RESEARCH PAPER

Mixed Matrix Pervaporative Membranes for Solvent Dehydration as a Next Step to Energy Intensive Distillation

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ABSTRACT

Pervaporation is an energy-efficient and selective alternative to distillation for dehydrating organic solvents that form azeotropes with water. The traditional hydrophilic polymers, including PVA and PAN, are, however, limited by flux selectivity trade-offs, undesirable swelling, and structural instability of highly interactive solvent systems. Mixed Matrix Membranes (MMMs) are matrices of polymeric materials that incorporate inorganic nanoparticles and thus become important in improving water sorption, molecular sieving, mechanical stability, and long-term life. This article critically reviews the state-of-the-art MMMs in dehydrating major industrial solvent-water mixtures, P-NP (Polar & Non-Polar), considering fillers like carbon-based nanomaterials, metal-organic frameworks (MOFs), zeolites, metal oxides, and metal nanoparticles. Particular emphasis is given on polymer-filler interfacial compatibility, dispersion quality, structure-property relationships, and the contribution of fillers in altering transport pathways. The article includes comparative performance of various P-NP solvents, ethanol, methanol, DMC, IPA, DMF, THF, and acetone systems, showing the continuing problems of interfacial voids, nanoparticle agglomeration, hydrolytic instability, and insufficient long-term testing. Necessary directions, including 2D nano-architectured fillers, stimuli-responsive MMMs, green fabrication paths, and AI-assisted membrane design. These are mentioned as the ways to attain scalable, durable, and high-performance dehydration membranes. This review provides a comprehensive, critical framework for advancing MMM-based pervaporation technologies towards industrial deployment.

Keywords: *Industrial Solvents, MMM, Pervaporation-dehydration, Polymer–Filler Interface, Solvent–Water Separation, Membrane Stability.*

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1. INTRODUCTION

Pervaporation has emerged as a strategically important membrane-based separation technique for dehydrating organic solvents used in the chemical, pharmaceutical, agrochemical, and electronic-materials industries. Its main advantage is its ability to overcome the thermodynamic limitations that restrict traditional distillation processes. Many commonly used industrial solvents, such as ethanol, methanol, dimethyl carbonate (DMC), isopropanol (IPA), dimethylformamide (DMF), acetone, and tetrahydrofuran (THF), form azeotropes or near-boiling mixtures with water [1]. Consequently, separating these mixtures by distillation becomes highly energy-intensive, operationally complex, and inefficient [2,3]. Conventional distillation typically requires substantial latent-heat input and, in many cases, the addition of entrainers. These factors, combined with environmental and safety concerns, limit its ability to achieve the ultra-low moisture content demanded in downstream operations such as fuel-grade ethanol production, pharmaceutical crystallization, catalyst-sensitive organic reactions, and semiconductor manufacturing [4,5]. Pervaporation addresses these

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**Author for Correspondence: swapna.rekha@gmail.com* limitations by selectively removing water through sorption and diffusion within dense hydrophilic membranes, independent of vapor–liquid equilibrium [6]. This enables deep dehydration without chemical additives, while significantly reducing energy consumption. Metal-organic framework (MOF)-based mixed matrix membranes (MMMs) have attracted significant interest because of their distinctive characteristics of the pervaporation process through the synergistic combination of polymeric matrices with a combination of inorganic fillers, namely, enhanced mechanical strength, higher permeability, and improved selectivity Figure 1 [7]. Although there are many articles on MOF-based MMMs in recent years, the given review is concerned with how the filler design and the microstructure could be improved to enhance MOF-based pervaporation membranes [7]. Despite these sustainability benefits, the large-scale adoption of pervaporation has been hindered by the limitations of existing polymeric membranes. Although hydrophilic polymers such as poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN) have been widely studied due to their water affinity and ease of fabrication, they suffer from flux–selectivity trade-offs, high swelling in polar solvents, and structural relaxation during operation [8,9].

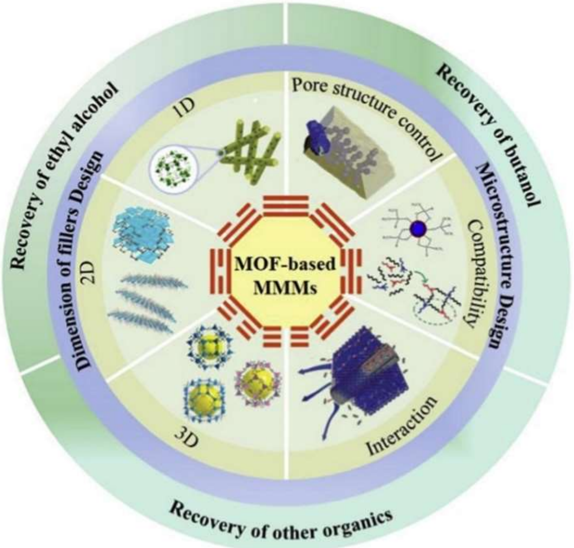

Figure 1: Schematic of pervaporation principle and MMM concept (polymer matrix + nanoparticle filler) adapted [7].

The above weaknesses have prompted the creation of mixed matrix membranes (MMMs) that incorporate the inorganic nanoparticles into a polymer matrix to enhance performance [10]. Various parameter can play a role in selective water transport, inhibition of polymer swelling, and enhanced long-term stability, and the performance levels achievable by these polymers alone are very challenging with pristine polymers. Incorporating nanomaterials such as graphene oxide (GO), carbon nanotubes (CNTs), metal-organic frameworks (MOFs), zeolites, and metal oxides (TiO_2, SiO_2, ZnO, Al_2O_3) provides improved hydrophilicity, molecular sieving, enhanced nanochannels, and greater mechanical strength [10-11]. These features promote selective water transport, suppress polymer swelling, and improve long-term stability. However, despite their potential, MMMs face several persistent challenges, including nanoparticle aggregation, polymer filler incompatibility, interfacial voids, poor dispersion reproducibility, and difficulties in scale-up [12]. These issues highlight the need for more sophisticated membrane-design strategies rather than simple material combinations like hybrid process integration using MMM with concept [13]. Some of the best membranes used in these separations are now being offered by MMMs, and three areas can be identified to improve such membranes: further analysis and refinement of the inorganic phases and further understanding the compatibility between polymer and the inorganic phases. This review provides an in-depth and analytical evaluation of polymer-nanoparticle composite membranes in the context of pervaporation dehydration, with a specific focus on PVA-based and PAN-based MMMs that are the most common in recent studies and represent the most promising options within the industrial context. Although some of the MMMs prove to be much better than pristine polymers, their translation to industrial practice is restricted by fabrication variability, lack of standardized testing rules, and environmental and regulatory issues on the use of nanoparticles. The review analyzes five broad groups of inorganic fillers, namely, carbon-based nanomaterials, metal oxides, metal nanoparticles, MOFs, and zeolites, and critically reviews the structure-property relationship, polymer-filler interaction, operational stability, and mechanistic effects of each of these fillers in enhancing transport in pervaporation.

2. Fundamentals of Pervaporation and Mixed Matrix Membranes (MMMs)

Pervaporation utilizes a solution–diffusion mechanism whereby molecules are absorbed into the membrane, diffuse through the polymer matrix, and evaporate under vacuum or sweep gas conditions. This technique, which avoids vapor–liquid equilibrium, is particularly valuable for challenging separations [14]. The permeation flux is defined by Fick's laws, with the permeability coefficient derived from solubility and diffusivity components. Selectivity is evaluated through separation factors or permeance-normalized parameters, crucial for assessing membrane performance in industrial dehydration contexts. For water-solvent separations, membranes must be engineered to enhance water permeability while minimizing organic molecule passage. This involves optimizing hydrophilicity, chain mobility, and transport pathways [15-16]. Mixed matrix membranes (MMMs) were created to address the limitations of conventional polymers, where the polymer provides structural integrity and the nanoparticles serve as selective modifiers or sieves. The polymer-filler interface significantly influences MMM performance, with ideal adhesion fostering high-quality contact and improved separation. However, poor compatibility can lead to increased rigidity and reduced segment mobility, ultimately affecting flux and selectivity. Non-selective leakage can occur from inadequate filler dispersion or interfacial defects. The key challenge in MMM development is controlling interfacial morphology [17-18]. Common polymer matrices for dehydration pervaporation include poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN). PVA's high hydrophilicity and crystalline structure make it suitable for water-selective applications, though it swells in polar solvents, impacting structural stability. Crosslinking and nanofillers can enhance its dimensional stability. PAN offers better resistance to swelling and higher mechanical strength but generally exhibits lower aqueous selectivity than PVA. However, its robustness and compatibility with various inorganic fillers make it advantageous for industrial solvent dehydration applications [19-20].

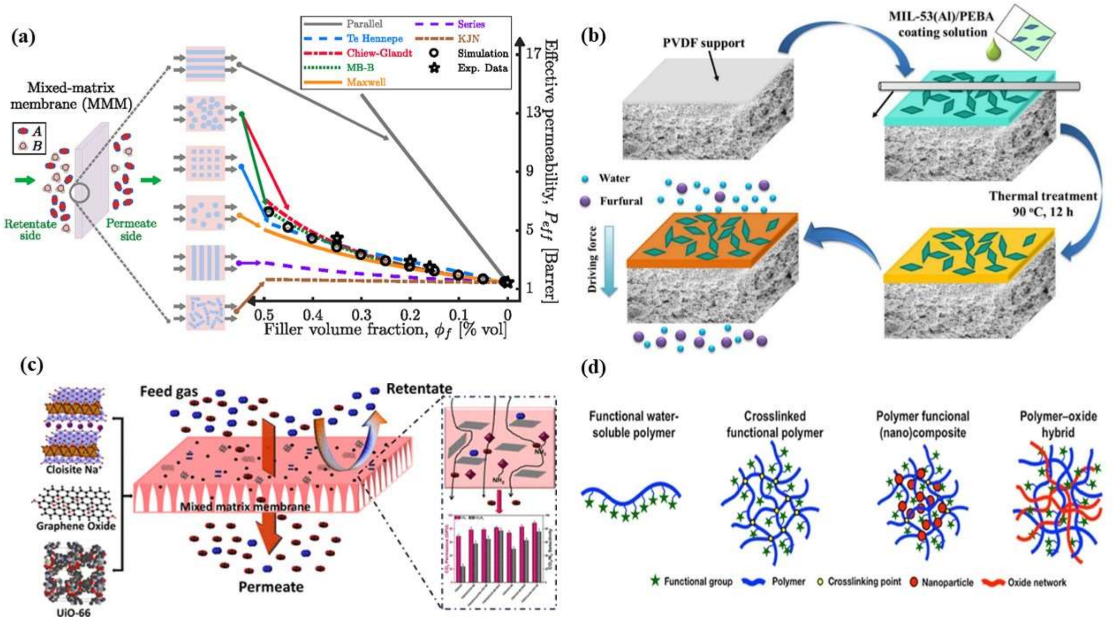

Figure 2: (a) Permeation pathway through polymer, filler, and interface region, adapted, (b) MMMs incorporating MIL-53(Al) MOFs, adapted, (c) Nanofillers in Mixed Matrix Membranes, adapted (d) Polymer nanoparticle interaction modes, adapted

To guide future advancements in Mixed Matrix Membranes (MMMs), the document illustrates the permeation process and analyzes existing permeation models against experimental results (Figure 2a). It details the basic transport process involving sorption, diffusion, and desorption. MMMs, incorporating functional inorganic fillers, can effectively separate water from solvents. A comparison highlights PVA and PAN's advantageous tunability relative to other materials like chitosan and polyimides. Understanding the interplay between polymer and filler properties is crucial for developing next-generation membranes that achieve high performance in diverse industrial applications [21-23].

3. POLYMER MATRICES USED IN MMMS

Pervaporation (PV) dehydration membranes utilizing mixed-matrix (MMM) concepts commonly incorporate hydrophilic polymer scaffolds. These scaffolds enhance the flow, selectivity, and mechanical/thermal stability of water transport routes. Common polymers include poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), chitosan, poly(dimethylsiloxane) (PDMS), polyimides, and poly(ether-block-amide) (PEBA), with PVA being the preferred choice for its high hydroxyl content, which improves water affinity and sorption capabilities. However, neat PVA presents challenges, such as swelling and dissolving in water, which can reduce size-exclusion and selectivity. To mitigate these issues, various crosslinking methods, including glutaraldehyde and citric acid, are applied to control swelling and balance permeability with stability [24-25].

Recent studies highlight advancements in glutaraldehyde and citric acid crosslinking and their effects on PV performance. The integration of hydrophilic nanofillers, such as zeolites and layered hydroxides, into crosslinked PVA matrices has been shown to enhance water flux by creating rapid transport pathways. PAN offers high thermal stability and can serve as both a substrate for aggressive separations and a base for thin, selective coatings, though it often requires modification to enhance its hydrophilic nature for drying applications [26-27]. Chitosan, a derivative of chitin, is favoured for its biodegradability and water sorption capacity, but requires careful formulation due to its sensitivity to pH and limited chemical stability. PDMS is commonly used in organophilic contexts but can be adapted for VOC removal when combined with suitable fillers. Polyimides provide excellent thermal and chemical resilience but may necessitate hydrophilic modifications for effective dehydration. Lastly, PEBA serves as a versatile block copolymer that combines elasticity and strength, evidencing promising results in dehydration selectivity when integrated with metal-organic frameworks (MOFs) or zeolites. Overall, the performance of PV membranes hinges on the careful selection of polymer matrices and the incorporation of fillers, optimizing the balance between water flux, mechanical stability, and selectivity [28-29].

3.2 Controlling Parameters of Polymer Matrix

Crosslinking, Swelling Control, and Interfacial Chemistry etc. are the basic controlling parameters of polymer matrix. Controlling surface swelling and crosslinking is arguably as important as selecting the polymer surface. Commonly used agents like glutaraldehyde and maleic anhydride are used to divide PVA and chitosan covalently, thereby decreasing equilibrium swelling and increasing chemical/thermal stability but excessive crosslinking decreases free volume and can also lower flux. The methods of counterbalancing these effects are partial crosslinking, post-treatments, maintaining micro-scale hydrophilic pathways, and functionalization of filler surfaces to bond to polymer matrix to allow counterbalancing non-selective gaps. This compatibility between interfaces (functionalization of fillers to silanes, polymers or ionic groups) minimizes non-ideal voids, which allows selectivity to be maintained at high filler contents. According to recent reviews of MMM, the most effective PV performance has been conclusively achieved through polymer chemistry tuning, crosslinked density tuning, and filler surface treatment [30].

3.3 Design Guidelines & Trade-offs

Polymer selection for dehydration mixed matrix membranes (MMMs) involves multi-objective optimization. Polyvinyl alcohol (PVA) and chitosan, known for their high water affinity, require crosslinking to mitigate swelling. Other polymers such as polyacrylonitrile (PAN) offer robustness, [31-32]. Polydimethylsiloxane (PDMS) is specifically used for organophilic applications. The design of MMMs entails binding a hydrophilic selective matrix to optimized fillers and crosslinking to stabilize flux without plasticization and interfacial issues. Literature indicates that achieving high flux while maintaining selectivity necessitates integrated control over polymer chemistry, crosslink density, and the filler-matrix interface. Studies highlight that carbon molecular sieve fillers, when uniformly distributed in polyethersulfone (PES) membranes, enhance selective transport due to impermeable interfaces [33-35]. Additionally, the incorporation of diethanolamine (DEA) improves filler-polymer compatibility, reducing voids and enhancing selectivity and permeability in pervaporation applications. The review emphasizes advancements in Pebax-based nanocomposite films for challenging applications like olefin/paraffin separation, water treatment, flexible electronics, and antimicrobial surfaces. It also surveys various fillers and evaluates the performance of resulting nanocomposites table 1. Guidelines for material selection, compatibilization methods, and performance enhancement strategies are discussed, featuring methods to address inherent nanocomposite drawbacks, including those involving MIL-53(Al) metal-organic frameworks (MOFs) (Figure 2b) [36-38].

4. NANOFILLERS IN MIXED MATRIX MEMBRANES

4.1 Carbon-Based Nanofillers

The document discusses the various carbon-based nanomaterials, including graphene, graphene oxide (GO), reduced graphene oxide (rGO), carbon nanotubes (CNTs), and carbon nanofibers (CNFs), emphasizing their properties and applications in mixed matrix membranes (MMMs) for separation technologies. These materials are favored as fillers due to their ability to be chemically altered, their layered structures, and their significant effects on the hydrophilicity and rigidity of membranes. GO is highlighted for its utility in dehydration processes because its surface is rich in oxygen-containing groups that attract water molecules, enhancing water sorption and creating tortuous pathways in polymers like polyvinyl alcohol (PVA) and polyacrylonitrile (PAN), which aids in blocking organic permeation [39-41].

CNTs and CNFs differ in their effects due to their high aspect ratios, forming aligned nanochannels that facilitate water transport, contingent on proper interfacial compatibility. Agglomeration of CNTs may necessitate functionalization to promote better interaction with polymers. While rGO has superior stability compared to GO, it demands further modification for improved dehydration selectivity. The paper also introduces a method for modifying UiO-66, a metal-organic framework, using Cloisite Na-MMT clay to create a blended material with GO incorporated into a polysulfone matrix, demonstrating advancements in MMM applications [42]. Table **2,** reported water–ethanol, water–DMC, and water–methanol separation data using carbon-based MMMs discussed in [43-46].

The discussion includes how the effectiveness of CO2 separation is improved through the incorporation of specifically designed nanomaterials like amine-functionalized carriers and addresses the complexities of interactions between polymers and nanofillers crucial for optimal performance. Key insights into the importance of the arrangement of nanosheets and their functionalization on the separation efficiency further underscore the findings. Tables 2&3 and Figure 2(c&d) referenced indicate data on water separation efficiencies and show how these carbon-based nanomaterials can be effectively integrated into polymer matrices, resulting in robust performance in pervaporation applications. Overall, the document illustrates the evolving role of carbon nanomaterials in enhancing the performance of separation technologies through tailored structural and chemical properties [47-50]. Table 3 demonstrates the efficiency of major carbon-based nanomaterials, namely GO, CNTs, GO - CNT hybrids, graphene, and its variants in mixed-matrix membranes pervaporation (Figure 3) [45, 51-59].

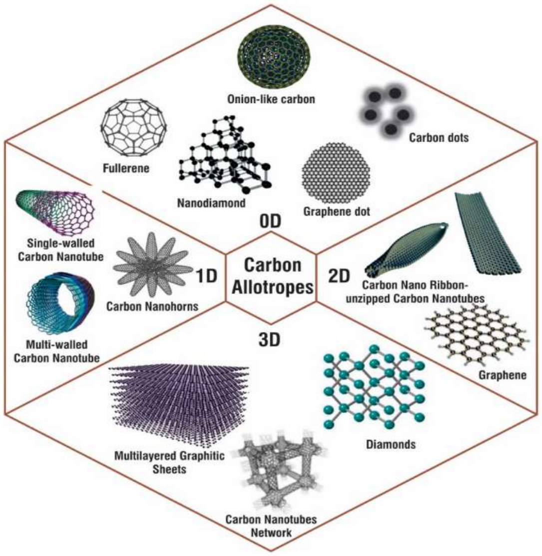

Figure 3. Various nanoforms of carbon allotropes with examples for 0D, 1D, 2D, and 3D carbon nanostructures, adapted

Chemical, mechanical, thermal, and electrical properties of different allotropic forms are also closely related to the structure and state of hybridization of carbon. Thus, these properties enable the same material to be used across diverse applications. Although operating the scanning electron microscope (SEM), cross-section images failed to record any apparent variation between the pristine and the electron irradiated CMS membranes, the scan of an energy-dispersive X-ray spectrometer (EDS) indicated an asymmetric chemical composition with an oxygen-rich surface of the CMS film following the electron irradiation [60]. The images of the CMS films using the high-resolution transmission electron microscopy (HR-TEM) demonstrated the maze-like structure of the amorphous carbon membranes. The respective Fast-Fourier Transformed (FFT) patterns reveal continuous rings with strong contrast differences in the images of the TEM that denote the representative pattern of disordered carbon strands. In addition, the loss of radial intensity at 3.94 min^{-1} in the pure CMS following the process of electron irradiation is a pointer to having produced condensed ultra-micropore sizes. The more elongated ultra-micropores cause less availability of the transport channels to the large gas molecules, hence, selective selection of the closely-sized gas pairs.

4.2 Zeolite Nanoparticles

Zeolites (4A, 13X, NaA, and ZSM-5) are the most established inorganic fillers to be used in dehydration applications because of their high hydrophilicity, high rigidity of microporosity, and clear aluminosilicate structures [61]. The pore sizes of zeolites 4A and NaA are optimal for water molecules, and therefore, they can act as molecular water traps within the polymer structure. They are highly intrinsically water adsorbing with a high sorption rate that facilitates fast sorption-based transport and are thus among the earliest and most successful PVA and PAN membranes [62-63]. Nanoparticles of zeolites enhance the rigidity of the membrane structure and prevent the relaxation of polymer chains during long-term exposure to polar solvents. They have a crystalline microporous structure, which guarantees the exclusion of organic molecules, in particular, with a higher kinetic diameter. Despite having larger pore apertures (approx. 5.5 Å), ZSM-5 has added mechanical strength and thermal stability without negatively affecting the overall dehydration performance of the blended system in hydrophilic polymers [64]. Unless functionalized appropriately, their inorganic surface might not be compatible with polymer chains, which causes microvoids to form. Dispersion and interfacial adhesion could be enhanced greatly through surface modification with silane coupling agents (e.g., APTES, GPTMS) or partial ion exchange. Besides, high loadings (>20–25 wt%) may result in particle-to-particle aggregation, thus decreasing permeability and creating nonselective areas of transport [65]. Despite these drawbacks, zeolite-filled MMMs tend to continue to take a leading role in the comparison of the performance of new nanomaterials [66]. A role of zeolites particularly 3A, 4A, NaA, 13X as highly successful inorganic fillers of hydrophilic MMMs in pervaporation. The classical LTA-type zeolites (3A, 4A and NaA) regularly yield very high separation factors (2000-7000) due to their micropores (3-4 A) that are suitable for adsorbing water but not bigger alcohols. The leading one is Zeolite 4A, which is the standard filler of PVA membranes as it provides high flux and high molecular sieving in the optimal loadings (10-15 wt. Zeolite 3A is highly water-selective but with slightly reduced flux because of tighter pores, whereas NaA is similarly water-selective and has high hydrophilicity, with PVA being highly compatible with its structure and hydrophilicity, although PAN-based systems confer greater chemical stability [67-69]. The hierarchically-ordered zeolites have been receiving increased attention within the past 15 years because of their exceptional properties, which are studied in catalytic reactions with industrial applications [70]. Hierarchical zeolites therefore, incorporate the inherent (catalytic) characteristics of the traditional zeolites and the ease of access and transport through the supplementary pore system [71]. So far, there are already many different types of synthetic strategies reported that enable to addition of another system of meso- or macropores evident in addition to the inherent microporosity of the classical zeolites [72]. The different synthetic pathways, which have been reported to date, the different physico-chemical techniques, which are needed to fully characterize the hierarchical pore system, and selective applications, which are of technical interest or could be of interest, are presented in this critical review.

4.3 Metal–Organic Frameworks (MOFs) in MMMs

Metal-organic frameworks (MOFs) have become one of the most versatile and high-performance types of fillers in mixed-matrix membranes (MMMs) because of their exceptionally controllable pore architecture, ultrahigh surface area, and extensive chemical functionalization opportunities. Their modular, crystalline structure enables the formation of pore aperture, topology, hydrophilicity, and flexibility of their framework to be tightly regulated, and also, when embedded in hydrophilic polymer matrices, provides highly selective water transport routes [73]. ZIF-8, UiO-66, MIL-53, and HKUST-1 -1000-104], are some of the most popular MOF in the process of dehydration pervaporation. Zeolitic imidazolate framework with sodalite cages (~ 11.6 A) and pore apertures (~ 3.4 A), ZIF-8 is a hydrophobic zeolite framework that has size-selective channels that inhibit organic diffusion and allow water diffusion via defect sites or flexible linkers [74]. It has an aperture of approximately 3.4 Å, which offers molecular-sieving properties and which is selective against water and bigger organic molecules [75]. However, it is hydrophobic, and therefore water transport is mainly a result of size exclusion and not due to selectivity through sorption. UIO-66, in its turn, contains hydrophilic groups of zirconium oxide, which facilitate water adsorption to a considerable extent, making it one of the most promising MOFs in dehydration MMMs [101]. MIL-series MOFs (e.g., MIL-53, MIL-101) add the effects of breathing and flexible pore geometry, which adjust under working conditions, a property that can be beneficial to selectivity combined with causing instability depending on the polymer matrix [76-78]. Conversely, UiO-66, which is constructed on Zr -O clusters, is hydrophilic in nature and has an excellent structural stability, thus, becoming especially useful in water-selective PV, as its –OH sites and unsaturated metal centres provide high water sorption and water hopping rates at the matrix-filler interface. The advantage of MIL-53(Al/Cr/Fe) is its breathing effect framework flexibility that enables it to contract/expand pores with or without the presence of sorbate molecules, and thus, exhibit greater sorption-diffusion selectivity against water in low alcohol concentration [79]. HKUST-1 (Cu-BTC), with its open metal sites, is very reactive to polar penetrants, but being hydrolytically unstable in humid environments restricts the longevity of PV application unless it is coated with a polymer or its linkers are modified. One of the lessons of the recent MMM research is that hydrophilic and hydrophobic MOFs act completely differently when it comes to applications in water-selective membranes. Hydrophilic MOFs (UiO-66, MIL-53) are more likely to increase water sorption and promote hydrogen bonding, and usually increase flux and selectivity. Contrastingly, hydrophobic MOFs (ZIF-8, ZIF-7) play a secondary role through the use of molecular sieving, defect attenuation, and enhanced free volume, which leads to moderate flux, but increased selectivity [80]. Consequently, selection of MOF needs to be in conjunction with the hydrophilicity of polymer matrix, intended separation mechanism, and stability demands. In spite of their strengths, MOFs have long-term issues: hydrolytic degradation, structural collapse when used in long-term humid conditions, instability of metal-linker bonds, and interfaces between particles and the polymer. Ligand functionalization, mixed-linker routes, core shells, and hydrophobic surface coatings, are the current operational strategies to enhance the long-term performance and stability of PV. The significant benefit of MOFs is the possibility to create uniform microchannels without degradation of structural integrity even at moderate loading (1-15 wt%). Nevertheless, the compatibility problems are typical: low dispersion or adhesion of the polymer and the MOF usually results in interfacial cavities, dominating over the benefits of molecular sieving [81-82]. Surface modification, the replacement of ligands, grafting of polymers, or attachment of hydrophilic functional groups has become imperative in the attainment of defect-free MMM structures. The long-term water stability of some of the MOFs is another factor: although UiO-66 is one of the most stable, some MOFs, such as HKUST-1, may hydrolyze in the presence of high humidity, which reduces their resistance to pervaporation operation [83].

4.4 Metal Oxide Nanoparticles & Metal Nanoparticles

The interaction of nanoparticles with polymer chains is often based on the hydrogen bond or the dipolar type of interaction that may cause a decrease of polymer mobility, swelling inhibition, and overall selectivity [84]. TiO_2 is a filler that is mostly researched because it has a hydrophilic surface, photocatalytic, and mechanical strengthening capabilities [85]. Metal oxides such as TiO_2, SiO_2, ZnO, Al_2O_3, and Fe_3O_4 are very common due to their enhanced chemical stability, their ability to have their surface modified easily, combined with their capability to alter the morphology of the membrane in Figure 4(a).

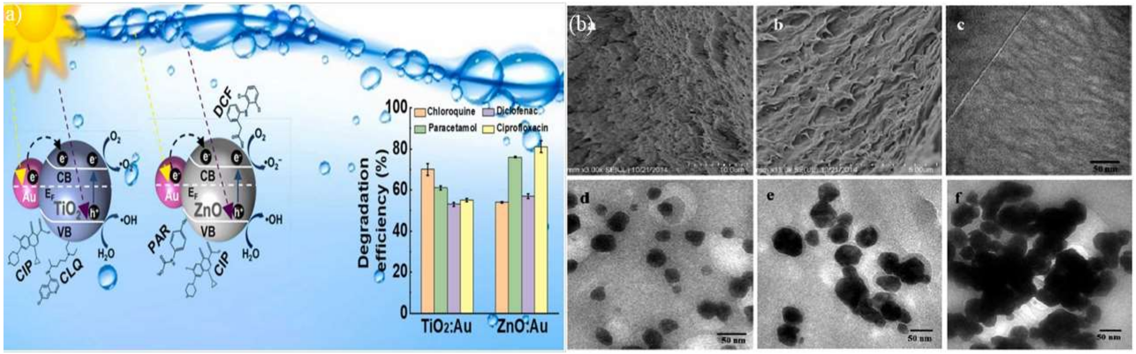

Figure 4. (a) Correlation between nanoparticle content and separation factor, adapted (b) Electron micrograph and schematic of Ag nanoparticle-loaded PVA MMM, adapted.

ZnO and Al_2O_3 have the potential to enhance the rigidity and decrease the free volume of the polymer, preventing organic diffusion and promoting the uptake of water via hydroxyl-rich surfaces. SiO_2 nanoparticles, particularly the mesoporous ones, are advantageous in terms of being tunable in terms of pore structures and high surface area, whereas Fe_3O_4 has other advantages such as magnetic responsiveness [86], useful for alignment or controlled dispersion. Exhibit an increased flux and selectivity as a function of particle size, surface chemistry, and loading. They, however, can also be subject to agglomeration because of high interparticle interaction, and therefore, great caution is required in the process of synthesis and dispersion. The potential results of excessive loadings include brittleness or phase separation, suggesting that optimization of the particle concentration (which is usually 0.5-15 wt%) is essential to achieve balanced performance. Metal nanoparticles such as silver, gold, copper, and iron are becoming of interest with regard to pervaporation MMMs because of their special catalytic and antifouling characteristics. They are highly surface reactive (their size is usually 10-50 nm), thus being able to interact dynamically with polymer chains and permeant molecules [7,55,87]. Silver nanoparticles and iron oxide nanoparticles showed high antimicrobial properties, which may be useful in membranes that are vulnerable to biofouling conditions [88-91]. Gold nanoparticles are costly but offer a high level of chemical stability and controllable surface chemistry, and are not as commonly applied in large-scale composite membranes [92]. Copper and iron nanoparticles can function as catalytic sites that alter local sorption environments or form reactive species in the operating conditions [93]. Despite these promising attributes, metal nanoparticles are challenging: they can oxidize, jam up, or leak away in the continuous pervaporation mode [94]. Their use in the separation of water-solvent is usually indirect, to enhance stability and resistance to fouling, and not to directly control the transport of the molecules. Therefore, their use is still in development and needs more systematic investigation to assess the results in the long term and security shown in Figure 4(b), depicting about the Electron micrograph and schematic of Ag nanoparticle-loaded PVA MMM.

6. Performance Analysis of MMM in Pervaporation

A critical analysis of the state-of-the-art mixed matrix membranes (MMMs) in pervaporation dehydration indicates that much more progress has been made in terms of hybridizing polymer nanoparticles; however, the subject is characterized by complicated performance-trade-off, structural discrepancy and lack of industrial validation. The most effective systems that have been described in the literature have a combination of hydrophilic polymer matrices with highly functional inorganic fillers that are able to aid water sorption, provide selective transport pathways, and prevent excessive swelling. However, the most efficient MMMs have their limitations in terms of stability over time, filler-polymer compatibility and scaling of processes [95-98]. This part critically analyzes the best performing MMMs, the underlying forces defining their transport behavior and their sustainability concerns which remain a limiting factor to their practical use.

6.1 Best Performing MMMs from Literature

Among the wide range of polymer–filler systems investigated, several MMM configurations have continued to show the best dehydration behavior. The PVAGO based membranes are still among the most researched systems which can be explained by the outstanding hydrophilicity of graphene oxide, adjustable functionality, and two-dimensional nanochannels that allow the fast selective passage of water [99-101]. GO incorporation has been known to enhance flux and selectivity at relatively low loadings (0.210 wt%), as long as the dispersion is uniform and the interfacial adhesion is preserved. Nevertheless, reproducibility in the long run can be affected by the fact that GO tends to restack and that it can be damaged in the course of operation [102]. Critical examinations also point out that various improvements described may have to do with the formation of microvoids and not be inherent with the benefits of transport that GO itself has to offer, and the actual mechanism behind the accomplishments. Another type of high-performance systems are PVA–zeolite MMMs, and especially those that make use of zeolite 4A, NaA, or 13X [103-105]. Zeolites offer rigid, hydrophilic micropores and absorb water selectively as well and the well-defined pore geometry facilitates molecular sieving. The old benchmark material of zeolite 4A/PVA membranes is always associated with high separation factors in both ethanol-water and DMC-water systems [106]. Nevertheless, recent reviews have revealed that the reproducibility of the dispersion of zeolites and the regulation of interfacial compatibility (particularly, the prevention of interfacial voids) can be considered unresolved concerns. Besides, the operational durability can be diminished by the mechanical brittle nature of high zeolite loadings. MMMs based on PANs, which include MOFs like ZIF-8, UiO-66, or MIL-series structures, have also become a promising top competitor in high-temperature or chemically sensitive solvents [107]. The resistance of PAN to swelling, together with the modular pore structures of MOFs, makes it possible to move water through PAN even in harsh environments. A case in point is ZIF-8/PAN, which has shown effective results in the process of separating ethanol and water along with methanol and water [108-110]. Nevertheless, water-selective pervaporation of many MOFs is complicated by their hydrophilic nature, thus requiring post-synthetic modification or hydrophilic functionality to be incorporated. Moreover, the stability of MOFs in aqueous mixtures is very heterogeneous; certain MOFs dissolve or lose their crystallinity over time, which puts a huge gap between the laboratory and industrial functions [111]. Overall, while each of these systems showcases distinct advantages, a critical analysis will show that the enhancement of the performance is frequently contingent upon delicate compositions, a particular system of solvents, and optimal conditions of operation. This makes comparison difficult and indicates that the allegations of high performance being universal should be understood with a question mark.

6.2 Influence of Key Factors

Further insight into MMM performance is achieved by considering the underlying factors of performance that are physicochemical in nature and determine the process of water sorption, diffusion, and selective transport. Polymer crosslinking density is considered to be one of the most powerful parameters. Increased crosslinking usually increases selectivity by decreasing the mobility of polymer chains and eliminating swelling in particularly high polar solvents like methanol or DMF [112-114]. Nevertheless, over-crosslinking brings about low free volume and available flux. Critical evaluation shows that some of the best-performing MMMs have been based on intermediate levels of crosslinking between structural rigidity and adequate permeability. The loading of nanoparticles is also a crucial part, and several studies have shown that it has a percolation threshold beyond which fillers form continuous or semi-continuous networks that contribute greatly to the transport [115-116]. This is threshold in that, below it, the improvements are frequently of a minor nature or are dominated by interfacial effects; whereas, above that threshold, agglomeration is inevitable, resulting in the development of voids or filler-laden defects. The ideal loading is diffuse in relation to the size of particles, their shape, surface chemistry, and affinities of the polymer [116,117]. Reports of dramatic performance at very high loadings (>10 wt%) commonly have a lack of interfacial control and are likely to have non-uniform performance when scaled up. The solvent-polymer interaction parameter (χ) is also another consideration that determines the polymer swelling behavior, and is a determinant of selective sorption. Low χ values are characterized by high polymer and solvent interactions, hence swelling, and this reduces selectivity. As an example, methanol has especially difficult interactions with hydrophilic polymers, which reduces the separation factors. MMMs strive to control the χ by adding hydrophilic stiff nanoparticles that tend to bind water more than other particles to change the sorption equilibrium. But, according to critical reviews, the changes in χ tend to give solvent-specific effects instead of general improvements. Finally, polymer crystallinity and chain mobility significantly affect transport properties. High crystallinity decreases the available free volume and increases selectivity, at the expense of low flux. Nanoparticles are known to be numerous nucleating agents that enhance or reduce crystallinity in relation to surface chemistry. The only problem with the literature is that such structural changes are frequently reported only qualitatively, without the precise method of differential scanning calorimetry (DSC) or X-ray diffraction (XRD). Thus, a portion of the performance improvements that are reported can be due to changes in crystallinity that are not intended, but not because of the inherent transport properties of the nanoparticles themselves.

6.3 Long-term Stability

Although the temporary gains in flux and selectivity are often highlighted, the long-term stability is one of the biggest issues of MMM-based pervaporation systems[118]. Effects of ageing, such as polymer relaxation and rearrangement of chains, the formation of microcracks, can considerably change the transport behaviour over time. Physical aging in hydrophilic polymers like PVA results in a decrease in free volume and decreases the flux when operating over an extended period. MMMs could increase such effects in case nanoparticles cause a breakage of polymer packing or serve as stress concentration sites. The other important stability issue is nanoparticle leaching, which is a major issue with metal oxides, MOFs and metal nanoparticles. Pervaporation can destroy interactions between polymer and filler due to mechanical stresses and repeated swelling-deswelling cycles, which lead to attachment and loss of fillers and poor performance. This is a problem that is rarely evaluated in laboratory research, but is a bane of industrial implementation, where months or years of continuous operation are anticipated. There is also the chemical compatibility in solvent systems, which is an under-researched area in most reports. Some polymers can be plasticized, chemically attacked to some degree by methanol, THF, acetone and water-rich environments may hydrolyze or degrade sensitive nanomaterials like ZIF-8 or MIL-series MOFs. Nanoparticles of metals can be oxidized or restructured on the surface, which affects their interaction with the polymer matrix [119]. Critical evaluations also point out that most of the MMMs that have worked well have been tested at low temperatures but the processes performed in industries usually need to operate at temperatures that are 80–120°C. Finally, despite the remarkable achievements that have occurred in the development of the advanced MMMs, the discrepancy between laboratory performance and real-life reliability is wide [120]. To obtain industrially viable pervaporation membranes, more systematic investigations regarding the long-term structural stability, interfacial strength, and solvent compatibility, which have been poorly covered in the literature so far, will be required.

7. CHALLENGES AND FUTURE DIRECTIONS

Despite the substantial progress achieved in developing mixed matrix membranes to operate in pervaporation dehydration, there has been a small move between laboratory prototypes and technologies that can be used in industries. Critical evaluation of available literature indicates that the bottle-necks exist which are linked to filler dispersion, interfacial compatibility, long-term stability, scalability, environmental sustainability, and regulatory acceptability. Moreover, the to-be-developed innovations should incorporate new nanoarchitectures, intelligent functional materials, and data-driven designs frameworks to circumvent the inherent drawbacks of polymer-nanoparticle hybrid systems. This part consolidates the major challenges preventing further implementation of MMM-based pervaporation technologies and describes the new research directions that can transform the sphere.

8. 0 Technical Challenges in MMM Fabrication

Among the most basic issues of MMM fabrication is the homogeneous dispersion of nanoparticles in the polymer material. Defects due to poor dispersion result in agglomeration, which causes selectivity and mechanical integrity defects. According to the literature, nanoparticles, including GO, MOFs, zeolites, and metal oxides, have high surface energies, which predetermine their clustering under mixing and evaporation of solvents. Even with surface functionalization (e.g. silanization, amine functional groups), it is hard to obtain reproducible distributions at higher loadings. The problems tend to increase in the course of membrane casting, where the rate of solvent evaporation and shear environment can affect ultimate morphology. Very connected to dispersion is the problem of interfacial voids. The polymer filler interface is very sensitive to the transport mechanism, but discrepancies in surface chemistry, rigidity, and thermal expansion tend to create nano or micro gaps. The voids may serve as non-selective routes that enhance flux at the cost of water selectivity. Although many papers have suggested surface modification, polymer blending, or compatibilizers to address the interfacial defects, the outcome differs depending on the systems, and a universal interfacial engineering strategy has to emerge. The other problem that is be resolved is the absence of standardized testing protocols. The variability in the content of the feeds, temperature, membrane thickness, downstream pressure and methodologies make cross-study comparisons challenging. The values of flux and selectivity that are reported in the literature are usually optimized in laboratory conditions and not in industrial scenarios. Moreover, not many studies have error bars, long-term testing, or statistical analysis, which restrict the credibility of performance claims. At present, there is a significant gap between laboratory membranes and pilot-scale prototypes.

8.1 Environmental and Regulation

Besides technical challenges, environmental and regulatory concerns regarding Mixed-Matrix Membrane (MMM) deployment are increasingly prioritized in research. A significant issue is the life-cycle environmental impact of polymer-nanoparticle membranes. Despite pervaporation being energy-efficient, the preparation of nanoparticles often involves non-toxic solvents, high-temperature reactions, and questionable energy efficiency, raising sustainability concerns. Comprehensive life-cycle analyses (LCA) are scarce, as are assessments of the ecological footprint from production to disposal. Additionally, the safety of nanoparticles, which can leach into the environment during production and disposal, poses regulatory challenges, particularly for materials like Ag, Cu, Fe, ZnO, TiO2, and MOFs. Current studies mainly focus on short-term nanoparticle leaching, failing to address long-term exposure in industrial applications. Regulatory bodies are increasingly demanding data on nanoparticle behavior and management at end-of-life. Furthermore, concerns arise from toxic precursors and solvents used in membrane manufacturing, although emerging green-solvent technologies offer potential environmental benefits, albeit still at an exploratory stage [121-124].

8.2 Emerging Trends

In response to current weaknesses in mixed matrix membranes (MMMs), new research is focusing on SMART MMMs, which are stimuli-responsive membranes that can adjust permeability or selectivity based on environmental factors like temperature and pH. Although mainly conceptual, these membranes may enhance industrial processes by preventing fouling and allowing process intensification. Innovations also include nano-architectured metal-organic frameworks (MOFs) with improved stability and precise pore regulation. However, challenges remain regarding scalable production and chemical stability. Artificial intelligence is being employed to optimize membrane design and performance, utilizing data analytics and digital twins to facilitate real-time monitoring and predictive maintenance. Additionally, renewable polymer matrices such as cellulose derivatives and biodegradable materials present sustainable alternatives, though concerns over stability and lifespan need further investigation before industrial application.

9.0 Conclusion

Mixed Matrix Membranes (MMMs) show promise in addressing the limitations of traditional polymeric membranes for pervaporation dehydration of solvent-water mixtures. Despite advancements with various nanomaterials integrated into PVA and PAN matrices, achieving industrially viable performance remains challenging due to factors like optimal filler dispersion and morphological control. Persistent issues such as interfacial gaps, nanoparticle agglomeration, and stability hinder scalability. Environmental and regulatory concerns regarding nanoparticle synthesis exacerbate these challenges. Future work should emphasize interface engineering, standardized testing, and understanding solvent-polymer-filler interactions. Innovative approaches, including nano-architectured fillers and AI-assisted design, hold potential but require validation in industrial contexts. Ultimately, successful commercial application hinges on bridging material innovation with sustainable, scalable technologies.

Author Contributions

Conceptualization, Investigation, Writing- Original Draft, editing: AM & PA; Writing- Review, Methodology and Supervision: SRP; Project Administration, Resources: HD, Project Administration, Visualization, Supervision: KN, All authors have read and agreed to the published version of the manuscript.

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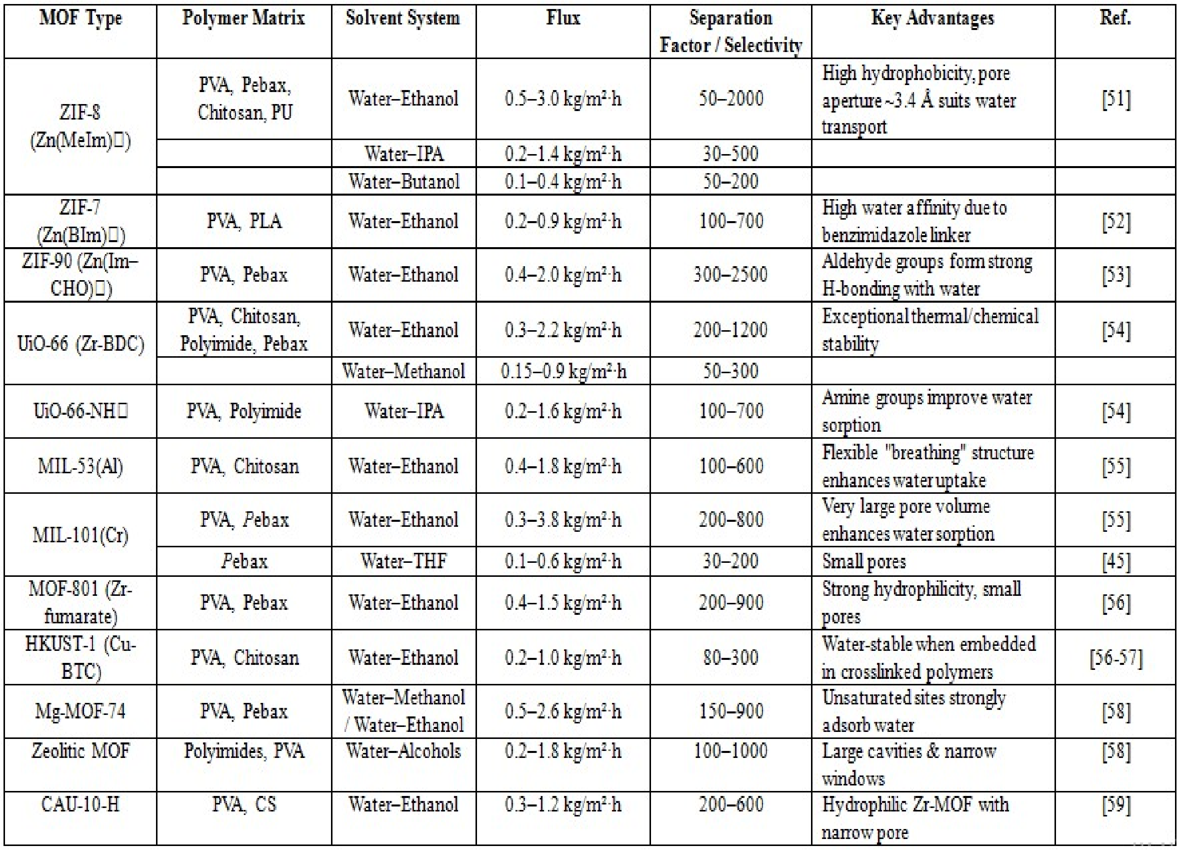
Table 1: Polymers used in pervaporative MMMs

Polymer Matrix	Water Permeability Behavior	Water Selectivity	Thermal & Chemical Stability	Swelling Resistance	Ref.
PVA (Polyvinyl Alcohol)	High water affinity → high water sorption and permeability due to abundant –OH groups	High intrinsic water selectivity; improved further with hydrophilic fillers (GO, MOFs, zeolites)	Moderate thermal stability; good chemical stability when crosslinked; otherwise prone to dissolution/swelling	Moderate thermal stability; good chemical stability when crosslinked; otherwise prone to dissolution/swelling	[33]
PAN (Polyacrylonitrile)	Lower water permeability than PVA due to lower hydrophilicity; permeability increases with filler functionalization	Lower than PVA intrinsically but improves with zeolites/MMMs (e.g., 4A, 13X)	Very high thermal and solvent stability; stable even in DMF/THF; excellent mechanical strength	Naturally good swelling resistance; suitable for aggressive solvents; maintains dimensional stability even in harsh organic media	[34]
Chitosan (Biopolymer)	High water sorption due to amine and hydroxyl groups; good permeability in aqueous systems	Excellent water selectivity for alcohol/water systems	Moderate chemical stability; limited long-term resistance; sensitive to pH and solvents; crosslinking needed	Prone to excessive swelling; crosslinking with GA reduces swelling significantly	[35]
PDMS (Polydimethylsiloxane)	Very low water permeability (hydrophobic); high permeability to organics, not water	Poor water selectivity; excellent for organophilic PV (VOC removal)	Excellent thermal and chemical stability; very stable elastomeric polymer	Swelling occurs in organic solvents; swelling is less of an issue for water-rich systems because PDMS is hydrophobic	[36]
Polyimides (PI)	Moderate water permeability; inherently less hydrophilic than PVA/PAN	Needs hydrophilic modification to achieve high water selectivity	Very high thermal & chemical stability; excellent for harsh conditions; stable under aggressive solvents	Very good swelling resistance; rigid aromatic backbone resists plasticization	[37]
PEBA / Pebax (Polyether-Block-Amide)	Soft ether blocks provide moderate–high water permeability; tunable permeability through block composition	Good water selectivity when combined with MOFs/zeolites	Good thermal stability; moderate chemical stability; plasticization possible in strong solvents	Moderate swelling resistance; improved by fillers; polyamide hard blocks add rigidity	[38]

Table 2: Reported water–ethanol, water–DMC, and water–methanol separation data using carbon-based MMMs

Polymer matrix	Carbon filler (loading)	Solvent feed (wt% water) / Temp	Flux (g·m□^{2}·h□^{1})	Separation factor (or selectivity)	Ref.
PVA (crosslinked)	Graphene oxide (GO) — 2.0 wt% (optimal)	Ethanol–water (10 wt% water) / not stated	145	3059	[43]
PVA (crosslinked)	GO + carboxylated CNT (GO–CNT–COOH hybrid) — low wt% (hybrid)	Ethanol–water (10 wt% water) / 23 °C	870 (0.87 kg·m□^{2}·h□^{1})	523	[43]
PVA (crosslinked)	GO (1 wt%)	Ethanol–water (90 wt% EtOH) / 40 °C	137 (0.137 kg·m□^{2}·h□^{1})	263	[43]
PVA (modified / PTES hybrid)	Organosilica / GO-like hybrid (not pure carbon)	Ethanol–water (85 vol% EtOH) / 40 °C	145	1026	[44]
PVA (double-crosslinked GO interlayer)	GO (0.1 wt%) interlayer design	Ethanol–water (feed omposition not always identical) / not stated	4,391	1,491	[45]
Polyimide / other sturdy polymer	rGO / reduced GO	Ethanol–water (10/90 wt%) / 20–50 °C	(reported permeation) selectivity > 12 (total flux lower)	Selectivity > 12 reported	[46]

Table 3: Summary of MOF-based MMMs for pervaporative dehydration of solvents.



MOF Type	Polymer Matrix	Solvent System	Flux	Separation Factor / Selectivity	Key Advantages	Ref.
ZIF-8 (Zn(MeIm)□)	PVA, Pebax, Chitosan, PU	Water–Ethanol	0.5–3.0 kg/m²·h	50–2000	High hydrophobicity, pore aperture ~3.4 Å suits water transport	[51]
		Water–IPA	0.2–1.4 kg/m²·h	30–500		
		Water–Butanol	0.1–0.4 kg/m²·h	50–200		
ZIF-7 (Zn(BIm)□)	PVA, PLA	Water–Ethanol	0.2–0.9 kg/m²·h	100–700	High water affinity due to benzimidazole linker	[52]
ZIF-90 (Zn(Im–CHO)□)	PVA, Pebax	Water–Ethanol	0.4–2.0 kg/m²·h	300–2500	Aldehyde groups form strong H-bonding with water	[53]
UiO-66 (Zr-BDC)	PVA, Chitosan, Polyimide, Pebax	Water–Ethanol	0.3–2.2 kg/m²·h	200–1200	Exceptional thermal/chemical stability	[54]
		Water–Methanol	0.15–0.9 kg/m²·h	50–300		
UiO-66-NH□	PVA, Polyimide	Water–IPA	0.2–1.6 kg/m²·h	100–700	Amine groups improve water sorption	[54]
MIL-53(Al)	PVA, Chitosan	Water–Ethanol	0.4–1.8 kg/m²·h	100–600	Flexible "breathing" structure enhances water uptake	[55]
MIL-101(Cr)	PVA, *P*ebax	Water–Ethanol	0.3–3.8 kg/m²·h	200–800	Very large pore volume enhances water sorption	[55]
	*P*ebax	Water–THF	0.1–0.6 kg/m²·h	30–200	Small pores	[45]
MOF-801 (Zr-fumarate)	PVA, Pebax	Water–Ethanol	0.4–1.5 kg/m²·h	200–900	Strong hydrophilicity, small pores	[56]
HKUST-1 (Cu-BTC)	PVA, Chitosan	Water–Ethanol	0.2–1.0 kg/m²·h	80–300	Water-stable when embedded in crosslinked polymers	[56-57]
Mg-MOF-74	PVA, Pebax	Water–Methanol / Water–Ethanol	0.5–2.6 kg/m²·h	150–900	Unsaturated sites strongly adsorb water	[58]
Zeolitic MOF	Polyimides, PVA	Water–Alcohols	0.2–1.8 kg/m²·h	100–1000	Large cavities & narrow windows	[58]
CAU-10-H	PVA, CS	Water–Ethanol	0.3–1.2 kg/m²·h	200–600	Hydrophilic Zr-MOF with narrow pore	[59]