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Zeolites-Mixed-Matrix Nanofiltration Membranes for the Next Generation of Water Purification

Mahboobeh Maghami and Amira Abdelrasoul

Abstract

Designing high performance and antifouling membranes are in a great need to remove water contaminations and to regulate the quality of drinking water. Mixed-matrix membranes (MMMs) could offer a solution to the permeability and selectivity trade-off in nanofiltration (NF) membranes. MMM could offer the physicochemical stability of a ceramic material while ensuring the desired morphology with higher nanofiltration permeability, selectivity, hydrophilicity, fouling resistance, as well as greater thermal, mechanical, and chemical strength over a wider temperature and pH range. Zeolites are fascinating and versatile materials, vital for a wide range of industries due to their unique structure, greater mechanical strength, and chemical properties. This chapter focused on zeolite-MMM for nanofiltration. Several key rules in the synthesis procedures have been comprehensively discussed for the optimum interfacial morphology between the zeolites and polymers. Furthermore, the influence of the zeolite filler incorporation has been discussed and explored for water purification. This chapter provided a broad overview of the MMM's challenges and future improvement investigative directions.

Keywords: mixed-matrix membrane, filler, zeolites, hydrophilicity, interfacial, morphology

1. Introduction

Both polymeric and ceramic membranes have been the center of interest for their tremendous contribution in the water treatment industry. Despite their advantages, these synthetic membranes have limitations in terms of operation and strength. Over the years, researchers have been attempting 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 new materials has been to associate the advantageous characteristics of the two types of membranes boosting the overall process efficacy. Conventionally, objectives such as enhancements 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. Nevertheless, material advancement in membrane technology and nanotechnology has made it possible to fine-tune the process efficiency and has successfully paved the path for the synthesis of MMMs for different applications. Aside from the water purification applications, the advent of MMMs has revolutionized other areas also where separation or purification is of big import. Some of these potential applications reported in literature include water purification, medical industry, catalytic, and gas separation. Nevertheless, MMMs have not even crossed the laboratory-scale barrier because the MMM technology is nevertheless in a developmental phase and only a few lab-scale developments have been described thus far.

2. Types of MMMs

MMMs can be defined as incorporating of dispersed nanomaterials such as zeolite, carbon molecular sieve, and carbon nanotubes incorporated in a continuous polymer phase. **Figure 1** presented a schematic of an ideal MMM structure including the dispersed phase and the polymer matrix [1].

MMM could offer the physicochemical stability of a ceramic material with promising the desired morphology with higher permeability; selectivity; higher hydrophilicity; high fouling resistance; high thermal, mechanical, and chemical strength over a wider temperature; and pH range [2–7]. These types of MMMs are named as inorganic filler-based MMMs, organic filler-based MMMs, biofiller-based MMMs, and hybrid filler-based MMMs, depending on the type
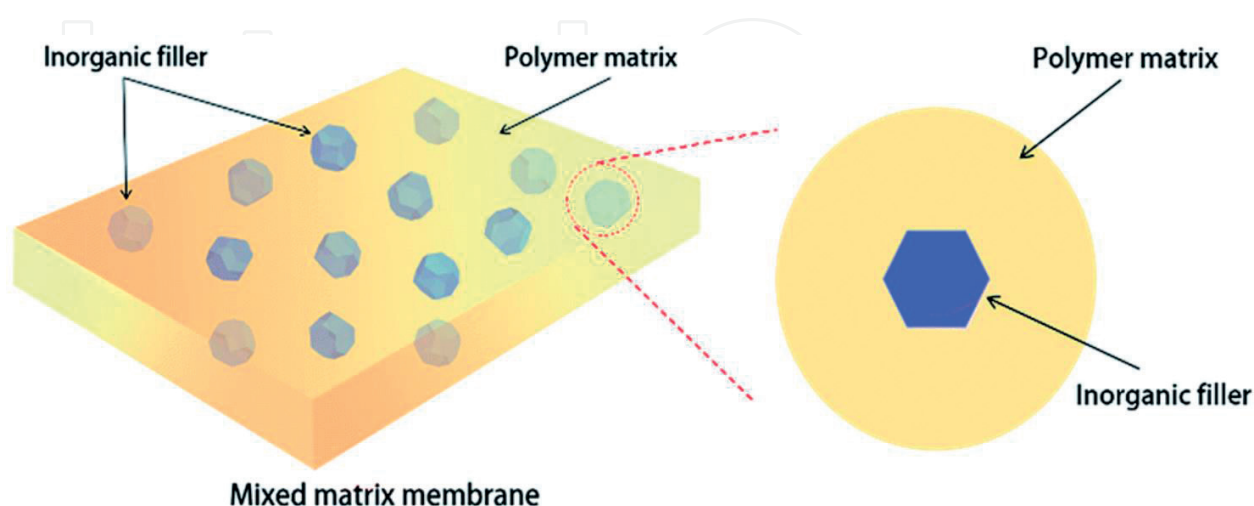

Figure 1. Schematic diagram of an ideal MMM structure [1].

of the dispersed fillers in the polymer matrix, as presented in **Figure 1** [1]. This chapter will focus on inorganic filler-based MMM, especially zeolite-MMM.

2.1. Inorganic filler-based MMMs

The field of inorganic filler-based membrane is a promising type of membranes, which has been explored extensively over the recent years. In the polymeric matrix, the 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 solgel, 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, mechanochemical synthesis, and electrodeposition. Currently, different types of inorganic fillers have been added to the polymeric phases. Some of these fillers are zeolite [8], silica [9], TiO_2 [10], carbon nanotubes [11], and silver [12]. There are two methods to incorporate inorganic fillers into membrane structure by blending with the solution or by attaching the fillers to the surface through different techniques [4]. Inorganic-based filler MMMs have been employed in water industry for the adsorptive removal of pollutants, disinfection and/or microbial control, catalytic degradation, and desalination [13]. They also have potentials to provide both high superior selectivity and the desirable mechanical and economical properties. Researchers believe that a suitable combination of polymers and inorganic fillers should offer superior permeability and selectivity compared to simple materials. In this review, zeolite-MMM will be comprehensively studied, as a promising membrane for several applications.

2.1.1. Zeolites-MMMs

Zeolites are microporous crystalline aluminosilicate materials with uniform pore and channel size; thus, they are used in various fields such as catalysts in the petrochemical industry, ion exchangers, and absorbents for softening and purification of water [14–16]. Incorporation of zeolites into a polymer matrix has attracted great attention in membrane technology, due to several excellent advantages such as permeability improvement of the selective component, in addition to the enhancement of the thermal stability, the mechanical strength of a polymeric membrane [17], thermal resistance and chemical stability [18–20]. On the other hand, zeolites are expensive. Limitation in both polymeric and zeolite offers the need to synthesize the novel polymer-zeolite-MMM. The interaction of zeolites in the membrane matrix and its shape-selective catalytic properties could improve permeability and selectivity separations [21]. There have been numerous attempts to incorporate zeolite particles in polymer matrices for gas separation due to its superior separation and size exclusion and in water purification applications [22, 23].

Rezakazemi et al. [24] studied the gas transport properties of zeolite-reinforced polydimethylsiloxane (PDMS) MMM. The filler was dispersed homogenously in the matrix without any voids at the zeolite-polymer interface. It was confirmed that the homogenous incorporation of filler in the matrix resulted in higher permeability for the MMM compared with the polymeric membranes.
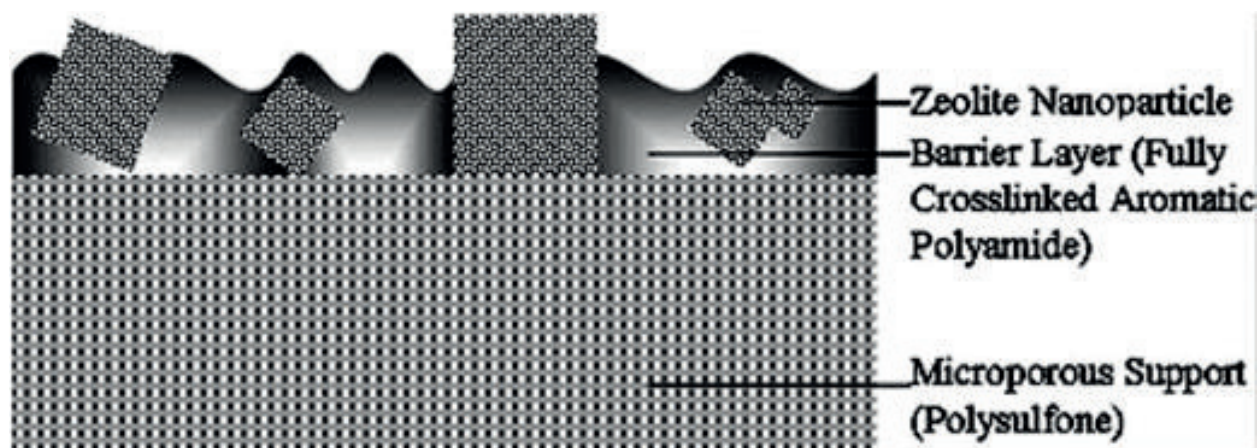
Figure 2. Schematic cross section of zeolite nanocomposite membrane (zeolite-MMM) [26].

Ciobanu et al. [25] reported that zeolite-polyurethane membranes demonstrated improved properties. The good interaction between the polymer and the zeolite at the interface was confirmed, and the membrane swelling was reduced. Consequently, the water flux through membrane increased with increasing zeolite concentration.

Hoek et al. [26] studied the formation of mixed-matrix reverse osmosis membranes by the interfacial polymerization of thin-film nanocomposite polysulfone supports impregnated with zeolites. **Figure 2** represents the cross-sectional image of zeolite nanocomposite reverse osmosis membrane, which is utilized for water purification through desalination process. It was found that increasing the zeolite nano-filler concentrations resulted in smoother, more hydrophilic, and more negatively charged MMM. As a consequence, the MMM membrane demonstrated high flux and a slight improvement in salt rejection compared to thin-film composite (TFC) membrane without zeolite nanoparticles due to changes of membrane morphology.

3. Interfacial morphology of zeolites-MMMs

To obtain the optimum interfacial morphology between the zeolite and polymer, several key roles should be considered. The first one is to promote the adhesion between polymer matrix and molecular sieve phases by modifying the zeolite surface with silane coupling agents [27–29]. The second one is to introduce low molecular weight materials (LMWMs) to fill the voids between polymer and molecular sieve phases [30, 31]. The third one is to apply high processing temperatures close to glass transition temperature (Tg) of polymeric materials to maintain the polymer chain flexibility during the membrane formation [32]. The fourth one is to prime the surface of zeolites by polymer [33].

.The polymer matrix plays an important role for permeability, and the inorganic filler has a controlling factor for the selectivity of the separation process. As a result, interfacial compatibility between the two phases has a profound impact on the separation performance for such

membranes. The addition of inorganic fillers has key impacts on the interfacial void formation, aggregation, pore blockage of the morphology, and the transport phenomenon. Consequently, the impregnation of zeolites has a significant influence on the overall performance of the newly developed MMMs. The formation of these interfacial voids is attributed to two main phenomena, the interaction between the polymer phase and the filler and the stress exerted during preparation [1, 32]. The presence of interfacial voids creates additional channels that allow for the solvent to pass through the membrane [34]. However, mechanical strength and rejection rate are also concerned by the channel density [35].

Figure 3 represents various structures at the polymer-zeolite interface region, and S represents the sieve in the polymer [36]. **Figure 3A** demonstrates a homogenous blend of polymer and sieve, indicating an ideal interphase morphology. **Figure 3B** shows polymer chain rigidification due to the shrinkage stresses generated during solvent removal. **Figure 3C** confirmed poor compatibility between zeolite and polymer matrix morphologies, due to the formation of voids at the interfacial region. **Figure 3D** indicates sealing surface pores of zeolites by the rigidified polymer chains. Overall, the interaction between polymer and zeolite is related to chemical nature of the polymer and sieve surfaces, and the stress encountered during material preparation, which are critical factors to form the interphase.

These features are a challenge and should be controlled or avoided for the synthesis of the targeted zeolite-MMM for several applications. The formation of relatively nonselective defects at the interface between the zeolite particles and the polymer medium will result in MMMs, which fail to demonstrate their performance [37]. Therefore, despite the good properties of the polymer-zeolite-MMMs, they still face some challenges to overcome.
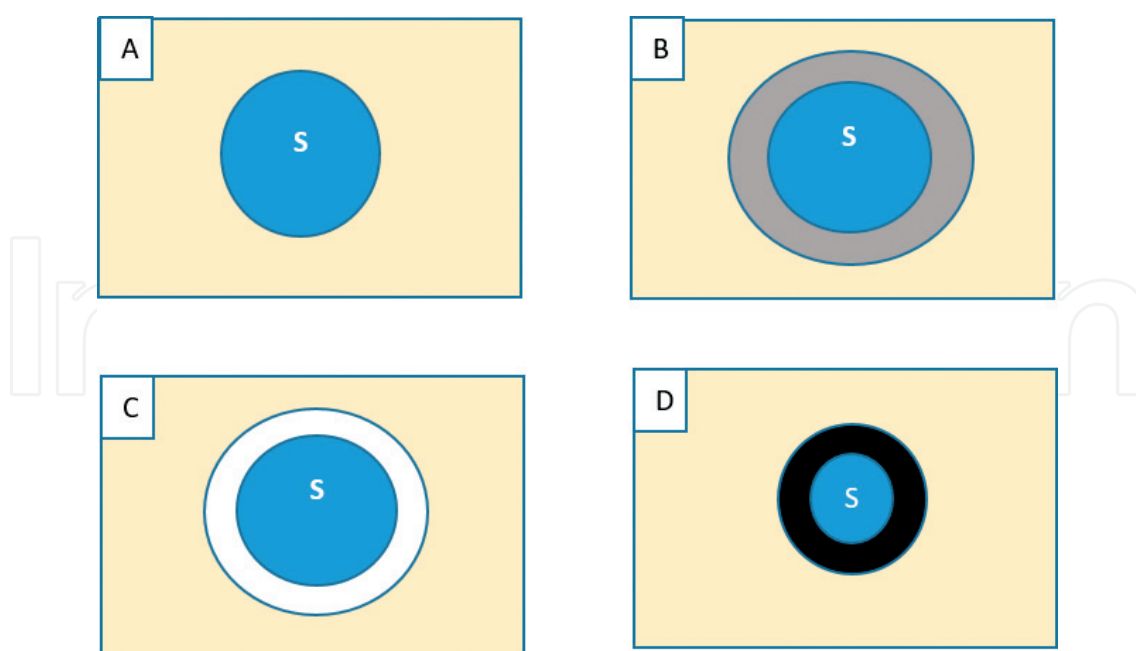

Figure 3. Illustration of various structures at the polymer-zeolite interface region [36]. (A) Homogenous blend of polymer and sieve (B) Rigidified polymer layer around the sieve. (C) Interfacial void around the sieve. (D) Sieve partial pore blockage.

4. Interfacial modification of zeolite-MMMs

Several strategies have been offered to improve the polymer-zeolite interaction and, hence, to avoid nonselective voids. These methods are included in incorporation of a plasticizer into the polymer solution that can decrease the polymer glass transition temperature (Tg) [32]. Consequently, polymer chain flexibility maintains during membrane preparation either by annealing the membranes above glass transition temperature of polymer [38, 39], or external surface of zeolites can be modified by coupling agents. The surface-initiated polymerization is the most frequent technique to improve the polymer-filler adhesion in polymer-zeolite-MMMs [40]. Furthermore, adding the low molecular weight additives (LMWAs) to the membrane formulation can act as a compatibilizer or the third component to prepare glassy polymer/LMWA blend membranes [31, 41]. Priming method can be also used to reduce the stress at the polymer-particle interface and to minimize agglomeration of the particles. Consequently, the interfacial interaction between the two components will be improved through coating the surface of the filler particles with a dilute polymer dope [31]; and eventually, minimizing of zeolite-solvent/zeolite-nonsolvent interaction, especially asymmetric MMM [42]. Therefore, the obtained hydrophobic surface can suppress the zeolite particles from acting as nucleating agents. As a result, it will minimize the voids induced by the unfavorable interaction between polymer and zeolite particles.

4.1. Interfacial modification with silane agents

Silane coupling agents were commonly proposed to modify the zeolite surface in order to improve compatibility of the inorganic filler with the polymeric matrix [43, 44]. It is known from literatures related to the silanation of zeolites that silane coupling agents have two types of reactive groups: the first type is the hydroxyl groups of zeolites, which could make hydrogen bonds with the amino silane agent [43], and the second one is the organo-functional group, such as amino and epoxy, which could be used to bond polymer chains to the zeolite. Therefore, improving adhesion between the zeolite and the bulk polymer phases in the membrane was achieved [45]. **Figure 4** shows a schematic silanation of zeolite surface with 3-aminopropyldimethylethoxysilane (APDMES) coupling agent [45].

Junaidi et al. [46] indicated that the glass transition temperature of MMMs is influenced by silane modification. In other words, the Tg of the zeolite-MMMs increased with the increasing of silane concentration on the surface of the zeolite particles. As a result, the silane modification of zeolite affects the mechanical properties of continuous phase due to the formation of the hydrogen bonding between the zeolite particles and polymer matrix and the movement reduction of the polymer chains [47, 41].

Pechar et al. [48] investigate the effects of silane grafting on the separation performance of MMM for permeation. The 3-aminopropyl trimethoxy silane (APMS) was added to modify SAPO-34 zeolite before the impregnation into the asymmetric polysulfone (PSf) MMMs through dry-wet phase inversion method. Both PSf and modified SAPO-34 membranes showed great enhancement in terms of selectivity and permeability compared to the original PSf membrane.
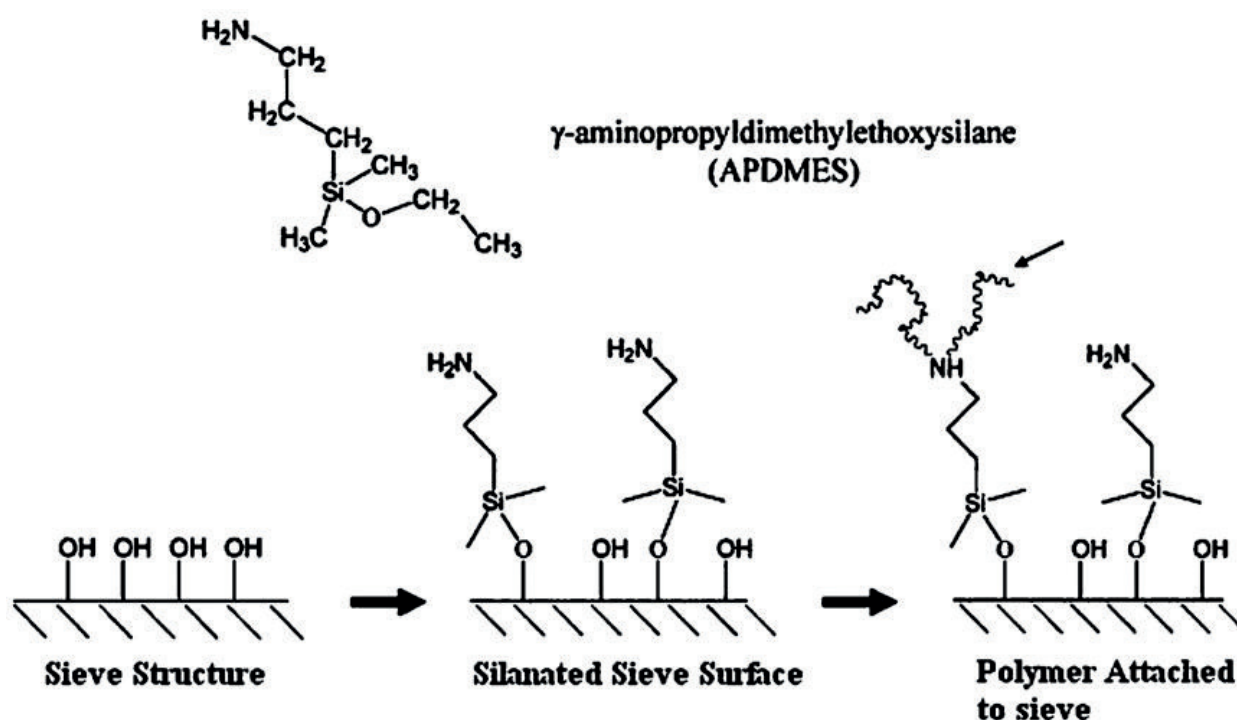
Figure 4. Schematic of the envisioned coupling reaction [45].

The increment of CO_2 selectivity and permeability was correlated to the diminishing of the interfacial voids, when SAPO-34 zeolite was modified using APMS in ethanol.

Sen et al. [49] studied the use of 3-aminopropyltrimethoxysilane (APTMS) influence to modify ZSM-2 zeolite to synthesize polyimide MMMs. Although micrographs showed the absence of voids, however, the modified ZSM-2-MMM performance for CO_2 selectivity and permeability was dropped relatively, similarly, to the performance of pure polymeric membrane, due to the pore blockage of the ZSM-2 zeolite [50].

In order to overcome this problem, other researchers such as Li et al. [28] modified zeolite 3A, 4A, and 5A using 3-aminopropylmethyldiethoxy silane (APMDES) in toluene solvent. Hence, rigidification of polymer chain and partial pore blockage reduced through this modification process. As a result, they showed high improvement for both of the selectivity and permeability of CO_2 than those MMMs containing zeolite without the modification and without major blockage the zeolite pores. Therefore, in some cases, surface modification by the silane coupling agents was recommended to enhance interfacial adhesion but hardly improved permselectivity.

4.2. Addition of low molecular weight materials (LMWMs)

Adding low molecular weight additives (LMWAs) to the membrane formulation acts as a compatibilizer or the third component to improve the compatibility between zeolite and polymer matrices. The low molecular weight materials induce a hydrogen bond with hydroxyl and carbonyl moiety. In addition, the formation of hydrogen bond confirms its solubility in the

solvent used to make the polymer dope solution. It should be noted that LMWMs should be solid at room temperature, in order to prevent their evaporation during membrane fabrication, consequently losing their ability of forming interfacial voids [31]. Once hydrogen bonds are formed between polymer chains and LMWMs, the free volume of polymers decreases, which results in a decrease in their permeability, whereas increase in their permselectivity.

kulprathipanja et al. [51] reported mixed-matrix membranes for the use in gas separation by blending polycarbonates (PC) with an additive p-nitroaniline (pNA) and incorporating zeolite 4A particles as filler. The permeability of all gases was measured using differential scanning calorimetry (DSC) analysis through PC/(pNA)/zeolite 4A membranes, which were lower than those through pure PC membrane. The incorporation of pNA was essential, since pNA acts as a facilitator for provision of better interaction between rigid, glassy polymer PC, and zeolite 4A particles. Therefore, the incorporation of a molecular weight additive with functional groups into zeolite-MMMs can be used as a tool to improve the structure and performance properties of the membranes.

One of examples of LMWMs is 2,4,6-triaminopyrimidine (TAP) containing three primary amine groups, which are able to form hydrogen bonds with both hydroxyl and carbonyl groups [31]. Furthermore, it had been reported that the carbonyl groups of polyimides (PI) could interact with amine groups of urethanes through the hydrogen bond formation.

Park et al. [31] used TAP to obtain the interfacial void-free PI membranes filled with zeolites. TAP enhanced the contact of zeolite particles with polyimide chains presumably by forming the hydrogen bonding. As a consequence, the void-free PI/zeolite 13X/TAP membrane showed the higher gas permeability for He, N_2, O_2, CO_2, and CH_4 with little expense of selectivity compared to the PI/TAP membrane having the same PI/TAP ratio, while the PI/zeolite 4A/TAP membrane showed lower permeability but higher permselectivity. The difference between both membranes was influenced by the pore size of zeolites. In addition, the molecular sieving effect of zeolites seemed to take place when the kinetic diameter of penetrants approached the pore size of zeolites.

4.3. Annealing

One of the largest challenges in designing zeolite-MMMs is poor contact between polymer and zeolite defects. Many efforts made to overcome to this problem associated with the zeolite-MMMs through the annealing of zeolite-MMMs above the glass transition temperature (Tg) [32]. In other words, Tg is considered as a qualitative estimation to compare the polymer chain rigidity of mixed-matrix membranes at different zeolite types with simple polymer membrane, and it also leads to a better contact between zeolite and polymer chains [52]. Annealing process at temperature above the Tg results into the formation of stronger bond between polymer matrix and zeolite. Despite advantages of annealing in relaxing the stress imposed to the hollow fiber membrane, it results in higher packing density of polymer chains. Therefore, there are drawbacks associated with annealing. In addition, it did not lead to significant improvement in the morphology of the membranes. Annealing at high Tg formed sieve-in-a-cage morphology, which will be difficult to create a good contact between the polymer and the

sieve [32]. In order to overcome to this disadvantage of annealing, incorporation of a plasticizer into the polymer solution can decrease the polymer Tg and thus maintain polymer chain mobility and flexibility during membrane fabrication [53]. Therefore, to develop membrane fabrication technology, a quench method after annealing membranes above Tg can be effective in gas separation process by forming frozen polymer chains quickly [54]. Therefore, it will have a higher free volume in the polymer matrix and subsequently higher permeability without the loss of selectivity.

4.4. Priming method

The dilute polymers are the same as the bulk polymers used for the preparation of MMMs. Coating the surface of the filler particles with a dilute polymer dope is known as the priming method [55]. The agglomeration is considered responsible for the defects between the polymer matrix and zeolite particle phases [56]. Since more agglomeration occurs in the polymer matrix when smaller particles are used, especially at high particle loadings, therefore, large zeolite particles are used to form practical mixed-matrix membranes. Therefore, zeolite particles were primed by increasing the amount of polymer. It should be considered that polymer effectively coats the zeolite particles before adding remaining bulk polymer and mixing with the priming polymer [57]. The purpose of priming is to reduce stress at the polymer-particle interface, to increase the compatibility between zeolite and polymer in MMMs, and to minimize agglomeration of zeolite particles [58, 59].

5. Zeolite nanofiltration MMM for water purification

Water treatment is increasingly important to remove water pollutants and solve water problems. Drinking water may compose of hazardous substances such as toxins and endocrine disrupting compound. Therefore, it would be urgent to invent more sustainable and reliable treatment process to remove water contaminations and to regulate the quality of drinking water. Development of cost-effective membranes is in a great need to effectively replace the conventional water treatment technologies to produce water that meet or exceed stringent standards. Nanofiltration (NF) membranes with pore size of 0.001 μm are among the potential alternatives which can filter wastewater from low organic content up to high organic content.

Recent studies have demonstrated that the zeolite-MMMs were applied to design nanofiltration membranes to enhance permeability, selectivity, stability, surface area, or catalytic activity in water purification and separation processes [60, 61]. Nevertheless, there are only few studies performed on zeolite-MMMs for water treatment; it is determined that the size of zeolite was designed to match the expected polyimide active film thickness, thereby providing a preferential flow path through the nanochannels of zeolites [62, 63]. Thin-film nanocomposite (TFN) membranes have been used by incorporating zeolite particles into the PA rejection layer. It has shown that the incorporation of zeolite in a PA layer could improve its water permeability without significant loss of salt rejection under high pressure during water purification process [64]. The main reason for that is nanochannels of zeolites with great

sub-nanometer pores in zeolite nanoparticles that behave as preferential flow channels for water molecules. The zeolite-PA-based TFN membranes are considered as superior separation performance for RO applications due to their enhanced water permeability of active layer [65].

Nanofiltration (NF) is widely used in many treatment processes, such as water softening, seawater and brackish water desalination, and removal of micro-pollutants such as sewage treatment and wastewater [66, 67].

Natural zeolite is considered as a suitable and desired material in the fabrication of NF membrane due to its strength against inflation in water. Furthermore, it can readily form a suspension to coat the membrane as a support [68]. In another research by Damayanti and coworkers, zeolite-based nanofiltration membranes demonstrated an excellent performance and high efficiency for removal of micro-pollutants for laundry wastewater treatment [69]. Membrane performance is measured based on the flux and rejection values. They studied the superior ability of zeolite nanofiltration to treat laundry wastewater as determined by turbidity measurements and phosphate removal as the two significant parameters. More importantly, another advantage of zeolite-based nano-membranes is that such membranes show an enhanced hydrophilicity when zeolites are used since they are hydrophilic in nature, which in turn contributes to enhanced removal of pollutants from wastewater.

In addition, the zeolite nanofiltration membranes showed improved separation performance and antifouling properties. In addition, a number of nanomaterials can be applied as potential
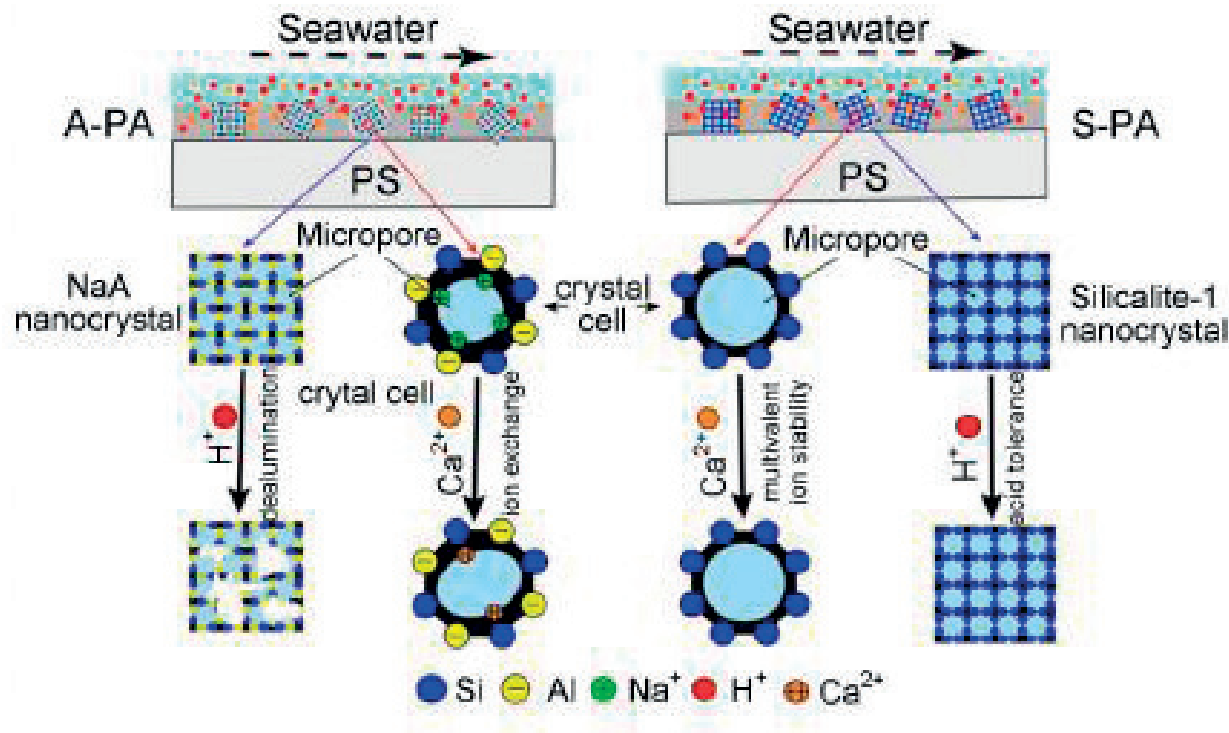

Figure 5. Schematic illustration of acid and multivalent ion resistance in thin-film nanocomposite membranes incorporated with NaA and silicate-1 zeolites [70].

water transport channels and modify the structure and surface properties of the membrane thin-film layers [70, 71].

In a systematic study by Zhang et al., it was shown that when silicalite-1 nanozeolites incorporated into polyamide (PA) thin-film composite membranes, they observed a higher membrane permeability as well as enhanced acid and multivalent cation resistance compared to NaA nanozeolite-incorporated membranes, as presented in **Figure 5** [70]. The effect of the silicalite-1 nanocrystals on the membrane properties was investigated. Contact angle measurements indicated that the silicate-1-PA (S-PA) membrane exhibited a more hydrophilic surface than the PA membrane by itself, in comparison with the PA and NaA-PA (A-PA) membranes. S-PA membranes evaluated by cross flow reverse osmosis tests showed greatly enhanced water permeability and improved acid stability. All of these results confirm that silicalite-1zeolites are superior compared to NaA zeolites in fabrication of thin-film nanocomposite membranes.

Furthermore, Yurekli showed filtration and adsorption processes by impregnation of zeolite nanoparticles in polysulfone (PSf) membranes for the removal of nickel and lead cations from synthetically prepared solutions [71]. The results also revealed that the sorption capacity and the water hydraulic permeability of the membranes could both be improved by simply tuning the membrane fabricating conditions. The coupling process suggested that the membrane architecture could be efficiently used for treating metal solutions with low concentrations and transmembrane pressures.

6. Future development

Recently, novel zeolite-MMMs have attracted great attention in membrane technology, due to the excellent advantages such as improvement in the permeability, selectivity, thermal stability, and mechanical strength of a polymeric membrane. However, the comprehensive understanding of organic-inorganic interfaces is in a great need. Zeolite-MMM performance suffers from defects caused by poor contact at the molecular sieve/polymer interface, 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. Moreover, some zeolite-MMMs for water purification application are considered potential hazards to humans and the environment, which also needs more study to determine the hazardous character of these nanoparticles and mechanism of nanoparticles embedded membrane fouling in industrial water purification in the future.

One of most difficulties associated with membrane technology is fouling for a long time. Although several strategies such as incorporation of antifouling nanoparticles and surface modification have been used to overcome this problem, intensive investigations are needed to stop regeneration of microbial colonies on membrane surface and to reduce the leaching of filler. The next-generation MMM should be developed with producing nano-size fillers without aggregation to improve their separation properties for membrane industry especially MMMs. There are several reasons to produce nano-size fillers, especially zeolite fillers such as

more polymer-particle interfacial area and enhanced polymer-filler interface contact by smaller particles. The potential of incorporating fillers such as zeolite particles has not been attained up to the expectation of zeolite-MMM performance, due to the smaller sizes, homogeneous distribution, agglomeration, price, availability, compatibility with polymer interface, their relation with water chemistry, better interfacial contact, and stability.

Despite many novel MMMs, fillers are being investigated, so far but their performances are restricted due to limited synthesis processes. Previously, the process fails to demonstrate their performance due to formation of relatively nonselective defects at the interface between the zeolite particles and the polymer medium on laboratory scale. Therefore, other major issues related to MMM is the interface defects that can lead to isolating zeolite fillers from the transport processes. Therefore, new techniques to achieve a perfect interface between inorganic fillers and polymers in membranes without compromising performance and scaling up these novel membranes under industrially relevant conditions are greatly needed.

In addition, many of these novel MMMs reported so far have been only tested on a laboratory scale and need further research to be used commercially in the industry. It is required to produce novel materials that can have high selectivity as well as nano-size fillers with incredibly small sizes. There are limitations on developing novel materials due to high prices or expensive synthesis processes. The molecular dynamic (MD) simulations of mixed-matrix materials could be an effective approach to predict diffusive performance of MMM, especially zeolite-MMMs, and to provide experimental guidelines for tuning the membrane permeability at the molecular level without high costs. Although there are many developed models for predicting the membrane performance, however, these models could not include the influence of inserting zeolite on membrane performance. Therefore, MD will be essential and effective to predict the morphology and intrinsic properties of these fillers and its interaction of the polymeric matrix.

Last but not least, factor is changing, and membrane morphology could change properties of membranes and subsequently will influence the membrane performance. Therefore, improving membrane performance in real conditions such as high temperature and high pressure and incorporating a plasticizer into the polymer solution would be possible and essential in order to provide better thermally and chemically zeolite-MMMs at different operating conditions.

Although development success of the synthesis and the application of MMMs impregnated with zeolites for water purification, however, the mechanisms behind these phenomena require intensive investigations for more advanced MMM technology.

7. Conclusion

Mixed-matrix membranes with zeolite fillers have attracted a lot of attention in membrane technology research due to its excellent advantages, such as high permeability and improved selectivity. Zeolite-MMMs could be considered an ideal candidate for purification industry since it combines the properties of polymeric matric and zeolite inorganic fillers. Application

and fabrication techniques of zeolite-reinforced polymeric membranes have been comprehensively reviewed in this chapter with the aim of optimizing interfacial interaction between the zeolite and the polymeric matrices. Compatibility between zeolite and polymer matrices can be improved with a number of methods, such as by applying high processing temperature during membrane formation, the silane modification and priming on the particle's surface, annealing that can relax the stress imposed to hollow fiber and result in higher packing density of polymer chains, and the introduction of a LMWA agent between the polymer matrix and inorganic particles.

There have been numerous attempts to incorporate zeolite particles in polymer matrices in water purification applications. The silicalite-1 zeolites are superior compared to NaA zeolites in fabrication of thin-film nanocomposite nanofiltration membranes. However, despite its advantages there are still issues and difficulties associated with zeolite-MMMs that have restricted their wider applications. Therefore, the advancements in the application and fabrication of zeolite-MMM need further intensive investigations. Future research should be conducted with the aim of developing new techniques that provide better understanding of zeolite incorporation into polymer structures. New materials should also be considered as a way of reducing the fouling concerns. Additional study is necessary for an improved understanding of the basic transport mechanism occurring through the MMMs. The next-generation MMMs must be developed with nano-size fillers and without aggregation so as to improve their separation properties severely needed in the membrane industry. Some results indicate that the nano-size zeolite particles incorporated in MMMs offer better performance in comparison with micro-size particles. New additives and modification agents should be produced to improve adhesion between polymer and inorganic fillers. In conclusion, despite of all the identified problems, MMM technology with zeolites could be considered a strong candidate for modern purification industry due to the remarkable properties of polymeric and inorganic zeolite materials.

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