic in nature, doping with TiO_2 led to decrease in contact angle due to hydrophilicity induced by the NPs. The anti-fouling performance of TiO_2/EPVC was analyzed by flux recovery experiment, in which pure water flux as well as flux of model foulant solution, 500 ppm bovine serum albumin (BSA) solution, was calculated in alternate cycle at different time interval as described by Rabiee et al. [59]. Similarly, SiO_2/PVC nanocomposite UF membranes were prepared by Yu et al. [69]. The hydrophilicity of SiO_2 NPs is due to the hydrogen bonding between hydroxyl group of water and SiO_2, which repels hydrophobic foulant protein, BSA molecule, resulting in good anti-fouling ability and higher flux recovery. Liang et al. [74] used ZnO-blended PVDF membrane to analyze anti-fouling performance. ZnO NPs were found to decrease the membrane surface contact angle significantly, and the flux recovery ratio reached near to 100%. Besides hydrophilicity, ZnO NPs also have antibacterial property, and are rather cheaper than TiO_2 NPs. The hydrophilic and photocatalytic nature of ZnO is comparable with TiO_2 as described by Miyauchi et al. [41].

Metal nanocomposite membranes were not widely studied because metal oxides NPs with special properties like photocatalysis, hydrophilicity, antibacterial, etc. [41] dominate over bare metal NPs. However, the only metal nanoparticles used with positive outcome were silver nanoparticles, due to their excellent antibacterial property and hydrophilicity. For example, Li et al. [84] used silver NPs with polyacrylic acid (PAA)-grafted PVDF membrane that was prepared in three steps. Firstly, PVDF membrane was prepared by phase inversion technique. Secondly, grafting of PAA occurs by wetting membrane surface with azobisisobutyro-nitrile (AIBN) and dipping into acrylic acid solution. Thirdly, silver ions from silver nitrate was made to bond with PAA brush, and then reduced to NPs by sodium borohydride. Similar surface modification of PSf with Fe_3O_4 NPs was reported by Homayoonfal et al. [87]. Three ways of synthesis was used for comparative study: Blending iron oxide NPs, UV photografting with acrylic acid/iron oxide dispersion, and depositing PA/iron oxide via TMC. Hydrophilic nature of iron oxide NPs led to decrease in contact angle with increasing NP concentration. Combination of different techniques and different metal/metal oxide NPs with different properties are continuously being researched for the common purpose of making anti-fouling or self-cleaning membrane. Next section deals with carbon nanotechnology-based membranes.

3.2. Carbon nanotechnology-based membranes

Carbon nanotechnology has attracted more attention since past decades due to their astonishingly different properties compared with their precursors and macro-sized or micro-sized counterparts. Carbon nanotube (CNT) is two-dimensional nanomaterial and an allotrope of carbon, known for their excellent surface adsorption, chemical, mechanical, and thermal properties [90]. It can be single-walled (SWCNT) or

Table 3
Metal/metal oxide NPs for membrane modification

Membrane base material	Method	Refs.
TiO_2		
PES	Blending and self-assembly	[44]
Polyamide TFC	Self-assembly	[45]
PSf, PVDF, PAN	Blending and pressurized deposition	[46]
Sulfonated PES (SPES)	Self-assembly	[47,48]
Polyamide coated PES	Self-assembly	[49]
PVDF	Blending	[50,51]
PES	Self-assembly	[52]
PES	Sol–gel	[27,53]
Poly (styrene-alt-maleic anhydride) alternative copolymer (SMA)/PVDF	Self-assembly	[54]
PSf	Blending	[55]
PSf	Sol–gel	[28]
PES	Blending	[56–58]
Emulsion PVC	Blending	[59]
PVDF/Sulfonated PES (SPES)	Blending	[60]
PVA coated PES	Self-assembly	[14]
PSf/Chitosan (CS)	Blending	[61]
PES	Blending of TiO_2 nanotubes	[62]
PVDF	Blending	[63]
PES	Blending of TiO_2 nanotubes stabilized by SDS	[64]
SiO_2		
PES	Blending	[65]
PVDF/Glycidyl methacrylate (GMA)	Blending	[66]
PVDF	Sol-gel	[29]
Polyamide laminated PSf	Dip-coating of commercial as well as as-synthesized NPs	[67]
PSf	Blending	[68]
PVC	Blending	[69]
PSf/PVA	Blending	[70]
PVC	Sol-gel	[71]
ZnO		
PES	Blending	[72,73]
PVDF	Blending	[74,75]
PSf	Blending	[76]
PVDF	Dip-coating of pre-treated PVDF as well as blending	[77]
PES	Nano-ZnO dispersion produced in DMF	[78]
Miscellaneous		
PVDF	Blending of Al_2O_3 NPs	[79–81]
CA	In situ reduction of $AgNO_3$ to Ag^0 NPs in DMF	[82]
PES	m-phenylene diamine (MPD) aqueous phase and silver (Ag) NPs dissolved in organic phase polymerized onto PES substrate	[83]
Polyacrylic acid (PAA) grafted on PVDF	Silver ion surface adsorption and reduction	[84]
Nafion resin	Blending of ZrO_2 sol prepared from tetrabutyl zirconate (TBZ)	[85]
PES	Blending of ZrO_2 sol prepared from zirconyl chloride	[86]
PSf	Fe_3O_4 NPs—Blending, surface deposition via acrylic acid as well as interfacial polymerization with polyamide (PA) and iron oxide NPs	[87]
PVC/CA	Blending of Fe_3O_4 NPs	[88]
PES	Fe_3O_4, SiO_2-coated Fe_3O_4, metformin-modified-silica coated Fe_3O_4, amine-modified-silica coated Fe_3O_4 Nanoparticles	[89]

multi-walled (MWCNT). Another form of carbon nanomaterial invented after CNTs is graphene, which is one-dimensional nanomaterial. Graphene possess surprisingly high surface area to weight ratio, hence good mechanical and thermal stability. Graphene oxide (GO) is oxidized form of graphene, and is hydrophilic in nature, unlike graphene which is hydrophobic. Preparation of GO was reported in many literature; however Hummers' method [91] and modified Hummers' method [92] is the most widely used technique. Graphene-based nanomaterials including nanoplateletes, nanosheets, reduced form of grapheme oxide (rGO), etc. have recently gained attention for their application in water desalination [93,94]. Some of the application of carbon-based nanocomposite membranes in recent years are listed in Table 4.

The as-synthesized MWCNTs are usually hydrophobic in nature; however, they are hydrophilized and used in membranes. Choi et al. [95] fabricated MWCNTs/PSf nanocomposite membrane by usual phase inversion technique. Before using MWCNTs, surface modification was done by treating with concentrated nitric and sulfuric acid. The result is that the surface of CNT is now functionalized by carboxyl and hydroxyl groups, thereby rendering them hydrophilic. Little more advanced step of modification was used by Qiu et al. [96] where acid-treated MWCNTs were rinsed with deionized water and after drying, were reacted with 5-isocyanato-isophthaloyl chloride (ICIC). This functionalized MWCNT/PSf blend membrane was used to analyze protein adsorption tendency. Roy et al. [98] prepared NF membrane modified with hydrophobic CNTs (functionalized with –COOH groups) as well as hydrophilized CNTs (functionalized with –CONHR groups). The base membranes used were hydrophobic PP flat membrane and hydrophilized PES flat membrane. These base membranes were interfacially polymerized by various methods as mentioned in the literature. The result was higher flux and improved solute rejection. On the other hand, Chang et al. [102] used PVP/GO in PVDF to study the possible interaction between PVP and GO. It was reported that the presence of carboxyl and hydroxyl groups in GO is responsible for forming hydrogen bonding with the hydrophilic PVP. Water flux increased with the increase in PVP content while BSA rejection decreased, owing to the increased porosity. Ganesh et al. [103] reported GO/PSf blend membrane, which was prepared by dispersing desired amount of GO in NMP and then, mixing them in PSf-NMP solution. The advantage of using NIPS method is that the hydrophilic nature of GO tends to draw them to the pore surfaces when immersed in water coagulation bath during phase inversion that is schematically presented in Fig. 2. Pure water flux was enhanced while the salt rejection decreased at higher pressure. However, salt rejection was higher for membrane with 2,000 ppm GO content compared to that with 1,000 ppm GO content.

Zhang et al. [106] modified PVDF membrane with GO-OMWCNT mixture. The zeta potential analysis proved that zeta potential of GO-OMWCNT mixture was found to be higher than GO and OMWCNT, which indicated good resistance to aggregation. AFM was used to measure interaction force between BSA molecule and membrane surface, for which BSA-immobilized tip was used. The result showed that neat PVDF membrane has stronger attraction with BSA tip, compared to nanocomposite membranes

Table 4
Carbon nanotechnology-based NPs for membrane modification

Membrane base material	Material/Method	Refs.
PSf	Modified MWCNTs/Blending	[95,96]
Brominated polyphenylene oxide (BPPO)	MWCNTs/Blending	[97]
PP as well as PES	MWCNTs/Surface coating	[98]
PES	MWCNTs/Blending	[99]
PAN	MWCNTs/Blending	[100]
Chitosan (CS) coated PES	MWCNTs/Blending with CS	[32]
PVDF	GO/Blending	[101,102]
PSf	GO/Blending	[103–105]
PVDF	GO-Oxidized MWCNTs (OMWCNT)/Blending	[106]
PVDF	GO-MWCNT/Blending	[107]
PES	GO/Blending	[108]
PVDF	Functionalized GO/Blending	[109]
PVDF	GO nanoplatelets/Blending	[110]
PVDF	GO/Water bath coagulation	[111]
PES	Functionalized MWCNTs/Blending	[112]

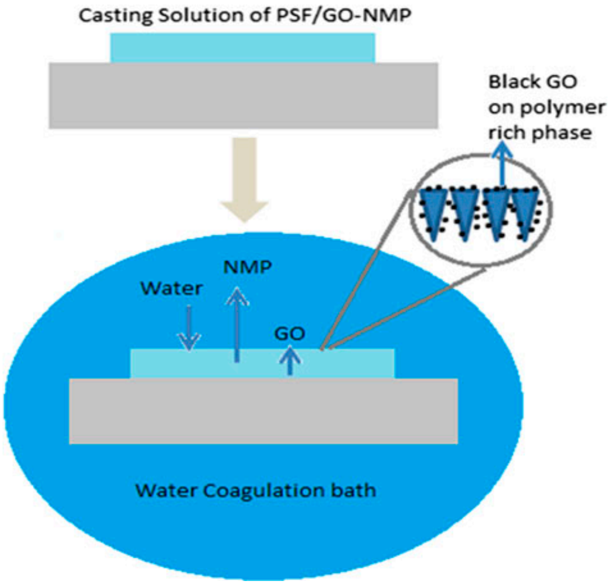

Fig. 2. Mechanism of NIPS resulting in GO nanosheets layering on the membrane and pore surface (Adapted from [103]).

containing GO-OMWCNT mixture. Xu et al. [109] reported the use of functionalized GO in PVDF membrane. The functionalization was done by dispersing GO and N,N´-dicyclohexyl-carbodiimide (DCC) in 3-aminopropyltriethoxysilane (APTS) for reaction. Like Zhang et al. [106], force extension curves between protein-immobilized tip and membrane were studied with AFM [109]. Different carbon-based NPs functionalized with various radicals are under research and development. Some metal/metal oxide nanocomposite membranes as well as carbon nanotechnology-based membranes were reviewed in the literature [42,113]. While the nanoparticles composites of metal/metal oxide NPs with carbon-based NPs for membrane processes are reported in various research papers as discussed in the next section.

3.3. *Nanoparticles composite membranes*

With the increasing demand of novel materials to combat water and energy crisis and for sustainable environment, entirely new kind of nanoparticles composites with enhanced properties compared to aforementioned NPs have been worked upon by many chemical and material science researchers such as coating of NPs over microspheres, decorating NPs with some other nanomaterials, incorporating NPs with some other nanomaterial, functionalization of NPs, etc. As described in the previous section, functionalized GO/PVDF membrane [109] lies under this category. GO was functionalized with organo-silane groups with the objective of improving the dispersion in PVDF polymer matrix due to increased interaction between polymer and nanoparticles composite. Various studies on membranes modified by nanoparticles composites (here referred to as "nanoparticles composite membranes") are discussed in this section. Zhang et al. [114] synthesized Cerium-doped non-stoichiometric nanosilica particles and blended them in PSf casting solution, which resulted in improved hydrophilicity, and hence improved permeate flux and rejection that was verified by filtration of oil-in-water emulsion. Similar studies were carried out to show the effect of addition of sulfated yttrium-doped non-stoichiometric zirconia (SO_4^{2-}/ZrO_2-Y_2O_3-SZY nanoparticles) on the oil rejection performance of PSf membrane. SZY/PSf nanoparticles composite membranes were prepared by well-known NIPS method. It was observed that oil retention as well as flux increased with increase in SZY NPs content [115,116]. Silver-loaded sodium zirconium phosphate (nanoAgZ) nanoparticles were used to modify PES membrane to evaluate anti-fouling performance using BSA filtration and anti-bacterial properties using *E. Coli.* and *Pseudomonas* suspension [117]. Hydrophilicity was improved with increase in NPs content which was verified by contact angle measurement. Mo et al. [118] prepared TiO_2-SiO_2/PA/PSf nanocomposite membranes by interfacially polymerizing PA layer onto PSf support membrane, and then allowing to react with 3-aminopropyltrimethoxysilane (APTMOS), and finally, dipping into TiO_2 dispersed in organic phase. Fig. 3 shows the basic mechanism of surface modification.

Self-assembly of GO-TiO_2 over commercial cellulose acetate (CA) membrane was reported in the research paper [119]. TiO_2 microspheres were prepared from TBT as precursor and added to aqueous solution of GO. After sonication and vacuum-drying, the GO-TiO_2 composites were self-assembled by spreading over membrane surface and applying nitrogen pressure. 20 mg/L Humic acid (HA) feed solution was used to analyze anti-fouling performance. Under UV illumination, photodecomposition of HA was

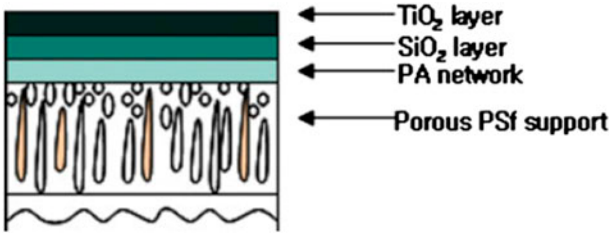

Fig. 3. Scheme of surface modification of PSf membrane with polyamide and nanoparticles composite (Reproduced with permission from Wiley Periodicals, Inc. [118]).

analyzed by TOC analyzer. TiO_2-GO nanoparticles composite possess enhanced photocatalysis because GO is able to extend the photoresponse range of TiO_2 from ultraviolet region with shorter wavelength to sunlight region with longer wavelength. Gao et al. modified the commercial PSf membrane using TiO_2-GO in following steps: (a) pouring TiO_2 aqueous solution onto membrane surface and depositing by stirring, (b) removing excess $TiO_2$and drying in oven, (c) pouring GO and depositing onto TiO_2-layered membrane, and (d) washing coated membrane with ethanol and exposing to UV light. Firstly, TiO_2 assembles on PSf as described in Fig. 1. Then, functionalized GO containing carboxyl and hydroxyl groups bonds self-assemble onto TiO_2 to form nanoparticles composite membrane [120]. Similarly, superhydrophilicity of SiO_2-GO [121] was exploited for preparing nanocomposite membrane of PSf [122]. The fouling performance was characterized by performing BSA rejection experiment and calculating permeate flux of water and BSA solution at different time intervals alternatively with washing cycles. It was found that SiO_2-GO/PSf membrane gave higher flux recovery, compared to GO/PSf and SiO_2/PSf [122]. Recently, Safarpour et al. [123] prepared reduced GO/TiO_2 nanocomposites with their different ratios to blend them in PVDF membrane; while contact angle measurement showed improved hydrophilicity, and BSA rejection was found to increase as well as flux recovery was improved as compared to bare PVDF membrane. Also, anti-fouling membranes were prepared with Ag-TiO_2 [124] and Ag-SiO_2 [125,126] NPs composites, and antibacterial effects of Ag-based nanocomposites were reported along with filtration experiment for flux recovery ratio.

Ag-TiO_2 nanoparticles composite membrane was developed by coating onto macroporous alumina support [124]. The evaluation was done in the photocatalytic membrane reactor equipped with UV light. Apart from antibacterial action on *E. coli* bacterial culture, photocatalytic degradation of rhodamine B dye was also tested. Flux recovery experiment was performed with and without UV light. SiO_2-Ag/PES nanoparticles composite membranes were prepared by Yu et al. [125] using TEOS and silver nitrate ($AgNO_3$) as precursors. The membrane anti-fouling performance was characterized by filtration experiment by calculating the flux recoveries, while the antibacterial properties were evaluated with two different bacterial cultures, viz., *E. coli* and *Staphylococcus aureus* (*S. aureus*). Similarly, Huang et al. [126] used the same starting materials for the preparation of nanoparticles composites, Ag-SiO_2 to modify PES. It helped to combine good antibacterial ability due to Ag with higher pure water permeability due to SiO_2. With the advances in nanomaterials science and technology, it has become easier to combine the properties of different materials by developing nanoparticles composites, and exploiting them in each and every field of science, engineering and technology which remains the task of researchers.

4. Characterization techniques

In the world of science and technology, invention and innovation starts from research and development. And to prove each and every new inventions,

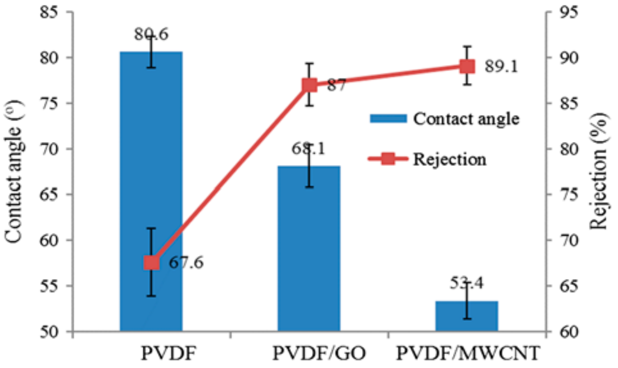

Fig. 5. Contact angle and rejection values plotted for different membranes (Data used from [107]).

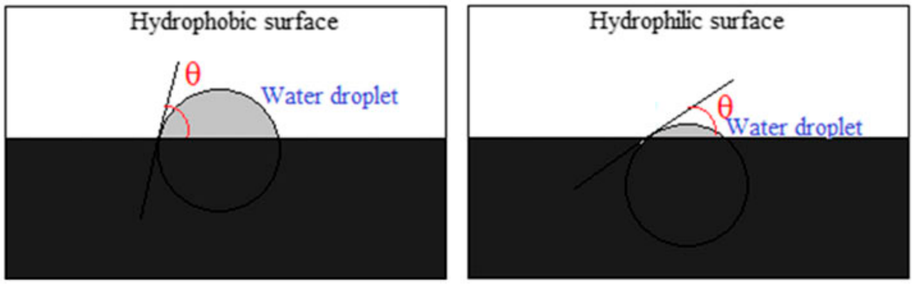

Fig. 4. Contact angle measurement between water droplet and membrane surface (Adapted from [84]).

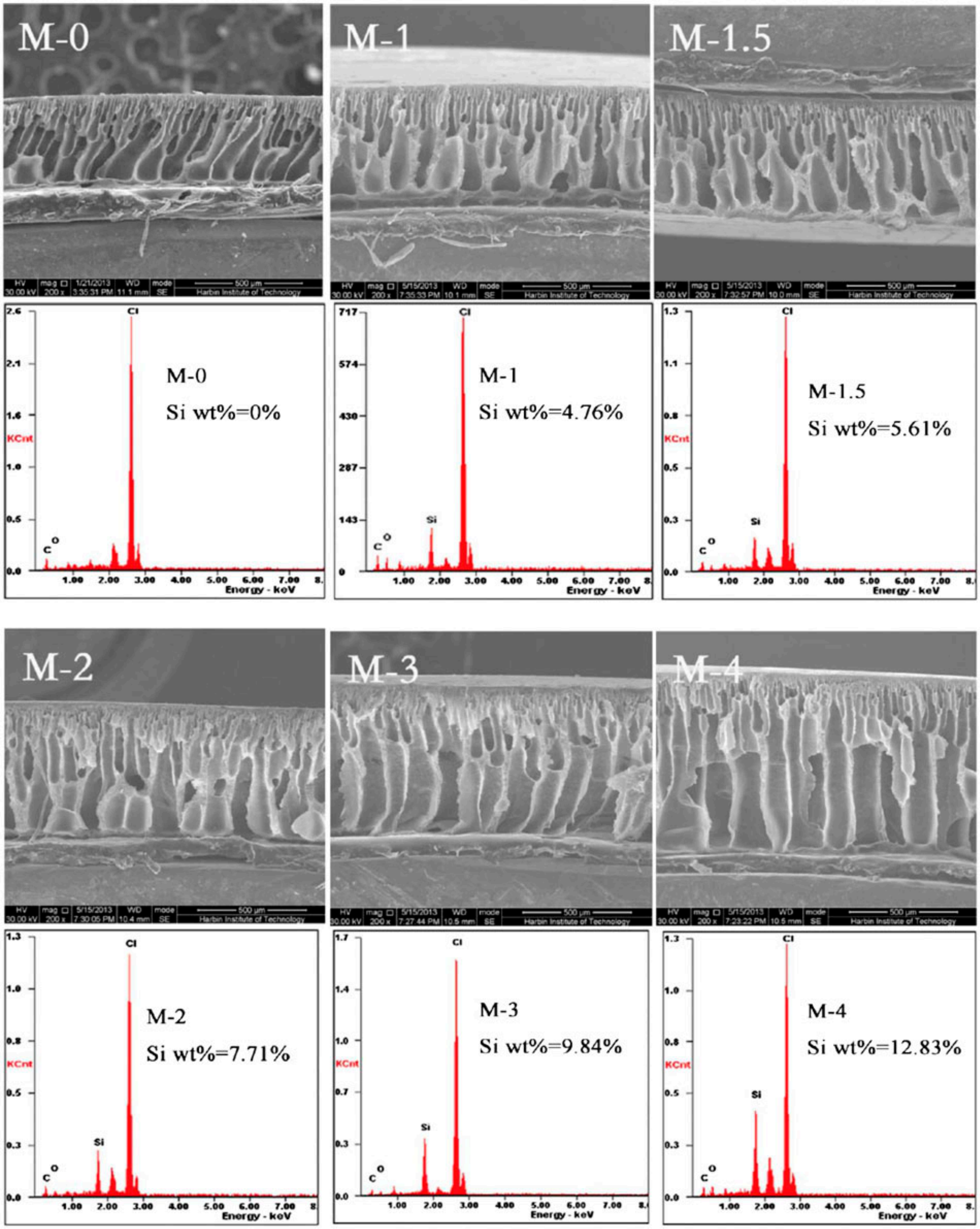

Fig. 6. SEM cross-sectional image and EDS spectrogram study of neat PVC and five different SiO_2/PVC membranes (Reproduced with permission from Wiley Periodicals, Inc. from [69]).

characterization techniques play vital role. SEM, TEM, AFM, X-ray diffraction (XRD), FT-IR, X-ray photoelectron spectroscopy (XPS), EDS, Dynamic Light scattering (DLS), contact angle measurement, TGA, zeta potential, etc. are common techniques used for characterization of nanocomposite membranes. The contact angle between water and membrane surface is the measure of the hydrophilicity of membrane surface. It was usually measured with contact angle goniometer applying sessile drop method. The initial contact angle of silver NPs modified PAA-grafted-PVDF membrane was measured as explained in Fig. 4. The higher the water contact angle, less will be the spreading of water droplet, indicating hydrophobic nature of surface, while lower contact angle means more wetting surface, and hence more hydrophilicity [84].

The effect of hydrophilicity on the BSA rejection of PVDF/GO and PVDF/MWCNT nanocomposite membranes can be seen in the Fig. 5 [107]. Almost, all the researchers working on the area of nanocomposite anti-fouling membranes have reported the use of this characterization technique to get basic idea about the nature of membrane surface. The surface morphology of different membranes can be compared by direct method of scanning electron microscopy (SEM). The comparison was usually made among neat unmodified membranes and membranes modified with different content of NPs. Energy dispersive X-ray spectrometer (EDS) equipped with SEM is used for chemical composition analysis of the membrane surface. SiO_2 content on the surface of SiO_2/PVC blend membranes was characterized nicely by SEM-EDS as shown in Fig. 6 [69]. We can observe that increase in the silica content of the membrane was proved by EDS spectrogram, showing the increasing accumulation of silica on the surface through silicon peaks. Atomic force microscopy (AFM) is used to study the surface roughness and topography by getting three-dimensional images, as well as to determine the interaction force acting between tip and membrane surface and getting force extension curves by immobilizing tip with, for example, protein foulants, especially BSA, as reported in some research papers [106,109]. A recent review by Johnson and Hilal [127] on membrane surface characterization using AFM mainly focuses on the versatility of the technique. Fourier-transform infrared (FT-IR) spectra of MWCNT/PSf membrane by the stretching vibrations helped to analyze the presence of various groups, viz., –OH, –CH, –C=O of ketones and carboxylic acid, C=C, C–O–C, S=O, etc. [95]. Functionalization over MWCNTs was verified by XPS spectrum showing peaks for C 1s, O 1s, N 1s, and Cl $2p^3$ [96]. FT-IR spectra was obtained for nanoparticles and their composites to characterize and compare GO and SiO_2-GO NPs so as to draw conclusion regarding anti-fouling and hydrophilic behavior based on functional groups, while XPS helped to verify and differentiate between GO and SiO_2-GO by the presence of peaks for silicon (Si) [122]. XRD technique verified the presence of iron oxide NPs in PSf membrane which was easy to conclude using XRD patterns [87]. DLS gives the particle size distribution of the colloidal suspension of NPs.

There are several techniques being developed for characterization of NPs in solid as well as in liquid state. Surface charge density and zeta potential of membrane surface can be characterized with sophisticated equipment. Zeta potential is the measure of tendency of the particles to resist aggregation. Higher the value of zeta potential, lower will be the aggregation, and more stable will be the NPs. Zeta potential of the modified PVC membranes were compared with neat PVC membranes using electrokinetic analyzer in the literature [128]. The detailed descriptions of the various methods of membrane characterization are available in literature [127,129,130].

5. Conclusions

Several conclusions can be drawn from this brief review on nanocomposite membranes. Some of them can be listed as follow:

(1) Most of the focus is made on MF, UF, NF, and RO membranes as their fouling tendency is higher than PV or GP membranes.
(2) Metal oxide NPs can be used in hydrophobic membranes to improve the anti-fouling performance. However, efficient surface coating method should be developed rather than using NPs blend membranes or entrapped membranes so as to ensure maximum utilization of NPs.
(3) TiO_2 NPs have been exploited enough since past decade so now, effort should be to use them as composites with GO, MWCNT, SiO_2, and Ag.
(4) Carbon-based nanomaterials can be hydrophilized as well as functionalized with metal/metal oxide NPs which can enhance the chemical properties of the latter while imparting the mechanical properties of the former.
(5) Development of novel nanomaterials will always keep the doors open for the research and development in the field of anti-fouling membranes.
(6) Hence, introduction of different characterization techniques becomes essential for membrane processes to get the proper insight into the behavior of materials at nanoscale.

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