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Mixed Matrix Membranes for Water Purification Applications

Danial Qadir, Hilmi Mukhtar, and Lau Kok Keong
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Membrane technology has been utilized for water purification application for a long time. Both polymeric and ceramic membranes have been center of interest for their tremendous contribution in this area. Despite their advantages, these synthetic membranes have limitations in terms of performance and durability. To meet the new demands and standards, mixed matrix membranes (MMM) have gained serious importance due to their ability to combine the features of the aforementioned membrane materials, offering better solutions in terms of performance, fouling, permeate quality and longevity. Besides such attractive features, MMMs have not yet reached sufficient maturity to challenge conventional membranes commercially. This review categorizes MMMs on its fuller basis into four types; (i) inorganic filler-based MMMs, (ii) organic filler-based MMMs, (iii) biofillers-based MMMs, and (iv) hybrid filler-based MMMs. A discussion is extended to modules and cost of these membranes along with the specific applications of each type of fillers. It also identifies the issues and challenges in the MMM area and highlights the domains that remain to be investigated.

Keywords: Water purification, synthetic membranes, mixed matrix membrane, filler types

INTRODUCTION

Water is indispensable for every human being and availability of safe drinking water should be assured as declared by United Nations Development Program in 2006 (1). A worrisome number 2.6 billions of human populations is suffering from deprivation of fresh water around the globe. It is estimated to cause the death of 3900 children each day while sickening a significant number among the population on a global basis (2). Water usage has been reported to be under great stress recently because of urbanization, climate change, industrialization, population and hyped food demands. These factors have asserted an extra pressure on water purification industry to meet the ever increasing demand (3). Previously, surface water and groundwater were appraised as sufficient freshwater resources, but industrialization has pushed mankind to meet the increasing fresh needs uncovering sea water, brackish water and wastewater as a valuable addition to the existing naturally fresh resources (4).

Many conventional and non-conventional technologies such as adsorption, disinfection, coagulation and flocculation have been employed to treat raw water to achieve the desired water quality for daily use (5). But many of these have failed to satisfy the new levels of water quality standards because of their inability to remove modern pollutants. Membranes have become the most viable option and alternate to the previous technologies (2, 6).

A membrane is a thin semi-permeable barrier that retains the contaminants and allow water to permeate, i.e., to pass through. The basic mechanisms of rejection for these contaminants involve sieving, diffusion or charge-charge interaction. A pressure difference across the membrane is the driving force for separation to occur (7–11). Figure 1 highlights the vital parameters for water filtration membranes.

Polymeric and ceramic membranes have been used extensively in water treatment industry. Both types of membranes have their pros and cons. Over the years, researchers...
have been trying to combine the effective features of both, polymeric and ceramic, materials in one new material called mixed matrix membrane (MMM) or hybrid membrane. The sole purpose of developing this new material has been to associate the advantageous characteristics of the two types of membranes boosting the overall process efficacy. Conventionally, objectives such as enhancement in permeability or selectivity, reduction in fouling and removal of specific contaminants have been attained either by combining two or more processes or by developing an integrated filtration process. However, material advancement in membrane technology has made it possible to fine tune the process efficiency and have successfully paved the way for MMMs in water filtration applications.

Apart from the water purification applications, the advent of MMMs has revolutionized other areas also where separation or purification is of great significance. Some of these potential applications reported in literature include blood purification (12, 13), toxins removal from human plasma (14), methanol fuel cell (15), sensors and biosensors (16), and wound dressing (17). Table 1 offers a brief comparison between available membrane types based on their materials and their characteristics. Membranes are developed for four different types of membrane types based on their materials and their characteristics. Membranes are developed for four different types

![Image](image-url)

**FIGURE 1** Vital parameters for membrane selection.

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<td>Water flux</td>
<td>Low-High</td>
<td>High</td>
<td>High</td>
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<tr>
<td>Salt rejection</td>
<td>Moderate-High</td>
<td>Low-Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Fabrication simplicity</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Improved stability</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>Tunable selectivity</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>Operational cost</td>
<td>Moderate-High</td>
<td>Low</td>
<td>NA</td>
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<td>Fouling</td>
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<td>techniques</td>
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</table>

TABLE 1  
Comparison of different types of membranes used for water purification [adapted from (11, 24, 27-30)]

**MIXED MATRIX MEMBRANES**

**Introduction**

MMMs can be defined as being an incorporation of nano-materials (solid, liquid or both) dispersed/embedded in a continuous phase. The continuous phase is a polymeric material and the dispersed phase contains porous (zeolite, carbon molecular sieve, activated carbon, carbon nanotubes) recently (24). It not only covers all the available membrane nanotechnologies but also discusses the limitations and research challenges (24). Also, comprehensive reviews on MMM synthesis, modification and application can be consulted for a better understanding of their use in various applications (25, 26).

This review categorizes MMMs based on their filler types for their applications in water purification industry. The major part of the review is devoted to inorganic filler-based MMMs because they are the most investigated membrane type compared to the other types discussed here. Moreover, this article covers the challenges and technological issues regarding MMMs in addition to future recommendations. The final part of the review discusses research areas that need to be explored for future advancements.
or nonporous material (silica, titanium oxide, fullerene. Figure 2 is a schematic of an ideal MMM (31). In general, MMM could offer the physicochemical stability of a ceramic material and the membrane forming ease of polymeric materials while promising the desired morphology with higher permeselectivity, higher hydrophilicity, high fouling resistance, high thermal, mechanical and chemical strength over a wider temperature and pH range (8, 9, 24, 32–39). Figures 3 and 4 are cross-sections of molecular sieve-based mixed matrix symmetric membrane and a zeolite nanocomposite membrane respectively, employed for water purification through desalination process (40). There are several methods developed over time to synthesize these membranes such as dispersion of inorganic filler in polymer solution, in-situ polymerization and sol-gel method (41–47).

It is believed that the polymer matrix plays a major role for permeability whereas the inorganic filler is a controlling factor for the selectivity of the separation performance. Hence, interfacial compatibility between the two phases is of enormous importance to serve the desired purpose for such membranes (32, 48). Because addition of fillers asserts their effects on the morphology, which subsequently alters the transport phenomenon and finally determines the overall performance of the newly developed membranes. Interfacial void formation, aggregation and pore blockage are some of the key effects witnessed in resultant MMMs (49–51). The formation of these interfacial voids is attributed to two main phenomena, one being the interaction between the polymer phase and the filler and two, the stress exerted during preparation (31, 52, 53). The presence of interfacial voids creates additional channels that allow for the solvent to pass through the membrane (51, 54, 55).

However mechanical strength and rejection rate are also concerned by the channel density (31, 53, 56). These features should be controlled or avoided by optimizing the synthesis process parameters acting on polymer concentration, filler concentration (57), casting technique or additional involvement of suitable material, i.e., additive or modification technique such as functionalization, coating etc. to develop a better compatibility between phases (31, 37, 47, 57–60). At the moment, efficient incorporation of nano-materials into polymeric phases in the lab could not be scaled-up for industrial application. Table 2 enlists the characteristics for which nanomaterials are aimed and employed in water filtration industry (61). Nevertheless, employment of these nanomaterials in membrane synthesis could be challenging since controlling the placement, dispersion and its shedding/loss during process is an intriguing task which has restricted its commercialization (62).

Types of Mixed Matrix Membranes

Because MMMs possess unique characteristics and no specific criterion is established yet to categorize them, many authors have defined their own criteria to identify the different types. A recent review by Yin and Deng defined four types (as given in Figure 5) on the basis of membrane structure and filler location in hybrid membrane structure (19). The four types of membranes are (i) conventional nanocomposite, (ii) thin film nanocomposite, (iii) thin film composite with nanocomposite substrate and (iv) surface located nanocomposite. In this review MMMs are characterized solely on the basis of their corresponding filler types. These types of MMMs are named as inorganic filler-based MMMs, organic filler-based MMMs, biofiller-based MMMs and hybrid filler-based MMMs. Each membrane type is illustrated next.

Inorganic Filler-Based MMMs

Examples of Inorganic Filler-Based MMMs. The field of inorganic filler-based membrane is an active MMM area, which has been explored extensively over the years. In any MMM, inorganic fillers attach themselves to support materials by covalent bonds, van der Waals forces or hydrogen bonds. These inorganic fillers are prepared through processes such as sol gel, inert gas condensation, pulsed laser ablation, spark discharge generation, ion sputtering, spray pyrolysis, photothermal synthesis, thermal plasma synthesis, flame synthesis, low-temperature reactive synthesis, flame spray pyrolysis, mechanical alloying/milling, mechano-chemical synthesis and electrophoresis (24). It is safe to presume that MMM has raised the bar in
terms of overall membrane performance. Balta et al. showed that the addition of ZnO particles in polyether sulfone (PES) membranes significantly increased the rejection of dye from 47.5% (PES only) to 82.3% (PES/ZnO). They deduced that permeation of PES/ZnO membrane improved due to the hydrophilic nature of ZnO and subsequent macrovoids formation in the PES/ZnO MMM (49).

Recently, Goh et al. introduced graphene oxide layers on polyamide imide (PAI) or polyether imide (PEI) hollow fiber membrane through the instant dip coating method

![Schematic cross section of zeolite nanocomposite membrane. Reprinted from (40) with permission from Elsevier.](image)

![Schematic of nanocomposite polymeric membranes (a) conventional nanocomposite (b) thin film nanocomposite (c) TFC with nanocomposite substrate (d) surface located nanocomposite.](image)

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<tr>
<th>Desirable nanomaterial properties</th>
<th>Examples of technologies enabled</th>
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<tr>
<td>Large surface area to volume ratio</td>
<td>Superior sorbents with high, irreversible adsorption capacity</td>
</tr>
<tr>
<td>Enhanced catalytic properties</td>
<td>Hyper-catalysts for advanced oxidation &amp; reduction processes to treat residual pesticides and pollutants</td>
</tr>
<tr>
<td>Antimicrobial properties</td>
<td>Disinfection without harmful byproducts</td>
</tr>
<tr>
<td>Multifunctionality</td>
<td>Fouling-resistant multi-functional filtration membranes that inactivate virus and destroy organic contaminants</td>
</tr>
<tr>
<td>Self-assembly on surfaces</td>
<td>Surface structures that decrease bacterial adhesion, biofilm formation and corrosion of water systems</td>
</tr>
<tr>
<td>High conductivity</td>
<td>Novel electrodes for capacitive deionization &amp; low cost, energy efficient desalination of high salinity water</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Sensitive sensors to detect pathogens and other priority pollutants</td>
</tr>
</tbody>
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Reprinted from (61) with permission from Elsevier.

![Table 2: Opportunities for engineered nanomaterials such as MMM in water treatment and reuse (61)](image)
(21). Their results showed a promising trend as permeability was noted up to 86% without any loss of its selectivity (i.e., 81% for divalent ions). In their study, the graphene oxide worked as an effective selective layer, which reduced the pore size distribution without creating any considerable hurdle (e.g., hydrodynamic resistance) for water permeability in the process. Furthermore they explained that additional effects of hydrodynamic resistance due to graphene oxide were nullified by its hydrophilic nature (21). In another study, Zindani et al. obtained similar results as they prepared an MMM by introducing the graphene oxide in PES matrix (63). They asserted that inclusion of graphene oxide in polymer matrix improved its hydrophilicity because of the acidic groups (e.g., carboxylic acid, hydroxyl and other groups) attached to its surface. In this work the graphene oxide PES addition enhanced the membrane selectivity and dye rejection up to 99% (63).

Srivastava et al. currently prepared a MMM for recovery of magnesium (Mg$^{2+}$) ions from natural waters (57). They embed BaCO$_3$ particles in a sulfonated PES matrix. The results showed satisfactory retention of magnesium ions in contrast to other cations such as Ca$^{2+}$ and Na$^+$. They explained that the improved rigidity of the PES membrane due to sulfonation only helped Ca and Na ions to pass through because of their smaller size (0.41 and 0.36 nm, respectively) in comparison with magnesium ions, which have a bigger hydrated ionic radius (0.44 nm). They also stated that inclusion of BaCO$_3$ played its role by adsorbing the Mg$^{2+}$ ions on its surface. It was also emphasized that to achieve the desired separation of retentive ions, the loading of nanoparticles was of great importance: an increased concentration of nanoparticles improved the selectivity (95–98%) of magnesium ions (57).

Mollahosseini and Rahimpour improved the ability of silver-laden membrane to retain the silver nanoparticles, which was previously a major issue for antimicrobial membranes (64). They claimed that by implanting some silver nanoparticles under a thin selective film, they enhanced the antifouling properties of the membrane used, inhibiting the leaching phenomena and therefore making a composite product suitable for antimicrobial purposes. This new membrane offered a lower flux but a better salt rejection than previously reported silver antimicrobial membranes. It was insisted to be due to the compact morphology of the reported membrane (64). Li et al. fabricated a MMM by including silica particles through hydrolysis of tetraethoxysilane (TEOS) into a polydimethylsiloxane (PDMS) matrix designed for the deoxygenation of water on a lab scale (65). They reported interesting results with an optimal TEOS/PDMS ratio that produced MMMs with not only a better water flux but also an improved selectivity (109.8–139). Here, the addition of the optimum amount of silica offered more free volume, more polymer-particle interfacial area and enhanced pore size, which resulted in better permeability (65).

Recently, many authors have reported halloysite nanotube-based MMMs and it seems to be a considerable addition to the inorganic fillers family because of the negative character and hydrophilic nature of these MMMs. These nanotubes have been inserted in different polymer matrixes with a variety of combinations (i.e., dextran, lysozyme, poly-sodium-4-styrene sulfonate) to achieve specific purposes such as mechanical strength (66), antibacterial property (67, 68), antifouling ability (69–71), high flux and high selectivity (55, 72). Table 3 highlights a comprehensive study of different polymer-based MMMs prepared by a variety of techniques through incorporation of novel inorganic fillers. A comprehensive and critical review on preparation methods, types of inorganic fillers and their specific characteristics for water purification applications is of great significance for polymeric nanocomposite membranes (73).

In short, it would be safe to speculate that MMMs could be a giant step in membrane area since targeted applications have proved them quite promising so far.

**Commonly Used Inorganic Fillers in MMMs**. As an essential part of MMMs, inorganic fillers are of a prime importance because they contribute to achieving the desired characteristics of the built MMM. In recent years, these fillers have been incorporated for various purposes such as: to enhance flux (43, 81), to improve selectivity (82), for disinfection (83), to alleviate membrane fouling (84, 85), as well as biofouling (85, 86) in water purification. In recent literature, different types of inorganic fillers have been added to the polymeric phases. Some of these fillers are silica (87, 88), zeolite (89–91), TiO$_2$ (45, 92), carbon nanotubes (93–95), multi-walled carbon nanotubes (CNT) (96–99), and silver (100, 101). Figure 6 (102) offers a schematic of different inorganic fillers utilized in preparing MMMs for water purification applications.

Literature reveals that inorganic fillers are either incorporated into the membrane structure by blending with the solution or it is attached to the surface by using different developed techniques (34). Currently, nanomaterials have been employed in water industry for the following purposes: adsorptive removal of pollutants, catalytic degradation, disinfection and/or microbial control, and desalination (61). Researchers firmly believe that a suitable combination of polymers and inorganic fillers should offer superior permeability and selectivity compared to existing materials.

Apart from other available inorganic fillers, CNTs are currently accepted as a vital development in water treatment applications, especially for desalination where these CNTs could reduce the cost and energy consumption significantly. Evolution of CNTs is highlighted in Figure 7, which shows how CNTs have been improved over the years for targeted demands. CNTs have been functionalized, aligned and sometimes both modifications are employed (103). Other carbon-based materials such as carbon molecular sieves and activated carbon could be of great interest as inorganic fillers. Because both fillers have shown promising results for applications such as gas separation (104) and especially adsorption (105, 106), their inclusion as a filler for water purification could be of great interest.
## Summary of previous studies on inorganic-based mixed matrix membranes for water purification applications

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<tr>
<td>Sen et al. (74)</td>
<td>Polyether sulfone (PES)</td>
<td>Spray-dried silica</td>
<td>Ultrafiltration</td>
<td>Permeability of MMM increased from (148.8–252.6) L.m⁻².hr⁻¹, because silica particles enhanced the hydrophilicity and provided extra pore channel. Interstitial pores on spray dried silica helped to retain the separation characteristics of new MMM because of its smaller pore sizes (2 nm).</td>
</tr>
<tr>
<td>El Badawi et al. (75)</td>
<td>Cellulose Acetate</td>
<td>Functionalized Nanotubes</td>
<td>Nanofiltration</td>
<td>Incorporation of CNTs into CA changed the membrane morphology by reducing the porosity BET area. Small inclusion (0.0005 wt% &amp; 0.005%) of CNTs raised the permeation rates by making the membrane more hydrophilic.</td>
</tr>
<tr>
<td>Silva et al. (76)</td>
<td>Polyvinylidene Fluoride (PVDF)</td>
<td>Multiwalled carbon nanotube (MWCNT)</td>
<td>Membrane Distillation</td>
<td>Incorporation of MWCNTs offered high permeates flux (9.5 × 10⁻³ kg/m²s) along with complete rejection (100%) of sodium chloride. A mixed matrix membrane with higher pore density and sponge like structure is synthesized and favored.</td>
</tr>
<tr>
<td>Ghanbari et al. (55)</td>
<td>Polysulfone (PSU) &amp; Polyamide (PA)</td>
<td>Halloysite Nanotube</td>
<td>Forward Osmosis</td>
<td>Improved antifouling behavior was observed for synthesized MMM. Addition of halloysite nanotubes enhanced the water permeability (5.18 × 10⁻¹² m/s.Pa), while water permeability to salt permeability ratio also increased to 33.88.</td>
</tr>
<tr>
<td>Yu et al. (77)</td>
<td>PES</td>
<td>Modified Silica</td>
<td>Loose Nanofiltration</td>
<td>Modified silica improved the operation stability of synthesized MMM loose nanofiltration membrane. Addition of modified silica particles increased the hydrophilicity and pore sizes of membrane resulting in increased water uptake (210.7%) and pure water flux (150.24 L/m².hr).</td>
</tr>
<tr>
<td>Jo et al. (78)</td>
<td>PES</td>
<td>Zinc Oxide (ZnO)</td>
<td>Ultrafiltration</td>
<td>A significant increase in anti-bacterial activity (up to 6.1) is noted due to addition of zinc oxide particles, which provided hydrogen peroxide on its surface, thus causing an inhibitory effect. Synthesized membrane also showed better antifouling capability with higher pure water flux than the pure membranes.</td>
</tr>
<tr>
<td>Mehwish et al. (79)</td>
<td>PVDF</td>
<td>Functionalized MWCNTs</td>
<td>Nanofiltration</td>
<td>Thiocyanate modified MWCNTs incorporated to PVDF membranes improved the mechanical &amp; thermal stability of the synthesized membrane, while raising the decomposition temperature to 580 °C and tensile modulus of 0.34 GPa. Higher fluxes and selectivity was found in the case of newly prepared membrane because of modified MWCNTs, which increased its hydrophilicity.</td>
</tr>
<tr>
<td>Zhang et al. (80)</td>
<td>PVDF</td>
<td>TiO₂</td>
<td>Ultrafiltration</td>
<td>TiO₂-added membranes showed better antifouling property compared to pure PVDF membrane. Addition of TiO₂ also improved the hydrophilicity and mechanical strength of resultant membrane.</td>
</tr>
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</table>
Moreover, introduction of metal organic framework (MOF)-based fillers in purification area is also gaining huge attention because of the distinctive features of this MOF sophisticated nanostructure that is highly porous, with tunable pores, high thermal and chemical resistance, catalytic character, and freedom to select organic linkers for targeted applications (107). For instance, selected MOFs, which are currently being used are MIL-53(Cr), MIL101(Cr), MIL-100(Cr), MIL-100(Fe), ZIF-8, UiO-66 (108). Table 4 summarizes the properties of common inorganic fillers and their application in water purification industry.

**Organic Filler-Based MMMs**

Organic filler-based membranes are modern type of MMMs in which organic fillers (such as cyclodextrin, polypyrrole, polyaniline (PANI), chitosan beads and semi-interpenetrating network polymeric nanoparticles) are introduced in substrate matrix, commonly through blending and phase inversion (119–125). Organic fillers have the distinct advantage of having more functional groups attached to them, hence making them more adaptable than inorganic fillers. Their ability to attach themselves on a substrate through chemical reactions or binding themselves, especially with a hydrophobic surface makes them a better option for developing specialized (antifouling, highly hydrophilic, specific component rejection or higher porosity) membranes (126, 127).

Fan et al. synthesized a nanocomposite membrane by blending PANI nanofibers in polysulfone polymer, resulting in a membrane of better permeability and antifouling ability (121). As a result, PANI nanofibers raised the water flux 1.6 times. This rise in water flux permeation was attributed to increased hydrophilicity of nanocomposite, since PANI fibers provided huge surface energy, which clustered the small water molecules, hence producing a more permeable polysulfone membrane.
Though rejection of PEG-20,000 and BSA by the PANI nanocomposite membranes did not sufficiently improve due to no change in pore size as of pure polysulfone membranes, yet the antifouling properties of the PANI membrane were improved due to the protonation ability and steric hindrance effect of PANI on polysulfone surface under acidic conditions (121).

In another study, Fan et al. investigated the optimal concentration of PANI nanofibers in nanocomposite membranes (122). As molar ratios of 1% and 15% improved pure water fluxes 1.6 and 2.4 times higher than simple polysulfone membrane due to hydrophilic characteristics of PANI. Another likely reason could be better interconnection between pores because of nanoparticles migration to the nanocomposite membrane surface, leaving behind some microvoids. Additionally, optimal inclusion of nanoparticles into membranes improved its features such as mechanical strength, porosity, hydrophilicity and permeation. On the other hand, PANI nanofibers made the membrane surface less adhesive to antifouling agents, thus improving the overall rejection of BSA. Figure 8 is a schematic of a nanocomposite membrane developed by adding PANI nanofibers in the polysulfone matrix, which explains the microvoid formation in nanocomposite PANI/PSU membranes, creating a higher flux (122).

Zhao et al. introduced PANI nanospheres and PANI oligomers into polysulfone membranes (129). These fillers similarly raised the pure water flux from 1.7 to 4 times higher than simple polysulfone (PSU) membranes. The PANI ability to produce interconnected pores in the membrane structure was also one key factor for enhanced pure water permeability. The addition of these PANI nanospheres and oligomers also improved significantly the rejection rate for BSA by creating relatively smaller pores (6.7–11.2 nm) and restricting adsorption on membrane surface due to the PANI hydrophilic nature in contrast to the hydrophobic character of BSA (protein size 8 nm) (128).

Zhao et al. also obtained the same results for PANI-based nanocomposite membranes with added polyvinylpyrrolidone (PVP) (129). They successfully enhanced the pure water flux, antifouling, separation efficiency and mechanical strength of resultant membranes with further PVP additions. Their study showed satisfying results because addition of PVP (below 0.5 wt%) with PANI organic filler in polysulfone matrix produced the aforementioned characteristics in the resulting membrane. BSA rejection through these membranes only occurs due to hydrophilic nature of nanofillers (PANI) on the surface and sieving mechanism due to larger sizes of BSA molecules, though addition of PVP did not affect the rejection significantly (129).

Adams et al. blended a β-cyclodextrin polyurethane into polysulfone matrix for removal of Cd²⁺ ions from water (119). The addition of β-cyclodextrin polyurethane increased the permeability of the MMM to 489 Lm⁻².h⁻¹ by providing more wide pores on surface, higher hydrophilicity and better connectivity between finger-like pores. On the contrary, β-cyclodextrin reduced the strength of the membrane because its inclusion created macrovoids in the structure, hence making

<table>
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<th>Inorganic fillers</th>
<th>Properties</th>
<th>References</th>
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<tr>
<td>Silver-based</td>
<td>Antibacterial, Good transport facilitator, Good selective barrier, High reactivity, anti-adhesion to protein, low toxicity to humans</td>
<td>(102, 109–115)</td>
</tr>
<tr>
<td>Iron-based</td>
<td>Highly reactive, larger surface areas in nanoform (F⁺), detoxification of organic and inorganic pollutants, reduce, removal of active metal ions, reductive dehalogenation of chlorinated organic compound, highly reductive, high adsorption capacity, hydrophilic, fouling resistant, magnetic oscillation, hydraulic turbulence</td>
<td>(102, 110, 112, 114, 116–118)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Hydrophilic, fouling resistant, anti-adhesion to protein, effective sorbents, ion exchange media for metal ions</td>
<td>(40, 102, 110, 114)</td>
</tr>
<tr>
<td>Silica-based</td>
<td>Hydrophilic, fouling resistant, anti-adhesion to protein</td>
<td>(110, 114)</td>
</tr>
<tr>
<td>Aluminum-based</td>
<td>High adsorption capacity, hydrophilic, fouling resistant, anti-adhesion to protein</td>
<td>(110, 114)</td>
</tr>
<tr>
<td>Titania-based</td>
<td>High adsorption capacity, hydrophilic, fouling resistant, anti-adhesion to protein, decomposition of organic compounds, reduced surface roughness, oxidative and reductive catalysts for organic and inorganic pollutants, killing bacteria</td>
<td>(40, 102, 110, 114)</td>
</tr>
<tr>
<td>Carbon nanotube-based</td>
<td>Antimicrobial, hydrophilic, high aspect ratio, biofouling resistant, anti-adhesion to protein, selective sorbents for organic compound</td>
<td>(40, 102, 110, 114)</td>
</tr>
</tbody>
</table>

![FIGURE 8 PANI/PSU nanocomposite membrane after immersion in water bath. Reprinted from (122) with permission from Elsevier.](image-url)
Highly hydrophilic MMMs

Molecular Weight Cut-off (MWCO) of newly prepared membrane increased from 0.2 to 4.8 kDa. Also this filler type made membranes porous up to 64% in comparison to nascent membranes (20%).

Inclusion of PA made the membrane more hydrophilic, hence increasing its permeability to 16 × 10⁻¹² m² Pa⁻¹ s⁻¹.

Filler Inclusion of PA made the membrane more hydrophilic, hence increasing its permeability/driving force claim-ability to 16 × 10⁻¹² m² Pa⁻¹ s⁻¹.

Flux recovery ratio up to 94.5% was achieved, which shows its superb antifouling ability.

Higher quality water purification

Flux recovery ratio up to 94.5% was achieved, which shows its superb antifouling ability.

Remarks

Nevertheless, limitin-concentration and incorporation method of biofillers in polymer matrix is of serious attention, since they stated significant decrease in membrane productivity under different biofiller concentrations (134).

Lin et al. used plant waste as biofiller in their study for cationic dye removal (139). They added biofiller, e.g., banana peel, tea waste and shaddock peel in polyethersulfone and reported the rejection up to 95% of cationic dyes. Addition of such biofillers provided the better charge interaction, hydrophobic interaction and hydrogen bonding, hence improving the overall rejection for developed MMMs. Further improvement in cationic dye removal from wastewater is also suggested if simple polymeric matrix is removed with biopolymers (139).

Other polymers have also been tested in various studies as Li et al. introduced aquaporin containing liposomes into polyanimide-imide (PAI) polymer matrix to synthesize a nanofiltration membrane with high permeability and higher rejection efficiency (137). Their study reveals that at optimal composition (liquid to protein ratio of 200), the resultant membrane showed the maximum pure water flux (36.6 Lm⁻².hr⁻¹), whereas rejection of divalent salts was as high as 95%. The high permeability of this membrane was attributed to the availability of more passage for water molecules provided by aquaporin. On the other hand, high rejection of membrane was the direct result of the liposomes’ selective layer. Nevertheless, the method of incorporation of aquaporin in any matrix is of vital importance, since aquaporin placed near the top surface or exposed to external environment would lose its activity (137).

Duong et al. developed a nanofiltration hybrid membrane (134). They introduced a selective layer of aquaporin incorporated triblock copolymer (AqpZ-ABA) on different gold coated alumina obtaining a gold-coated/ABA block copolymer/gold-AqpZ-ABA substrates by vesicle spreading method. A

### Table 5

Summary of organic filler-based MMMs

<table>
<thead>
<tr>
<th>Reference</th>
<th>Filler</th>
<th>Support matrix</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kotte et al. (130)</td>
<td>PEGylated Polyethyleneimine (PEI) nPs</td>
<td>Polynylidine Fluoride (PVDF)</td>
<td>• Fouling resistant MMM is developed.</td>
</tr>
<tr>
<td>Mukherjee et al. (131)</td>
<td>Polyaniline (PA)</td>
<td>PSU</td>
<td>• Molecular Weight Cut-off (MWCO) of newly prepared membrane increased from 0.2 to 4.8 kDa. Also this filler type made membranes porous up to 64% in comparison to nascent membranes (20%).</td>
</tr>
<tr>
<td>Liao et al. (132)</td>
<td>polyppyrrole nanospheres</td>
<td>PSU</td>
<td>• Offers &gt;10 times initial water permeability</td>
</tr>
<tr>
<td>Zhu et al. (133)</td>
<td>chitosan-montmorillonite (CS-MMT)</td>
<td>Polyethersulfone (PES) &amp; Polynylpyro-lidone (PVP)</td>
<td>• High pure water flux (68.82 L m⁻² h⁻¹)</td>
</tr>
<tr>
<td>Zhu et al. (54)</td>
<td>Quanternized Polyethylenimine (QPEI)</td>
<td>PES</td>
<td>• High flux recovery ratio up to 94.5% was achieved, which shows its superb antifouling ability.</td>
</tr>
</tbody>
</table>

### Biomaterial-Based MMMs

Incorporation of biomaterials (biofillers) such as (aquaporin, amphiphilics or lignin) into continuous matrix is an innovative technique to enhance the effectiveness of membrane technology. Biofiller-based MMMs delivered a better permeability, antifouling ability and certain functionalities such as mechanical reinforcement effect, which were either lacking or quantitatively low in nascent membrane (134–136). Two design strategies to synthesize these membranes are extensively reported in literature. In one strategy, aquaporin containing lipidd bilayer is coated directly on membrane substrate, while in the second strategy, vesicles or proteoliposomes (aquaporin are incorporated in liposomes/polysomes) are coated on the support surface (137, 138). Figure 9 presents a design of a vesicular membrane incorporated with a commonly used biofiller (Aqp i.e., Aquaporin).

Recent work by Kumar et al. proposed that the introduction of aquaporin filler in amphilic triblock polymer vesicles (PMOXA₁₅-PDMS₁₀-PMOXA₁₅) demonstrated an excellent ability for water productivity (permeability/driving force) claiming it to be 800-fold than the simple polymeric membrane (134).

These newly developed MMMs also offered the unique ability to achieve a controlled permeability. Also, they were found to be an excellent barrier towards urea, glucose, glycerol and salt by reporting their relative reflection coefficient higher than unity. Nevertheless, limiting concentration and incorporation method of biofillers in polymer matrix is of serious attention, since they stated significant decrease in membrane productivity under different biofiller concentrations (134).
A comparison of the obtained different membranes showed that gold coated-AQPZ-ABA membranes provided good improvement for water permeability (16.1 L h⁻¹ bar⁻¹) while rejection soared to 45%. Membrane defects were witnessed, however, which was thought to be the result of the method selected for AQPZ inclusion in the selective layer (136).

Manjarrez Nevárez et al. synthesized a propionated lignin-based nanocomposite membrane for metal ions rejection (135). They incorporated three different types of propinated lignin (kraft, organosolv, hydrolytic) in cellulose triacetate (CTA) through vapor induced phase separation method. Comparison showed that propinated kraft lignin (KL) improved the mechanical strength of the resultant KL/CTA membrane. Propination of kraft lignin increased the compatibility of the propyl group with cellulose acetate due to more available London dispersion forces between the biofiller and the substrate polymer. However, propination adversely affected the mechanical characteristics of developed membranes in the cases of organosolv (OL) and hydrolytic (HL) lignin.

Propination in OL and HL lignin increased the particle sizes of resultant biofillers, which diminished that adhesion between CTA and incorporated lignin nanoparticles, thus making the membranes less mechanically stable. Rejection results for propinated KL/OL/HL-based CTA nanocomposite membranes showed a better rejection of arsenic ions for OL-based CAT-membranes by raising the rejection percentage from 17% to 22.8%, while the other two lignins suffered reduction in As rejection due to antagonistic effects of divalent ions present in the solution. Yet, all resultant membranes were found good at rejecting cations but not anions (135).

A summary of recent works with biofiller-based water MMMs is compiled in Table 6. For detailed studies, the recent reviews by Zhu et al. (140–143) should be consulted. Also the works of Wang and Zhao (144–147) are important in the area of biofillers, especially aquaporin-Z-based MMMs.

Hybrid Filler-Based MMMs

Hybrid fillers are the recent addition to the MMM technology. This type of membrane contains two different fillers (independently or in composite form) added to the continuous phase. These hybrid materials are incorporated either to accomplish any targeted purposes or to improve the overall process effectiveness of the resultant membrane. In Figure 10, a conceptual multifunctional membrane is depicted with hierarchal nanofillers where, on different layers, different types of nanofillers are introduced to achieve diverse functionalities. Daraei et al. introduced the combination of iron (II, III) oxide and polyaniline into polyethersulfone matrix to be able to accomplish 85% of Cu (II) removal from water (153). The results showed that adsorption in this case was the dominating separation mode; else this membrane could offer a better reusability and durability (153).

A novel hybrid material Chitosan-montmorillonite (CS-MMT) was dispersed in polyethersulfone (PES) matrix by Zhu et al. (133). This novel hybrid filler CS-MMT raised the membrane antifouling ability due to its highly hydrophilic nature and also increased the membrane mechanical strength by restricting the polymer chain mobility forming interrelated structures. They showed that a high flux recovery up to 92% was achieved due to a loose active layer and the enhanced hydrophilic nature of membrane (133). Alpatova et al. also synthesized an antifouling MMM through inclusion of Fe₂O₃ nanoparticles and multiwalled carbon nanotube (MWCNT) in polyvinylidene fluoride (PVDF) (51). Addition of this hybrid filler raised the degradation of fouling compounds such as cyclohexanoic acid and humic acid, hence making the membrane more antifoulant than the nascent one. Additions of Fe₂O₃ enhanced the membrane hydrophilicity but an increase in Fe₂O₃ content caused a notable drop in the surface porosity of membrane. Furthermore, rejection studies were performed in
<table>
<thead>
<tr>
<th>Author</th>
<th>Filler</th>
<th>Polymer</th>
<th>Preparation method</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wang et al. (148)</td>
<td>Aquaporin Z i.e., AqpZ</td>
<td>Polyacrylonitrile (PAN)</td>
<td>Film rehydration method</td>
<td>- High pure water flux (22 L.m(^{-2}).h(^{-1}))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Rejections at 0.4 MPa are;</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>- 0.5% MgCl(_2) rejection (97%)</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>- 0.5%NaCl rejection (75%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Durable and stable at high pressures</td>
</tr>
<tr>
<td>Wang et al. (149)</td>
<td>Aquaporin Z</td>
<td>Hydrolyzed Polyacrylonitrile (HPAN)</td>
<td>Vesicle rupture method</td>
<td>- Novel method of membrane synthesis is introduced by employing double skinned structure on substrate surface.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Improved antifouling ability is achieved against humic acid foulants</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Biofiller enhanced the hydrophilicity and also reduced the roughness of membrane, resulting in increased permeate flux (15.6 L/m(^2).hr)</td>
</tr>
<tr>
<td>Ding et al. (150)</td>
<td>Aquaporin Z</td>
<td>Polysulfone</td>
<td>Vesicle rupture method</td>
<td>- A biomimetic forward osmosis membrane with high flux (23.1 L/m(^2).h) and low solute flux (1.7 L/m(^2).h) was prepared through novel method.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Synthesized membrane showed excellent stability and durability due to presence of supported lipid bilayer (SLB).</td>
</tr>
<tr>
<td>Ji et al. (151)</td>
<td>Zwitterionic nanoparticles</td>
<td>Polysulfone</td>
<td>Interfacial polymerization</td>
<td>- A highly permeable (109.7 L/m(^2).hr) and highly selective (NaCl/Na(_2)SO(_4)28.4) membrane is achieved.</td>
</tr>
<tr>
<td>Wagh et al. (152)</td>
<td>Aquaporin Z</td>
<td>Polybenzimidazole</td>
<td>Phase inversion + surface modification</td>
<td>- Zwitterionic nanoparticles provided the antifouling and hydrophilic characteristics to membrane.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- This modified membrane showed better performance in terms of hydrophilicity, antifouling ability, mechanical stability and flux recover (92.8%) than nascent membrane.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Membrane showed higher rejection of 88% and 86% against Bovine Serum Albumin and Lipase solutions, respectively.</td>
</tr>
</tbody>
</table>
presence of H$_2$O$_2$ to investigate the oxidation effects. H$_2$O$_2$ decomposition on membrane surface provided OH$^*$ radicals, which oxidized the humic acid and cyclohexanoic acid, hence improving the permeability and antifouling capability of the membrane (51).

Saf et al. introduced the reduced graphene oxide/polythiophene (rGO/PTh) into PES phase to design an antifouling MMM with high permeability (154). Inclusion of rGO/PTh hybrid filler increased permeability and protein rejection. In this MMM, rGO added porosity to the membrane surface, while PTh enhanced hydrophilicity even though rGO alone is hydrophobic (154). A research by Teli et al. demonstrated that MMMs containing hybrid fillers polyaniline (PANI)/phosphomolybdicacid (PMA) in PES offered a better antifouling activity and more efficient membranes than the simple PES membrane (155). A combined effect of hybrid filler was witnessed in this case since PANI increased the porosity of membrane, while PMA raised its surface hydrophilicity, hence increasing the overall permeability of pure water flux.

Recently, Zhao et al. reported the same results of improved antifouling ability by addition of hybrid filler (modified halloysite nanotubes + Ag particles) (70). It was observed that some halloysite addition did not affect the membrane structure but increased the permeate flux up to 250%, while antimicrobial activity was recorded as 99.9% for E. coli. The addition of halloysite increased the PES pore sizes and offered more space for water permeation, hence resulting in the observed increased flux of the resultant MMM (70). It must also be mentioned that, despite the significant contribution of hybrid fillers through combined effect, they could also cause adverse effects to the membrane overall efficiency. As surface pore blockage was sometimes observed in hybrid filler-based membranes, hence making the parameters such as selection of fillers and their composition most important for these MMMs (153, 155). A summary of other studies with hybrid fillers for MMMs as reported in literature is presented in Table 7.

**ISSUES, CHALLENGES AND OPPORTUNITIES**

Recent developments in membrane technology have undoubtedly established its legacy in various areas where separation is a core process. Gas separation as well as water treatment have extensively benefitted from membrane technology so far and advancements in these areas are still in progress. Nevertheless, these advancements have been restricted by some of the core issues that need serious attention from research community.

- Fouling has been one of the serious challenges for membrane industry for a long time. To tackle this issue, approaches such as incorporation of antifouling nanoparticles, surface modification, and integrated processing (e.g., post/pretreatment) have shown promising results. But future research should focus on two key issues; (i) to stop regeneration of microbial colonies on membrane surface and (ii) to mitigate the leaching of filler (39, 63, 92, 98, 158–169).
- Another challenging issue for membrane industry especially MMMs is identification and development of new filler materials. Even though enormous amounts of filler have been reported in literature, yet their price, availability, compatibility with polymer interface, better interfacial contact, stability, smaller sizes, homogeneous distribution, agglomeration and their relation with water chemistry have been of great concern (50, 102, 170–172).
- Some of these fillers have a toxic nature and their employment in water treatment application could be of great risk to humans and environmental. Hence, further opportunity lies in in-depth studies of the issues such as determining the hazardous character of these nanoparticles and mechanism of nanoparticles-embedded membrane fouling in water treatment industry (37, 102, 171, 173, 174).
One key area that demands extensive research is development of novel materials for continuous phase in MMMs. Even though many polymers (e.g., glassy, rubbery), polymeric blends and functionalized polymers have been employed, yet this area demands more research for water and even for gas separation applications through membranes. Many of these novel materials introduced so far have been only tested on a laboratory scale and need further study. Successful implementation of these materials lies in developing materials that not only offers high selectivity with very thin top (selective) layer, but also contains filler particles of incredibly small sizes. Many suggested that many novel materials could not gain popularity due to high prices or expensive synthesis processes, so a search for cheaper materials could also be a potential research area (32, 50, 167, 168, 175–178).

One key area that demands extensive research is development of new processes to fabricate the membranes. Because numerous novel membrane materials and fillers are being investigated around the globe but their performances are restricted because the synthesis processes have limitations. Current processes lack the ability to produce defect-free membranes even on laboratory scales as in the case of rigid polymeric membranes. Therefore, new techniques to achieve a perfect interface between continuous and dispersed phase in membranes without compromising performance represents the holy grail. Additionally, technological development to scale up these novel membranes is greatly needed (52, 112, 172, 176).

Finally, development of a transport model to predict the performance of new membrane types, especially MMMs, is in its initial stage and holds a lot of potential for research community today. Previously developed models have been improved and different parameters have been studied, yet studies in this particular area lack essential tools, experimental data or suitable models for anticipating the processes contributing to membrane separations. Furthermore, extensive research is needed to estimate and incorporate the morphology and intrinsic properties of these fillers to develop a more precise and advanced model. Also, models for prediction of membrane performance in the case of multivalent ion solutions, and for fouling, are in the earliest phases, but ultimately could offer a great opportunity to new researchers in the area (50, 168, 179–183).

**CONCLUSIONS AND FUTURE RECOMMENDATIONS**

Water purification industry has taken a giant leap since the development of the first membrane and its successful application for that very application. Membrane technology has effectively replaced conventional water treatment technologies with its considerable quality water product, while keeping the prices as low as possible. Nevertheless, over time, tightening regulations and increasing water demand have forced researchers to explore new horizons matching the new challenges. Polymeric and ceramic membranes have been effective in as long as they have lived up to current expectations and new demands. But the identification of new pollutants and their effective removal have pushed them to limits, forcing researchers to find new ways to deal with their persistent fouling problems.

### TABLE 7

<table>
<thead>
<tr>
<th>Reference</th>
<th>Polymer</th>
<th>Hybrid filler</th>
<th>Application</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mahmoudi et al.</td>
<td>PSU (15%)</td>
<td>Ag/GO nPs</td>
<td>Nanofiltration</td>
<td>Ag-laden Graphene Oxide (GO) caused the hydrophilicity by reducing the interface energy of resultant membrane. 0.5 wt% of nanoparticles in PSU matrix demonstrated the max. Pure water flux by increasing the porosity of membrane and no fouling.</td>
</tr>
<tr>
<td>Mehwish et al.</td>
<td>PVDF</td>
<td>Functionalized MWCNT-Ag</td>
<td>Nanofiltration</td>
<td>Hybrid filler increased the tensile strength of the resultant membrane. Salt rejection and permeability (4.7 to 5.8 ml/cm².min) is also observed to soar because of filler inclusion.</td>
</tr>
<tr>
<td>Alpatova et al.</td>
<td>PVDF</td>
<td>Fe₃O₄ + MWCNTs</td>
<td>Catalytic degradation of organs</td>
<td>Hybrid filler enhanced the antifouling capability of resultant membrane when added in optimized amount (0.2 wt% MWCNTs + 1% Fe₃O₄). Removal efficiency of cyclohexanic acid (CHA) was observed to be 48%, while for humic acid (HA) it was 53.1% approximately when H₂O₂ was added.</td>
</tr>
<tr>
<td>Duan et al.</td>
<td>PES</td>
<td>Halloysite + Cu nanoparticles</td>
<td>Antibacterial for water purification</td>
<td>Pure water flux of newly developed membrane was reported to be 212 L/m².h because hydrophilic hybrid filler raised affinity to water molecules. Copper nanoparticles increased the antibacterial activity (94.5%) by hindering the growth of bacteria on membrane surface.</td>
</tr>
<tr>
<td>Wang et al.</td>
<td>PES</td>
<td>Hybrid chitosan</td>
<td>Adsorption of toxins</td>
<td>Modified chitosan in nascent membrane increased its adsorption of toxins, e.g., copper, anionic dyes. It also increased its mechanical properties and acid–alkali resistance.</td>
</tr>
</tbody>
</table>
To alleviate these new issues, the idea of hybrid membranes or MMMs has surfaced, which actually offers combined features of polymeric and ceramic membranes by incorporating the inorganic particles into organic polymer matrix. This new type of membrane is claimed to be efficient in terms of its efficiency, permeability and selectivity; however, it has also developed its own complexities and difficulties, which has restricted its wider application. Some of the identified problems include the complexity of the synthesis process, high cost, identification of compatible inorganic particles, agglomeration, inorganic particle concentration, phase separation, control of morphology and structural defects. Additionally, the inclusion of inorganic particles into an organic membrane structure for water purification application is considered a potential hazard to environment and human health, which also needs to be addressed in the future. Despite all suspected problems, MMM could be considered a strong candidate for modern purification industry since it combines the properties of polymeric and inorganic materials.

Hybrid membranes, as an upcoming technology, need to be investigated for their immense potential. Future research should focus on developing new techniques to prepare inorganic materials and their incorporation into polymer structures. Some new polymers as well as new combinations should also be explored to meet the challenges. New materials should also be considered to alleviate fouling phenomena. Much work is required to understand the basic transport mechanism of hybrid membranes. New solvents, additives and agents should also be reviewed to achieve better adhesion between polymer and inorganic fillers. Interfacial studies are also required to understand the contact between these two different phases to improve their contact at interface. It can be concluded that MMM technology has great potential, although its success and competitiveness require a combined and persistent effort to resolve the problems identified here in order to compete with existing purification technologies.

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