

1 **A review of zeolite materials used in membranes for water purification: History, applications, challenges and future**  
2 **trends**

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12 **Keywords**

13 **Nano zeolite, polymeric based zeolite membrane, non-polymer based zeolite membrane, polyamide-zeolite**  
14 **nanocomposite membranes, supported zeolite membrane**

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1 **Abstract**

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3 This review provides a critical assessment of the potential of zeolite particles incorporated into polymeric membranes in view  
4 of improving the performance of these membranes. Zeolites are of interest due to their unique properties and extensive  
5 potential in separation processes. Significant investigations were carried out particularly over the last two decades to modify  
6 and improve conventional membrane synthesis and properties by the inclusion of zeolites. Zeolite membranes can be classified  
7 into three categories based on their employment in membrane structures for purification of drinking water and wastewater  
8 and for desalination: self-supported zeolite membranes, inorganic supported zeolite and zeolites mixed into the polymeric  
9 matrix or top layer. The focus of this review is on nano-sized zeolite particles incorporated into the polymeric structure of the  
10 membranes, with specific attention to the polyamide layer used in pressure-driven membrane processes such as reverse  
11 osmosis (RO). The incorporation of inorganic zeolite particles in the polymer matrix enhances the permeability without  
12 decreasing the selectivity, and increases the mechanical strength, fouling and chlorine resistance of the membranes.  
13 Agglomeration and defect formation are highlighted as the main obstacles to the fabrication of large scale high-performance  
14 zeolite membranes in order to identify strategies to solve these issues. Among the different strategies, adding a cross-linking  
15 agent to the interfacial polymerization process might be a promising method to fabricate homogeneous zeolite-polymer  
16 composite membranes with excellent performance. This paper provides a better understanding of the knowledge acquired in  
17 the development of polymer based zeolite nanocomposite membranes and gives perspectives for future research.

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## 1 **Introduction**

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3 There is a clear interest in developing more efficient water treatment technologies to meet increasing water demands in a  
4 (more) sustainable way, and to provide clean water as drinking water and for industrial use <sup>1,2</sup>. Membrane technologies are  
5 the preferred methods for water purification compared to conventional methods such as adsorption, coagulation, disinfection,  
6 flocculation and distillation. Membranes can be classified into two main categories, based on their synthesis materials:  
7 polymeric membranes (polyethersulfone, polyamide, polytetrafluoroethylene, polysulfone, polyacrylonitrile, and  
8 polyvinylidene fluoride as examples), inorganic membranes, which can be made of glass, metal, carbon, silica, zeolite or  
9 ceramic materials made of clay, metal oxides, or zeolites. In between these two categories there are mixed matrix membranes  
10 (MMMs), having typically inorganic particles in an organic matrix, or combinations of a polymeric top layer on a ceramic  
11 substrate and vice versa <sup>3,4</sup>. Polymeric or organic membranes are currently dominant membranes in water and wastewater  
12 treatment and desalination, due to their advantages: a low-cost operation without the need for chemical additives and thermal  
13 inputs, sufficient selectivity, excellent mechanical resistance, better tunability and simpler processability into different  
14 modules <sup>5-7</sup>. The polymeric membranes can be categorized into two common classes based on the structure of membrane;  
15 asymmetric membranes made through phase inversion method such as cellulose triacetate/cellulose acetate (CTA/CA) and  
16 Thin Film Composite (TFC) membranes made by interfacial polymerization (IP) <sup>8</sup>.  
17 Separation by a membrane occurs based on the concentration, temperature, electrical voltage, or pressure gradient across the  
18 membrane. The most widely used driving force in membranes for purification of water is pressure, applied in microfiltration  
19 (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Following the developments of the first generation

1 MF/UF asymmetric membranes consist of a thin top layer supported by a porous sublayer with the same polymer, there has  
2 been continuous effort to enhance the performance of membranes for the water purification industry<sup>9</sup>. Since the breakthrough  
3 development of thin film composite (TFC) membranes in 1977, made of a thin layer of polyamide on the top of microporous  
4 support layer with different polymer by the interfacial reaction between trimesoyl chloride and phenylenediamine<sup>10</sup> to produce  
5 high-performance membranes, they have been the subject of further study over many years.

6 Most thin film polyamide composites are produced from monomer reactants on a porous polysulfone and polyethersulfone  
7 support via interfacial polymerization<sup>11-14</sup>. Therefore, the permeability and separation performance of the membrane is  
8 determined by the IP process condition and polyamide physicochemical properties<sup>15-17</sup>. Trimesoyl chloride (TMC) and m-  
9 phenylene diamine (MPD) are two monomers that have been used frequently to make a polyamide layer. There has been  
10 growing interest in discovering the effect of monomer type on the improvement of membrane performance. Moreover, the  
11 effect of the support layer, ratio and concentration of monomers, reaction time and temperature, post-treatment, and also the  
12 use of additives was investigated<sup>13, 18-24</sup>.

13 Although early asymmetric membranes have a higher tolerance of active chlorine present in feed water and showed more  
14 biofouling resistance compared to composite polyamide membranes, advantages such as excellent flux and higher salt  
15 rejection, higher resistance for a wider pH range, flexibility to wider operating pressures without compacting, lower pressure  
16 requirements and enhanced durability made composite polyamide TFC membranes more fit for commercial use<sup>19, 25</sup>.

17 However, the trade-off between the permeability and the salt rejection, biofouling and fouling by colloidal particulates,  
18 chemical decomposition and oxidation by chlorination, and short lifetime are severely restricting the use of polyamide TFC

1 membranes<sup>26</sup>. Furthermore, these membranes suffer from the compaction effect: by applying pressure, the polymer structure  
2 becomes tighter over time, with a lower porosity, which declines the flux of the membrane<sup>14,27</sup>. Another challenge of current  
3 polyamide TFC membranes is their fairly low boron removal rate by single-pass RO systems to comply with the WHO  
4 standard for drinking water<sup>28,29</sup>.

5 In view of overcoming the restrictions of conventional polyamide TFC membranes, various strategies such as modification  
6 of the polyamide layer, incorporation of nanoparticles (NPs), or the manipulation of the interfacial polymerization procedure  
7 have been explored. The most effective approaches to enhance salt rejection and water permeability are surface modification  
8 and the incorporation of nanoparticles<sup>30-35</sup>. Application of different substrates, solvent treatment, and the addition of co-  
9 solvent in aqueous or organic solutions during the IP process are other strategies that have been investigated<sup>19</sup>.

10 The combination of different nano-sized materials with a membrane matrix have the potential to enhance the efficiency of  
11 conventional membranes and to mitigate their drawbacks, but also to add new functionalities such as antibacterial effects to  
12 the membranes, with fewer defects in the surface<sup>1,2,36</sup>. Therefore, researchers have investigated nano-sized materials such as  
13 carbon nanotubes (CNTs), graphene, graphene oxide (GO), aquaporins (AQP), nanofibers, nanoscale metal oxides, and  
14 zeolites in order to boost the membrane performance for water treatment with lower energy. Other nanoparticles of interest  
15 that have been incorporated into membranes include halloysite nanotubes (HNTs), aluminosilicates, metal alkoxides, and  
16 silver<sup>37,38</sup>. In particular, environmentally friendly/non-toxic nanoparticles are preferably used as additives into polymeric  
17 membranes. Therefore, carbon nanotubes, aquaporins, nano zeolite crystals are considered the most promising materials for  
18 high-performance membranes in desalination, water treatment, and water reuse<sup>37,39,40</sup>. Among these nanomaterials, zeolites

1 served as pioneer nanoparticles to be incorporated in membranes. They proved to be competitive candidates for the synthesis  
2 of membranes with superior performance in terms of ion rejection and permeability.

3 Zeolites are widely used in different areas due to their unique structures, selective sorption characteristics and diverse  
4 biological activities of silicates and aluminosilicates and the catalytic activity of aluminosilicates in their structure <sup>41, 42</sup>.

5 Zeolites have been extensively utilized as catalysts and sorbents in many industrial applications such as in the petroleum  
6 industry <sup>43, 44</sup>. They have been also used in chemical sensors to control industrial processes <sup>45-47</sup>, or as an anti-corrosion coating  
7 <sup>48</sup>, in radiation measurements <sup>49</sup>, energy recovery technologies <sup>50</sup>, solar energy and thermal adsorption storage <sup>50-53</sup>, gas  
8 separation and air purification <sup>54, 55</sup>, and measuring indoor air quality <sup>56</sup>. Zeolites are widely utilized in a range of environmental  
9 applications, including the remediation of pollution related to the disposal of hazardous materials in municipal, industrial and  
10 agricultural wastewater <sup>35, 57-59</sup>. They have also been employed in agricultural activities to modify and improve the physical  
11 properties of clay or sandy soil by increasing the water-holding and the cation exchange capacity of the soil, retaining water  
12 and nutrients in the soil which consequently leads to higher crops yields and prevents contamination of watercourses <sup>60</sup>.

13 Zeolites have been investigated as adsorbents for the removal of inorganic anions and organic compounds such as humic  
14 substances from aqueous solution <sup>61-64</sup>, fluoride <sup>65</sup>, nitrate <sup>66, 67</sup> and aluminum from contaminated water <sup>68</sup>, chemical and  
15 biochemical oxygen demand <sup>69</sup>, dyes from wastewater<sup>70-72</sup> and heavy metal from aqueous solution <sup>73-75</sup> and industrial  
16 wastewater <sup>76-81</sup>. They are also applied for the sorption of cesium from nuclear power plants wastewater <sup>82, 83</sup>, detection and  
17 monitoring and decontamination of water pollutants <sup>84</sup>, oil/water separation <sup>85</sup>, alcohol/water separation <sup>86, 87</sup>, and for treatment  
18 of ammonium-rich wastewaters <sup>88-91</sup>. Surfactant modified zeolite (SMZ) has been used to remove more than 99% of the viruses  
19 and 100% of E. coli bacteria from sewage effluent <sup>92, 93</sup>.

1 The wide range of potential applications of zeolites in various areas with positive perspectives have led to the exploration of  
2 the benefits of zeolites in membrane technologies. Applications of metal or ceramic supported membranes with zeolites on  
3 their top layer have been reviewed <sup>94-100</sup>. The progress and development of zeolite membranes in comparison with metal-  
4 organic frameworks (MOFs) were also described <sup>101, 102</sup>. Furthermore, the incorporation of zeolites in polymeric mixed matrix  
5 membranes have been reviewed regarding gas separation applications <sup>103, 104</sup>. However, to the best of our knowledge, an in-  
6 depth discussion of polymeric based zeolite membranes for water treatment and desalination applications was not yet made.  
7 The objective of this paper is to bring insight into what has been reported for zeolites incorporated into membranes for water  
8 treatment and desalination. This review can help researchers to acquire a profound understanding of fundamental aspects of  
9 zeolites when incorporated in membranes and provides suggestions for further research in this area.

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## 11 **Fundamentals of zeolites**

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13 Zeolites are crystalline solids that naturally exist in rocks, volcanoes and mines within many parts of the world. Most of the  
14 zeolite supplies are in Asia, Australia, and Europe <sup>44</sup>. Zeolites are eco-friendly, inexpensive, widespread, and chemically and  
15 thermally stable materials with unique pore characteristics and a high surface area <sup>59, 60</sup>. The word "zeolite" has Greek roots  
16 and has two parts: "zeo" means boil and "lithos" means stone. Thus, zeolite refers to "boiling stones". The flexibility and  
17 adaptability of zeolites have attracted scientists over several decades. The scientific investigation of zeolites started in northern  
18 Europe, where in 1756 a Swedish mineralogist, Alex Fredrich Cronstedt discovered this material and its particular adsorbent

1 properties <sup>44, 105</sup>. During the nineteenth century, many new zeolites and their unique properties were gradually identified and  
2 synthetic zeolites were introduced <sup>106</sup>.

3 The first researcher who introduced the extraordinary phenomenon of "molecular sieving" was James W. McBain. In this  
4 mechanism the size and shape of the microporous frame of the zeolite allows excluding salt molecules from water, leading to  
5 an extraordinary salt-water separation <sup>105, 107</sup>. In the middle of the nineteenth century, Eichhorn discovered the ion exchange  
6 properties of zeolites. Later zeolites have been applied as a cation exchanger and water softener. The introduction of X-ray  
7 diffraction in detecting the structure of zeolites, at the beginning of the twentieth century was a remarkable development in  
8 opening up new possibilities for the use of zeolites in environmental and industrial applications and that was a technical  
9 breakthrough to translate the scientific observations to practical applications <sup>105, 108</sup>. The International Mineralogical  
10 Association Commission declared in 1997 that any substance with a framework structure that has cavities occupied by water  
11 molecules and exchangeable ions and that shows freedom of movement, molecular sieving, solution-diffusion, dehydration,  
12 and catalysis properties, could be classified as zeolite <sup>44</sup>. This definition covers varieties of zeolites with different chemical  
13 structures such as aluminophosphates and metallosilicates (no silica or aluminum in the compositions) and zeolite-like  
14 materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs) that exhibit similar or even better  
15 properties and structures than silica-alumina zeolites. Therefore, categorizing zeolites can be complicated <sup>109</sup>.

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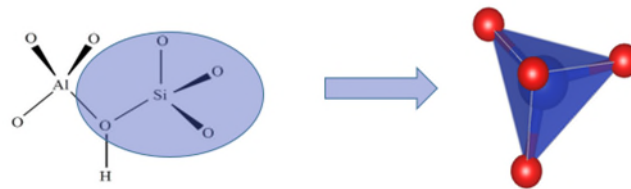
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1 *Chemistry, structure, and properties of zeolites*

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3 The chemistry of zeolites is related to their crystalline structure. Therefore, zeolite properties depend on their specific crystal  
4 structure and chemistry. Generally, the classical zeolites chemical formula is  $[(\text{Li}, \text{Na}, \text{K})_a(\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba})_d(\text{Al}_{(a+2d)}\text{Si}_{n-(a+2d)}\text{O}_{2n}) \cdot m\text{H}_2\text{O}]^{44, 110}$ . Figure 1 illustrates the zeolite structure characterized by a linked tetrahedral framework consisting of  
5 four oxygen atoms linked with cations (usually Si) and forming a three-dimensional silicate tetrahedral.  
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Figure 1- A unit of an elementary structure of the zeolite

10 Each Si-O and Al-O bond connects two cations and is shared between two tetrahedral blocks, thus producing a three-  
11 dimensional macromolecule of  $\text{SiO}_2$  and  $\text{AlO}_2$  tetrahedral blocks. To balance the net negative charge of the zeolite framework  
12 comprised of  $(\text{AlO}_4)^{5-}$  and  $(\text{SiO}_4)^{4-}$  it is bound to alkaline or alkaline-metals, such as  $\text{K}^+$ ,  $\text{Na}^+$  or  $\text{Ca}^{2+}$  in most cases, or  $\text{Li}^+$ ,  
13  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  in some other cases, on the external surface of the zeolite, by weaker bonds.

1 Nano-sized zeolites are particles with a size less than 200 nm with enhanced properties such as high external surface areas  
2 and adjustable surface charge <sup>111, 112</sup>. Nano zeolites are nanoporous, water-soluble nanoparticles composed of tetrahedral  
3 arrangement aluminosilicate framework bonded by four oxygen anions <sup>113, 114</sup>.

4 Zeolites with low Si/Al ratio (high Al content) in comparison with plain silica zeolites are more polar (higher negative charge)  
5 and hydrophilic because of the interaction of dipole H<sub>2</sub>O with the aluminosilicate framework. However, plain silica or high  
6 silica zeolites exhibit more hydrophobic behavior and provide more homogeneous and low defect surfaces <sup>115</sup>.

7 The crystal structures of zeolites usually have three units; primary building units (PBUs), (SiO<sub>4</sub>) and (AlO<sub>4</sub>) tetrahedral units  
8 and secondary building units (SBUs) formed by sharing oxygen with adjacent tetrahedral units and making simple geometric  
9 shapes in a variety of forms like single or double rings, polyhedral or complex units. Different types of SBUs with different  
10 orientations link together and make a unique structure of the zeolites unit as depicted in Fig. 2 and 3. In the third place,  
11 zeolites may contain several different framework structures called composite building units (CPUs) such as rings, cages, and  
12 different types of dissimilar morphology. These rings, cages, and chains may be joined to form complex composite building  
13 units of zeolites such as cavities, channels, and prisms and make a "molecular sieve"; the naturally porous structure of zeolites  
14 typically with a pore size below 2 nm. The pore size is determined by the size of the rings in the framework in different types  
15 <sup>116</sup>.

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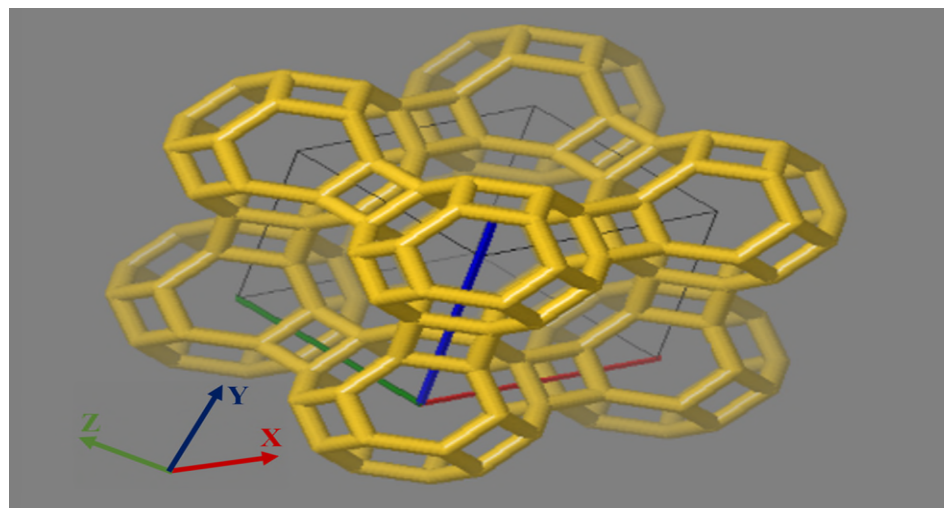


Figure 2- Linde Type A (LTA) zeolite unit framework

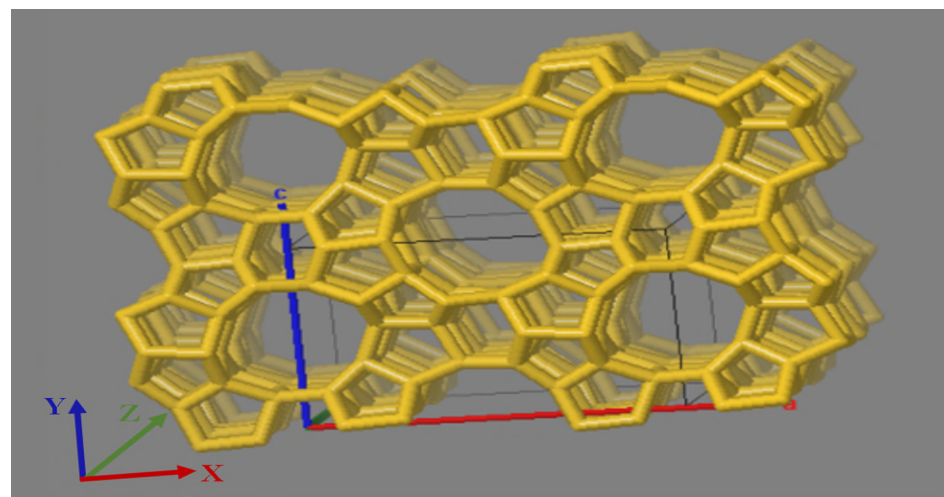


Figure 3- Mordenite Framework Inverted (MFI) zeolite unit framework (<http://www.iza-structure.org>)

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1 The particular structure of zeolites plays a significant role in their remarkable characteristics as it determines the mechanism  
2 of diffusion, in which only molecules with equal or smaller pore size than the zeolite structure are able to pass through the  
3 channels and cages, while the larger molecules are excluded.<sup>114, 117</sup>. Cation exchange and high absorbency behavior aligned  
4 with the molecule sieving feature make them a distinct choice in industrial applications and water purification<sup>118, 119</sup>. The  
5 ability to remove organic, inorganic, and organometallic compounds from aqueous solutions and the denitrification effect can  
6 be attributed to their absorption properties. Besides, the potential of tuning their pore size in synthetic types are important in  
7 selective catalysis and proton transfer in various industries<sup>44, 91, 117</sup>. As a result, the applications of zeolites are related to the  
8 crystal structure, chemistry, and their properties<sup>114, 117</sup>.

9

### 10 *Zeolite types*

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12 Based on their source, zeolites have been categorized into natural and synthetic ones. At least 80 types of natural zeolites and  
13 more than 200 synthetic zeolites were reported by 2019<sup>44, 120</sup>. Natural clinoptilolite zeolite is one of the most widely used  
14 types. Mordenite, chabazite, stilbite, analcime, phillipsite, and laumontite are other common forms of natural types<sup>51, 62</sup>. The  
15 natural zeolites have a powerful adsorptive potential and can be used as a cost-effective sorbent to remove contaminants such  
16 as organic pollutants, nitrogen, sulfur, formaldehyde, radon, heavy metals and more from wastewater and in desalination, due  
17 to their high ionic rejection properties<sup>49, 61, 121-126</sup>. The limited exploitation of natural zeolites resources across the world such  
18 as clinoptilolite and chabazite together with the occurrence of impurities (for instance quartz) that consequently decrease their  
19 efficiency in ion-exchange and adsorption, led to the production of synthetic and commercial types<sup>44</sup> for specific uses<sup>127, 128</sup>.

1 Synthetic zeolites have a more uniform composition than natural zeolites and can be manufactured at a larger scale in a smaller  
2 time frame than naturally occurring zeolites. The most general and usual synthetic types of zeolite are A, X, Y, faujasite  
3 zeolites ( FAU) , LTA, MFI and zeolite socony mobil-5 (ZSM-5) types <sup>51, 129</sup>. Higher surface areas and larger micropore  
4 volumes, lack of impurities, and adjustable pore size make them desirable options for research purposes <sup>43, 130</sup>. Synthetic  
5 zeolites can be made with a wide range of pore structures and they have shown a higher potential for trapping various  
6 contaminants from air and water <sup>118, 131</sup>, separation of oil-water mixtures <sup>132</sup>, and control of N<sub>2</sub>O emissions and radioactive  
7 sorption from water and wastewater <sup>82, 133-135</sup>. Synthetic zeolites such as ZSM-5 <sup>136</sup> and MFI <sup>137</sup> have shown a high efficiency  
8 in the remediation of pollutants from wastewater such as radon (Rn), cesium (Cs) and strontium (Sr) radionuclides and a  
9 significant adsorption capacity for all ions and toxic metal ions (Cr<sup>3+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>) <sup>136, 138, 139</sup>. Moreover,  
10 synthesized zeolites from fly ash demonstrated a high capacity as an adsorbent in removing heavy metals from aqueous  
11 solutions and wastewater <sup>73, 118, 131, 140</sup>. Synthetic zeolites can be specifically manufactured for particular purposes. For instance,  
12 Linde type A (LTA) zeolite, which has the same pore diameter as the polyamide active layer of thin film composite membranes  
13 (approximately 0.41 nm aperture) and a more negative charge and super-hydrophilic features compared to the conventional  
14 membranes, may be a suitable option for separation <sup>141, 142</sup>.

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## 1        **Zeolites in pressure-driven membrane technology**

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3 Inorganic membranes have some advantages such as a higher stability in a harsh environment and higher resistance to pressure  
4 drops, easier cleanability and longer thermal and mechanical stability compared to organic polymeric membranes <sup>94</sup>.  
5 Therefore, R&D activities focused on developing inorganic materials like zeolites such as MFI, MOFs, carbons and clay <sup>57</sup>,  
6 <sup>143-145</sup>. Application of zeolites in membranes can be mainly categorized as follows: self-supported zeolite membranes,  
7 inorganic supported zeolite membranes and crystal zeolite mixed into the polymeric matrix membranes. Self-supporting  
8 zeolite membranes are prepared on a removable cellulose or teflon support layer and they are fragile with no mechanical  
9 strength that makes them unfeasible for industrial applications <sup>146</sup>.

### 10 11        *Supported zeolite membranes*

12  
13 One of the main types of inorganic membranes are polycrystalline microporous zeolite membranes. Supported zeolite  
14 membranes are the most commonly used and preferred type of zeolite membranes. They have a zeolite microporous structure,  
15 which may contain a porous ceramic or metal support plus a thin and porous layer of zeolite on top that contains nanometer-  
16 size inter-crystal pores <sup>97, 146, 147</sup>. From the first effort of preparing zeolite membrane in 1987 from granular zeolite <sup>148</sup>, they  
17 have been widely explored and studied due to their unique properties such as molecular sieving, catalytic and selective  
18 sorption, lower fouling probability, flexibility and adaptability <sup>4, 54, 94, 101, 146, 149, 150</sup>. Some of the widely used zeolite framework  
19 structures in separation membranes are FAU, LTA, ZSM-5, MFI, mordenite zeolite (MOR). In particular, MFI zeolite

1 membranes including silicalite-1 and ZSM-5 (aluminosilicate) have been utilized more due to their pore size and simple  
2 manufacturing <sup>151</sup>. ZSM-5 is the most often used zeolite in the inorganic composite membrane due to its porous structure and  
3 ease of production <sup>152, 153</sup>.

4 Adsorption properties of zeolites and their molecular-sized pores determine how molecules permeate through them <sup>121</sup>.  
5 Experiments have revealed that separation based on shape selectivity merely occurs in high-silica zeolite types such as AL-  
6 free silicalite-1 (pure silica and shape-selective MFI membranes). These types of molecular sieving membranes progressed  
7 earlier due to their simple preparation and high chemical stability. On the other hand, zeolites containing a higher amount of  
8 Al in the structure showed a more negative surface charge, and the adsorption behavior governs the separation process <sup>154</sup>.  
9 Therefore, in some interaction-selective zeolite types such as hydrophilic LTA, the stable hydrophilic interactions with water  
10 inhibit the development of the Al-containing zeolite seeds to a defect-free zeolite layer. In general, fabrication of an Al-  
11 containing thin defect-free zeolite layer seems to be more challenging and they are unsuitable for an acidic environment.  
12 Apparently, positively charged additives to the crystallization batch used during synthesis can compensate for the negative  
13 charge <sup>154</sup>. However, some research suggested that when the distribution of zeolite pores size takes place in a range of  
14 components size in the feed flow, molecular sieving mechanism governs the separating process. The feed flow may pass  
15 through the interzeolite path or inter-crystal pores in the zeolite films (voids between pores) or through the intrazeolite path  
16 (zeolites inner pores) as illustrated in figure 4. The creation of inter-crystal pores in zeolite films could lead to the permeation  
17 of salts larger than zeolite pores and eventually decrease separation efficiency <sup>151, 155, 156</sup>.

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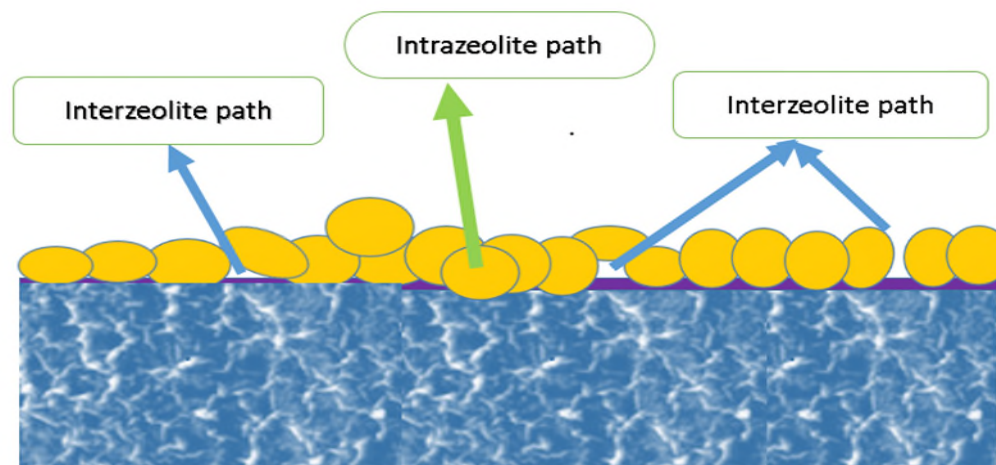


Figure 4- Schematic scheme of the flow path through a zeolite layer

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Since a high selective ability of inorganic zeolite membrane for separation of organic/ water mixtures, alcohols, and even organic/organic mixtures such as methanol /MTBE has been reported <sup>157-160</sup>, the idea of applying inorganic membranes on a porous alumina support for RO applications came from Kumakiri et al. in 2000 by hydrothermally synthesize zeolite type A to overcome the lack of membrane resistance to the organic solution and the durability problem at high pressure. The study demonstrated the possibility of using such inorganic membranes for RO applications, at pressures over 49 bar <sup>161</sup>. Later, the simulation of the zeolite membrane also suggested that these membranes are suitable for removing ions such as copper, chlorine and mercury from aqueous solution through the RO process <sup>114, 162</sup>. Hydroxysodalite (HS), a zeolite with 0.4 nm aperture, was applied for reverse osmosis based on size exclusion of hydrated ions with larger dimensions than the aperture



1 <sup>163</sup>. Furthermore, an experimental study of MFI and FAU zeolite types in reverse osmosis for desalination and wastewater  
2 treatment demonstrated a high rejection for monovalent ions and notably a better rejection for contaminant ions with higher  
3 charge density like bivalent metal cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and trivalent chromium ( $\text{Cr}^{3+}$ ) rather than monovalent such as  $\text{Na}^+$   
4 and  $\text{K}^+$  <sup>144, 147, 164, 165</sup>. MFI is a chemically stable type of zeolites; the use of MFI in a membrane was found to give a high  
5 resistance to chlorine (during hypochlorite cleaning) without loss of flux or ion rejection. This makes them a great candidate  
6 for desalination membranes <sup>166</sup>. The strong hydrophilic characteristic of NaA type of zeolites with pore size of 0.41 nm  
7 inhibited fouling in microfiltration (MF) <sup>167</sup>. Zeolite microfiltration membranes were investigated for recovery of water from  
8 oily wastewater and industrial wastewater treatment <sup>167, 168</sup>.

9 In table 1, an overview of some studies on non-polymer based zeolite membranes and their application is given. Two main  
10 methods exist in the fabrication of zeolite membranes, namely *in situ* growth and seeded secondary growth. *In situ*  
11 crystallization is the simplest method to synthesize a zeolite membrane on a support <sup>169</sup>. Difficulties in scale-up and lack of  
12 reproducibility are inevitable obstacles of the *in situ* approach compared to secondary growth. Thus, the formation of an  
13 aligned crystal zeolite layer through the secondary growth method, which consists of coating the support layer with zeolite  
14 seeds and hydrothermal synthesis post-treatment, is more reproducible and commonly used <sup>149</sup>.

15 The different methods of manufacturing inorganic zeolite membranes, the structure and nature of the support strongly affect  
16 the properties of fabricated membranes. In some studies, a low-cost support was used instead of the commonly used and  
17 expensive alumina in the structure of the zeolite composite membranes <sup>137</sup>. Despite the high production cost of inorganic  
18 zeolite membranes, they can be used where the structure and the function of organic polymeric membranes fail or barely

1 fulfill the expectations such as high thermal and chemical stability and biocompatibility. This is the case in the treatment of  
 2 complex wastewater containing radioactive elements and organic solvents <sup>147, 170</sup>.

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4 **Table 1: Non-polymer based zeolite membranes reported in the literature, with their synthesis method and observations made**

Type of Zeolite	Method	Fundamental reason	Result	Ref	Year-country
$\alpha$ -alumina-supported zeolite A (1 $\mu$ m)	hydrothermal method	Durability against heat and organic mixture in RO	Reveal the possibility of using in RO High-pressure stability up to 49 Bar	<sup>161</sup>	2000- Japan
$\alpha$ -alumina-supported MFI-type	in-situ crystallization	Experimental study of RO zeolite applications in desalination of complex mixtures	useful to treat different kinds of wastewater	<sup>147</sup>	2004- USA
$\alpha$ -alumina-supported MFI-type	in-situ crystallization	Ions separation from aqueous solutions by RO	ion rejection increase and water flux decreased in the order $rAl^{3+} > rMg^{2+} > rNa^{+}$ (depend on charge of ions and size)	<sup>171</sup>	2004- USA/New Mexico
$\alpha$ -alumina-supported MFI-type	seeding and secondary growth	Enhancement of water permeation of RO	Considerable increasing in water flux, while Al ion incorporate in zeolite framework and a slight increase in rejection	<sup>172</sup>	2007- New Mexico
$\alpha$ -alumina-supported MFI-type	in-situ crystallization	Separation and removal organics by RO	High rejection efficiency shows a strong dependency on ions charge and size, organic concentration affect slightly	<sup>63</sup>	2008-USA

5

6

7 In addition to the considerable cost of inorganic membranes including polycrystalline supported zeolite membranes, they have  
 8 some other disadvantages like brittleness and the difficulty in making highly selective (dense) membranes and controlling the  
 9 thickness of the manufactured membrane on a large scale due to the formation of defects (nonselective voids) <sup>57, 94, 143-145</sup>.

1 Moreover, the fabrication of a uniform zeolite film with minimum voids and high selectivity is one of the major concerns in  
2 developing inorganic zeolite membranes for industrial use <sup>151, 155</sup>. Although testing on lab scale suggested the potential of  
3 supported zeolite membranes, few barriers still prohibit real applications in water purification processes: mainly the lack of  
4 reproducibility to meet commercial and large scale requirements and the scale-up of the membrane. Despite the progress of  
5 preparing 100–200 nm zeolite membranes, low flux and moderately expensive membranes unit make supported zeolite  
6 membranes economically inefficient <sup>100, 173, 174</sup>. Moreover, inorganic zeolite membranes, unlike polymeric membranes, do not  
7 reveal plasticization behavior and are fragile. To tackle these challenges, composite organic-inorganic polymer membranes  
8 have the possibility to enhance the separation and the physicochemical stability and widen the industrial applications by  
9 combining the benefits of superior processing features of organic polymeric membranes and selective features (adsorption  
10 and molecular sieving) of the inorganic zeolite membranes. This gave rise to the idea of making thin and stable mixed matrix  
11 membranes (MMMs) with higher performance and more plasticization resistance by dispersing or embedding porous  
12 (zeolites, carbon nanotubes) or nonporous (silica, titanium oxide) inorganic material into polymeric matrix <sup>175</sup>. Recent research  
13 mostly targeted porous fillers as enhancer materials adapted in mixed matrix membranes to improve their performance and  
14 operational stability <sup>176</sup>.

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1 *Mixed matrix membranes*

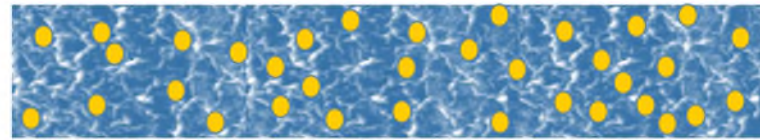
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3 Mixed matrix membranes (MMMs) or nanocomposite membranes could benefit from antifouling, mechanical and chemical  
4 stability, and separation features of inorganic materials, and cost-effective and formability features of polymers at the same  
5 time. Therefore, several studies focused on improving the performance and properties of these membranes by adding inorganic  
6 fillers as polymer reinforcement like zeolites, MOFs such as ZIF-8, carbon and clay into the structure or on the surface of the  
7 polymeric matrix <sup>177-191</sup>.

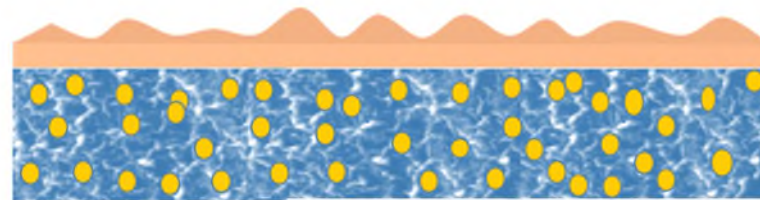
8 The selection of an appropriate inorganic material with hydrophilic and molecular behavior is a key factor in preparing a  
9 desirable mixed matrix membrane with a high affinity between organic particles and the polymer matrix <sup>188</sup>. Since the first  
10 report of incorporation of 5A zeolite into a polymer in the 1970s, a wide range of inorganic materials including zeolites as  
11 conventional porous fillers have been investigated <sup>176</sup>. However, few initial attempts using glassy polymers failed, and the  
12 separation performance of synthetic membranes declined compared to pure polymeric membranes due to defect formation  
13 and lack of adhesion between the inorganic particles and the polymer matrix <sup>176, 192</sup>.

14 Thus, further efforts focused on employing advanced porous materials such as MOFs and developing defect-free MMMs by  
15 adding some coupling agents or additives such as porous organic cages (POCs) and metal-organic cages (MOCs) aiming to  
16 provide more compatibility between polymer and filler <sup>176, 192</sup>. Mixed matrix membranes were prepared through dispersing  
17 inorganic fillers in the polymer solution, *in situ* or by the sol-gel method <sup>193</sup>. With the emergence of nanotechnology used for

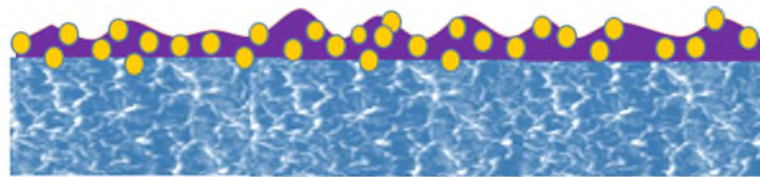
1 membrane synthesis, extensive research has been conducted on incorporating different types of nanomaterial into polymeric  
2 membranes <sup>194</sup>.  
3 Kim et al. divided ‘nanotechnology enhanced membranes’ into two categories: MMMs and thin film nanocomposite (TFN)  
4 membranes. Although, this categorization may not be complete and correct, it was taken over by Gupta and Roy <sup>195, 196</sup>.  
5 Later, Yin and Deng categorized nanocomposite membranes into four groups depending on the location of the NPs: 1)  
6 conventional mixed matrix nanocomposite membranes to synthesize porous membranes, 2) thin film composite membranes  
7 with nanocomposite substrate, leading to a higher initial permeance, less membrane compaction and reduced internal  
8 concentration polarization 3) surface located nanocomposite membranes, 4) thin film nanocomposite (TFN) membranes. This  
9 is illustrated in Figure 4 <sup>33, 197</sup>.



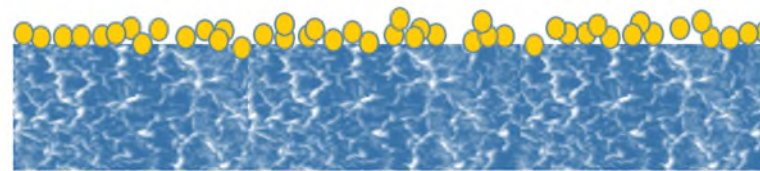
Conventional Nanocomposite



TFC with embedded NPs to substrate



Thin Film Nanocomposite



Surface Located Nanocomposite

- 1
- 2
- 3
- 4

Figure 5- Schematic of different types of nanocomposite membranes (adapted from <sup>33</sup>)

1 Among all modification strategies to address conventional TFC membranes problems, blending hydrophilic nanoscale  
2 particles into an ultra-thin (<500 nm) PA layer allowed for a significant improvement in the performance of the membranes  
3 due to the resulting enhancement in surface charge, roughness, and hydrophilicity <sup>198</sup>.  
4 Incorporating promising nanoparticles such as zeolites into polymeric membranes could lead to another breakthrough in  
5 membrane desalination by further enhancing the water permeability without salt rejection loss <sup>199</sup>. However, despite the fact  
6 that nanomaterials are being suggested as having the most promising potential in membrane desalination and water treatment  
7 technologies, each of these nanomaterials has specific limitations. Table 2 summarizes the highlights and limitations of the  
8 most used nanomaterials including zeolites for water purification applications.

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**Table 2: Highlights, benefits and drawbacks of nanomaterials in water desalination technologies** <sup>121 & <sup>39</sup> & <sup>31, 173</sup></sup>

Nanomaterial	Application	Desirable Properties		Drawbacks
<b>Carbon-based Nanomaterials (CNMs) such as CNTs &amp; Graphene</b>	Membranes FO	Large surface area Long-range of porosity Very high thermal and electrical conductivity Exceptional mechanical Strength Chemical stability Smooth graphitic walls Stiffness Rapid sorption-desorption mechanism High flux performance Anti-biofouling	CNTs: Highest strength to weight ratio in all material. Alleviate concentration polarization Low weight Excellent adsorptive properties against both chemical and biological contaminants Enormous potential in resolving the permeability-selectivity trade-off boundary contribute toward improving membrane-fouling resistance Stability and diversity	Specialized synthesis technique Large-diameter Assembling the nanotubes into compact and scalable vertically aligned carbon nanotube (VACNT) membranes for high-flux applications Health concerns & may impose some unwanted impact on environmental receptors Nanometer-sized diameters but micrometer-sized lengths Defects in the sealing of the interstitial spaces impair the selectivity Lack of experimental data on the high permeation flux
			Graphene: The strongest material ever tested Huge theoretical specific Low dimensional Excellent electrical conductivity Inherent hydrophobic	Saturate at a short period Non-porous
			GO: Higher resistance to chlorine Higher resistance to fouling Stable in acidic and alkaline solutions	Specialized synthesis technique Aggregation of GO nanosheets at high concentration
<b>Zeolites</b>	Membranes	The high surface area due to the porous structure Mechanical stable for long time exposure to the salty solution Extraordinary performance in ions removing Molecular sieve & cavities functioning Compaction	Agglomeration at high concentration leads to interstitial defects Reproducibility, especially on a large scale	



		<p>resistance and enhanced permeability  negative surface charge  Super-hydrophilic  Low cost  successful commercial adoption of TFN</p>	<p>Decreased in flux and rejection with the increase of water salinity due to the amount of salt trapped in the membrane matrix/defects  Less flux compares with other technologies</p>
<b>Metal NPs (Nano Ag)</b>	Membranes	<p>Anti-biofouling  High and wide range of antimicrobial activity  Ease of use  High conductivity  Low human toxicity</p>	<p>accumulation in the membrane skin layer  formation of macro-voids and ↓ rejection of significant toxicity  Leaching</p>
<b>AQP</b>	RO	<p>high permeability performance  high selectivity performance  High mechanical strength  Low energy  Able to stand on high pressure (5 bar or more)</p>	<p>Specialized synthesis technique  Limited to small area membrane  High cost  Limited fundamental and experiential knowledge of protein-support interactions for the incorporation of proteopolymersomes into a robust support  Unknown long-term viability under practical conditions of high pressure, salinity, fouling &amp; cleaning cycles  The obstacle in scaling up and stability for industry applications  Narrow operation window  Low sustainability  Need for special storage condition</p>
<b>Nano-TiO2</b>	<p>TFN  UF  Hollow fiber  Ceramic membrane  Reactive membranes  (groundwater)</p>	<p>Enhancement of surface area  High chemical &amp; thermal stability  Hydrophilicity  Efficient Photocatalytic activity  Low cost  Low human toxicity  Greater affinity for organic material</p>	<p>Usable for low contaminant concentrations in water  generation of toxic intermediate degradation products  60%–70% loss in system efficiency compared with the use of free-standing nanoparticles</p>

1 Although it is believed that the structural shape of nanomaterials including nanotubes or nanoparticles in the nanocomposite  
2 has a significant role in enhancing the performance of TFNs, the exact effect is not understood yet <sup>200</sup>.

3 Thin film nanocomposite membranes developed by embedding different types of nanoparticles into the polymeric matrix  
4 exhibit superior properties. Considering the fact that the top surface of the polyamide layer is negatively charged due to the  
5 presence of carboxylic (-COOH) and amino (-NH<sub>2</sub>) groups, various methods have been suggested for integrating  
6 nanoparticles on the surface of the membranes: NPs self-assembly, coating or deposition, chemical grafting, electrostatic  
7 attraction, and layer-by-layer assembly <sup>33, 142</sup>. However, the fabrication of a well-dispersed nanocomposite membrane without  
8 defect (pinholes or cracks) has been very challenging <sup>201</sup>.

9 Among all nanomaterials, zeolite nanoparticles are thought promising to produce composite membranes not only in view of  
10 better permeability and selectivity properties, high resistance to chlorine and high antifouling behavior but also for their low  
11 cost compared to GO, CNT and SiO<sub>2</sub> for commercial uses <sup>202</sup>. In view of addressing fouling as a major problem of TFC  
12 membranes in the desalination process, researchers have explored the modification of membranes by embedding nanoparticles  
13 such as zeolites in order to obtain antifouling and antimicrobial activities. Zeolites with higher surface roughness, tunable  
14 pore size and charge porosity could alter surface physicochemical properties of the membrane and improve the antifouling  
15 ability of the membranes <sup>198, 203-205</sup>.

16 Moreover, the 3-D structure of zeolites, contrary to 1-D and 2-D structures of nanomaterials such as CNT and GO, is beneficial  
17 for an easier embedment into the membrane structure without a need for orientation <sup>206</sup>. Inorganic nanomaterials such as

1 zeolites serve as a cross-linking agent in the polymeric matrix and mitigate the compaction effect in mixed matrix membranes  
2 <sup>193</sup>.

3 Polymeric based zeolite nanocomposite membranes are fabricated by the distribution of nano-size particles into the polymeric  
4 structure, mainly into the organic phase during the IP process or into the support layer <sup>2</sup>. Several methods are used to fabricate  
5 nano zeolite composite membranes for industrial applications. Solution blending is the most simple way in order to  
6 manufacture zeolite-polymer composite membranes <sup>2</sup>. Surface modification and functionalization of incorporated  
7 nanoparticles, modified IP techniques, the use of metal alkoxides, alignment of nanofillers or nanotubes are relatively effective  
8 approaches to have a better dispersion of the nanoparticles in the solution for IP process or provide stronger covalent bonds  
9 to the polyamide matrix <sup>207</sup>. Recently, several researchers have focused on the functionalization of nano-additives by amine  
10 groups to create better casting suspensions. Examples are the functionalization of nanoparticles with amino groups as a  
11 coupling agent with UZM-5 zeolite nanoparticles <sup>208</sup>, grafting NH<sub>2</sub> groups to nanoparticles to have a better dispersion of  
12 hydrophilic zeolites in the hexane phase, formation of a covalent bond between the NH<sub>2</sub> groups on the zeolite and the TMC  
13 molecules <sup>142</sup>. The first incorporation of nano zeolite in a polydimethylsiloxane (PDMS) polymeric membrane was reported  
14 by using the silicalite-1 type with 70 nm particle size applied into pervaporation for separation of a mixture of ethanol and  
15 water. Preparation of a defect-free filled polymer layer with silicalite–polyamide showed a drastic increase in both flux and  
16 selectivity at the highest loading amount, which could be related to the mesopores in the silicalite-1 structure acting as  
17 freeways and yield tiny voids <sup>209</sup>. Later in 2007, a new generation of composite RO membranes, the so-called thin film  
18 nanocomposites, was reported by embedding NaA zeolite nanoparticles to change the cross-linked surface of the polyamide

1 structure in the membrane <sup>210</sup>. The inclusion of NaA zeolite overcame the permeability and selectivity trade-off in the RO  
2 membrane, and a high flux was achieved without compromising salt rejection <sup>210, 211</sup>. A study on nano zeolite-Y for dye  
3 rejection also indicated a high rejection attributed to the negative charge of Y zeolite and a high flux because of providing  
4 preferential hydrophilic water channels through the membrane <sup>212</sup>. Hoek et al. studied the incorporation of different fillers  
5 such as copper, silver, silica, silver-zeolite and zeolite into polysulfone (PSF); it was concluded that only zeolite led to an  
6 improvement in both permeability and selectivity and overcome the trade-off between permeability and selectivity <sup>213</sup>. The  
7 unique properties of zeolite nanoparticles such as high surface area, enhanced chemical and physical activities, shape  
8 selectivity due to the presence of uniformly distributed micropores, novel surface selectivity, flexibility in adaption to a  
9 particular purpose and easy incorporation within membranes make them an ideal choice for industrial applications. Their  
10 unique inside framework provides the possibility for resident ions and molecules to flow smoothly into or out of the zeolite  
11 structure. The porous structure of zeolite with plenty of cavities and channels makes them a potential sorbent material <sup>121</sup>.  
12 A key feature of polyamide-zeolite nanocomposite membranes compared to other nanocomposite membranes is that zeolite  
13 particles can be designed and adjusted to be matched with the polyamide film thickness to achieve a “percolation threshold”,  
14 providing preferred flow passages for the feed water to permeate through the particles incorporated into the polymer <sup>141, 214</sup>.  
15 The negative charge of zeolite nanoparticles and their hydrophilic properties lead to a higher affinity to water molecules and  
16 the retention of anions. Besides, additional flow paths are provided by the nano zeolites incorporated into the polyamide <sup>141</sup>,  
17 the Donnan effect, diffusion-solution, sieving mechanism are other mechanisms that take place for transport of water  
18 molecules through nanocomposite membranes <sup>30, 37, 215</sup>.

1 Despite increasing attention to utilizing the benefits of mixed matrix membranes including TFNs in the water purification  
2 industry, the fabrication of these types of membranes is not yet sufficiently mature to replace conventional membranes. In  
3 particular, aggregation and defect formation are still challenging issues for commercially used upscaling <sup>7</sup>.

4 In the following section the focus is on the research activities that have been conducted so far on the performance of zeolite  
5 incorporated TFN membranes (mostly RO), concerning fouling resistance, permeability-selectivity trade-off, and chlorine  
6 tolerance.

7

### 8 **Nano zeolites in pressure driven membranes**

9

10 Incorporating zeolite nanoparticles into the polymeric structure of membranes, particularly into the polyamide layer of a TFC  
11 membrane as the latest generation of composite membranes was carried out to improve the characteristics of the thin film  
12 composite layer; for instance, to increase the hydrophilicity and surface charge density for making smoother and more  
13 negatively charged surfaces and therefore, overcoming trade-off issue between selectivity and permeability of TFC  
14 membranes, offering more energy-saving and fouling resistance properties in composite membranes. Positive consequences  
15 of employing these nanoparticles in different types of membranes such as ultrafiltration (UF), nanofiltration (NF), reverse  
16 osmosis (RO) attributed to the exceptional super hydrophilic surface and the mesoporous framework of zeolite nanoparticles  
17 which provide preferred flow passages for feed water.

18

1 *Ultrafiltration (UF)*

2

3 Ultrafiltration membranes as a low cost treatment, suffering from fouling and consequently flux declining over operation  
4 time. It is understood that hydrophilic zeolites can help to prevent fouling <sup>167</sup>.

5 Recent research found that uniformly embedding LTL zeolite nanoparticles onto the membrane surface (surface located  
6 nanocomposite) of low pressure membranes such as polysulfone UF membranes provided a higher permeability and lower  
7 fouling resistance membrane without considerable particle agglomeration <sup>179</sup>.

8 Han et al. added NaA zeolite as one of the most hydrophilic particles in different concentrations to mitigate the hydrophobicity  
9 of poly phthalazinone ether sulfone ketone (PPESK) based UF membranes. A higher retention and better antifouling ability  
10 was obtained at 3 wt.% NaA concentration compared to commercial UF membranes. However, a concentration over 3 wt.%  
11 caused particle aggregation on the surface. They suggested adding hydrophilic nanoparticles to the casting solution to make  
12 a denser skin layer and larger macro voids (finger-like pores) in the membrane sublayer because they are able to absorb vapor  
13 (water) from the air. The rejection of PEG 6000 enhanced from 77.9% to 96.8%, while the flux moderately decreased <sup>216</sup>.

14 Nanoparticles embedded into the support layer have been explored to provide more binding opportunities for foulants and  
15 thus enhance the fouling resistance <sup>30, 217, 218</sup>. Uniformly embedding Linde type L (LTL, 80 nm) zeolite to the UF membrane  
16 via *in situ* embedment was successfully performed by Dang et al. <sup>179</sup>; they suggested that the higher resistance to fouling

1 should be due to the anti-adhesion ability of nanoparticles. In this method of nano zeolite embedding no considerable  
2 agglomeration was reported up to the coverage ratio of 40%.  
3 Some studies have demonstrated that zeolite has the potential to overcome the trade-off between permeability and selectivity  
4 <sup>219</sup>. Liu et al. incorporated zeolite 4A on a polysulfone (PSF) UF membrane to break through the trade-off and examine the  
5 influence of zeolite particle size, zeta potential, and channel dimensions. It was found that a higher roughness and  
6 hydrophilicity and negatively charged surfaces with smaller pore sizes increase fluxes due to the ample nanoscale paths (0.5–  
7 0.8 nm) for water flow, and rejection as well, via a combination of the Donnan effect and steric hindrance. Modified  
8 membranes exhibited fouling resistance, and good mechanical, and thermal stability <sup>220</sup>.

9  
10 *Nanofiltration (NF)*

11  
12 Nanofiltration (NF) membranes mostly made via interfacial polymerization are designed to have a higher permeability at low  
13 applied pressure compared to reverse osmosis and higher rejection of ions and organic matters compared to UF membranes  
14 <sup>152</sup>. Incorporating nanoparticles via dispersing in aqueous or organic solutions or support layers led to an improvement in the  
15 NF performance <sup>32, 221, 222</sup>.

16 In view of a uniform dispersion of nanoparticles in the fabrication of polysulfone based thin film nanocomposite NF  
17 membranes, a novel method was reported by Dang et al. <sup>32</sup>. In this approach, a uniform *in situ* embedded preparation of a  
18 support layer with nano zeolites was employed before interfacial polymerization to make the polyamide layer <sup>179</sup>. A higher

1 roughness was obtained, but no change in hydrophilicity. Nevertheless, a two times higher permeability was achieved; the  
2 rejection of  $\text{MgSO}_4$  and negatively charged pharmaceuticals was similar to a reference TFC membrane but lower for NaCl  
3 and positively charged pharmaceuticals. This could be due to internal pores in the zeolite structure and undesirable defects on  
4 polyamide.

5

## 6 *Reverse Osmosis (RO)*

7

8 Thin film composite reverse osmosis (RO) membranes with a dense thin polyamide layer on the top comprise 53% of the  
9 global desalination capacity, and are therefore the dominant technology for seawater desalination.<sup>31, 201, 218</sup>. However, the RO  
10 process has some challenges: chemical consumption for cleaning, operating cost, permeability-selectivity trade-off,  
11 concentration polarization, sensitivity to chlorine and solvents, and fouling<sup>19, 211, 223</sup>. These factors lead to a reduction of  
12 permeability, deterioration of permeate quality, enhancement in energy consumption, and shortening membrane life<sup>19, 39</sup>.

13 Over two decades, many researchers have been studying zeolite membranes for RO desalination of brackish and seawater,  
14 and tried to enhance the performance of RO membranes to remove pollutants from water by adding zeolite nanoparticles;  
15 transport mechanisms were less studied<sup>28, 29, 152, 224</sup>.



1 Table 3 summarizes different approaches in synthesizing zeolite-polymer composite reverse osmosis membranes. Results  
2 indicated that zeolite-based thin film composite membranes experienced a higher performance in comparison with bare  
3 polyamide thin film RO membranes. In addition, they offer more resistance to compaction and fouling <sup>14</sup>.  
4 Several researchers suggested a mesoporous structure and the super hydrophilic surface of the zeolite membrane offers an  
5 exceptional flow path for water molecules with almost 0.27 nm diameter through internal micropores (0.42 nm aperture  
6 diameter) of the zeolite crystals <sup>14, 141, 199, 225</sup>. Another hypothesis is that the low cross-linking degree of TFN membranes could  
7 be a reason for the increased water flux <sup>226</sup>. The lower hydraulic resistance for transporting water molecules through NaA  
8 nanoparticles micropores and size exclusion for salts (common hydrated ions approximately is 0.6–0.9 nm diameter) within  
9 inside pores of the NaA, would lead to a superior performance of the zeolite added RO membranes <sup>211</sup>. The hydrophilic  
10 properties of NaA nano zeolite due to hydroxyl groups yield a better compatibility with polyamide hydrophilic bonds and  
11 fewer voids. However, the presence of alkaline Al in the structure of NaA and the higher potential for ion exchange (sensitivity  
12 to acid and multivalent ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup> and Sr<sup>2+</sup>) leads to durability issues over operation time and less resistance to  
13 acidic feed water and seawater, which limits their application for desalination <sup>227</sup>. Generally, in order to control scaling,  
14 moderate acidification on the feed side of the RO membranes is applied that can lead to dealumination reactions and removal  
15 of Al from the NaA zeolites structure <sup>227, 228</sup>. Therefore, replacement of alumina-free silicalite-1 zeolite with 0.55 nm pore  
16 size and very similar hydrophilic properties and compatibility, but more stability features compare to NaA zeolite was  
17 suggested <sup>227, 229</sup>. The obtained membrane of Huang et al. study showed an excellent permeability compared to NaA zeolite  
18 incorporated membrane, which was attributed to the silicalite-1 larger pores size and increased water diffusion rate and a

1 higher chemical stability. Thus, silicalite-1 could have a great potential for incorporation into the polyamide layer of  
2 composite RO membranes to be used in large scale applications for complex feed water and seawater<sup>227</sup>.

3 The study of other types of zeolites like Y and NaX (both types with 0.74 nm pore size) demonstrated a higher permeability  
4 but a deterioration in rejection or stable salt rejection, which could be attributed to larger water flow paths (macro voids) made  
5 by these nano zeolites. However, these composite TFN membranes still benefit from an increased physical and chemical  
6 stability and improved surface properties<sup>201, 230</sup>. The exchange of silver ( $\text{Ag}^+$ ) cations with sodium ( $\text{Na}^+$ ) cations of LTA  
7 nanocrystals in the aqueous solution of the IP reaction to synthesize a zeolite-polyamide TFN RO membrane, produced a  
8 superior permeable RO membrane with small changes in salt rejection. In addition, silver form of LTA (AgA), with smaller  
9 pore dimensions (0.35 nm), provided a more negative zeta potential and an increased hydrophilicity. Accordingly, these  
10 membranes have a higher fouling resistance compared to sodium form (NaA) and pure TFC membranes<sup>225</sup>.

11 Since pore-filled zeolite TFN membranes also have a high water permeability, Lind et al. suggested that the presence of nano  
12 zeolite might alter the kinetics of the IP process. Interaction between monomers and nano zeolite particles might alter the  
13 polyamide structure by making defects or voids, which would be more passable to salts ions and deteriorates the separation  
14 process<sup>141, 225</sup>. However, Huang et al. found that the addition of NaX zeolites in the organic phase during the IP process, in  
15 contrast with dispersing them in the aqueous phase, leads to more cross-linked and homogeneous zeolite-polymer composite  
16 membranes with excellent salt rejection<sup>211</sup>. Since the cross-linking degree of the active layer and the good dispersion of nano  
17 zeolite are correlated with rejection of salts (such as chlorine ions),<sup>28</sup> and increase the chlorine resistance of the polyamide-  
18 zeolite composite membrane<sup>26, 162</sup>, adding cross-linking agents during the IP process might improve the permeability without  
19 compromising rejection. A recent simulation study of an MFI zeolite membrane estimating the rejection of copper, mercury

1 and chlorine reported 100 % rejection for copper and mercury ions and 97.6% rejection for chlorine ions while keeping a high  
2 water flux. Therefore, this type of zeolite membranes with perpendicular pores that allow for water transport through all  
3 dimensions of the zeolite crystals could be a competitive candidate to boost current membranes used in water purification  
4 applications <sup>162</sup>.

5 The role of different sizes of zeolite particles on the separation of nanocomposite RO membranes needs to be more  
6 investigated. It is commonly believed that particle size has a strong influence on the performance of zeolite TFN membranes  
7 <sup>187, 231</sup>. Smaller nano zeolites provide more interfacial area between the polymeric matrix and nano zeolites, giving a better  
8 exclusion of salts <sup>232</sup>. Moreover, smaller zeolites enhance the permeability but larger zeolites provide more desirable surface  
9 properties <sup>233</sup>. Nevertheless, small nano zeolites might cause intense agglomeration and consequently undesirable defects on  
10 the nanocomposite membranes <sup>232, 234</sup>. Therefore, choosing a zeolite with proper pore size might have a great effect; this  
11 should come along with a good dispersion in the polymer.

12 Another challenge encountered by current RO membranes in desalination is the low rejection of boron ions, which are found  
13 naturally as uncharged boric acid in seawater <sup>28</sup>. The concentration of boron in seawater is above 4-5 mg/l, and according to  
14 the World Health Organization (WHO) standard it should be under 2.4 mg/l for drinking water <sup>235</sup>. Boric acid tends to form  
15 hydrogen bonds with the surface of membranes and passes through the RO membrane. Since methods like using multiple  
16 stages or manipulating the pH of feed water to remove boron are inefficient and need a high cost <sup>28</sup>, a promising boron removal  
17 method could be achieved by employing nano zeolite in RO membranes. With respect to boron removal, it is reported that  
18 incorporating zeolite 4A into RO composite membrane enhances the boron rejection while improving the water flux, with a  
19 reduction of salt rejection <sup>235</sup>

**Table 3: polymer base nano zeolite RO membranes**

<b>Type of Zeolite</b>	<b>Method</b>	<b>Fundamental reason</b>	<b>Result</b>	<b>Ref</b>	<b>Year-country</b>
silicalite-1 nano zeolite	IP	Overcome ion sensitivity of NaA in seawater desalination	Enhance permeability and chemical stability Higher water diffusion rate larger flow channel and pores	<sup>227</sup>	2013-China
NaX	hydrothermal method + Dispersing in the aqueous solution+ Ultrasonication	Enhancement performance of polyethersulfone ultrafiltration support membrane	Higher permeability with no change in salt rejection Higher physical, chemical, and thermal stability	<sup>230</sup>	2011- Iran
NaX	hydrothermal method	Enhancement performance of polyethersulfone ultrafiltration support membrane	Higher permeability with no change in salt rejection Higher physical, chemical, and thermal stability	[120]	2011- Iran
NaA	IP in-situ on polysulfone supports	Improving the efficiency of water treatment technology	High Permeability Nearly constant rejection	<sup>210</sup>	2007-USA
Linde Type A(LTA)	coating on polysulfone base UF by IP+ additive	Separation performance of RO	Inverse correlation between flux and zeolite size observed High flux with slightly high rejection) at high flux) probably due to defect formation	<sup>141</sup>	2009-USA
NaA	IP by dispersing them in an organic phase	explores the behavior of nano zeolites added to the organic phase	Composing a higher cross-linked and homogeneous zeolite membrane and achieve excellent rejection	<sup>211</sup>	2013- China
Linde type A (LTA) with Ag & Na cations(NaA & AgA)	IP And the hydrothermal method	A better understanding of separation performance, fouling resistance and interfacial properties of TFN RO membranes	AgA made TFN RO produced higher flux and rejection, more hydrophilic and smoother surface and more fouling resistant behavior rather than NaA	<sup>225</sup>	2009-USA
zeolite Y	Pre-seeding assisted IP	producing organic-inorganic membrane for water purification using	high water flux with an insignificant loss for rejection (>95%) (more control over the pore size to make defect-free TFN)	<sup>201</sup>	2010-Japan

surface-modified NaA	surface modification with OTS	Overcome the agglomeration Problem in TFN membrane and improve the dispersibility of zeolites	Mitigating of zeolites aggregation Enhancement of permeability and slightly rejection compare to the original zeolite TFN	35	2011- China
Zeolite X	oxidative polymerization and coating	corrosion reduction and energy recovery in RO desalination plants	Better anti-corrosion properties	<sup>236</sup>	2019- Egypt
Silicalite	IP	desalination	fourfold higher flux but rejection significantly dropped	<sup>237</sup>	2012-Australia

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#### 4 **Zeolite composite membranes challenges**

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6 Although zeolite nanoparticles have been successfully employed in the polyamide layer, reducing the fouling resistance and  
7 the cleaning cost of common polymeric membranes, they could lose their function in the long term <sup>198, 205, 229</sup>. Nanoparticles  
8 could be leaching out after a while of operating, and cause safety concerns and hazards for the environment <sup>238</sup>. Therefore,  
9 degradation of membranes and loss of their properties over time need to be further investigated. In addition to this challenge,  
10 agglomeration, defect formation and complicated synthesis process are other hindrances in the manufacturing of defect-free  
11 nano zeolite composite membranes.

12

#### 13 *Agglomeration*

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15 One of the challenges in the fabrication of thin film nanocomposite membranes including zeolite membranes is agglomeration  
16 or the poor binding/adhesion of the nanoparticles to the polyamide layer, which results in a lower suspensibility of

1 nanoparticles inside the casting solutions. Therefore, agglomeration and poor particle dispersibility due to the non-polarity of  
2 the organic solvent are responsible for defect formation on the structure of membranes. Agglomeration mostly occurs for  
3 using smaller particles and in high nanoparticle loading amounts<sup>30, 237, 239-241</sup>.

4 Due to van der Waals forces between nanoparticles, they attract each other and agglomerate<sup>242</sup>. Furthermore, the high surface  
5 energy of nanoparticles might lead to severe agglomeration on top of the TFN membrane, and therefore the formation of  
6 larger particles that do not match with polyamide structure<sup>35</sup>. Thus, agglomeration causes a poor dispersion of nanoparticles  
7 on the polyamide layer and a reduction of their active surface area<sup>142, 207, 242</sup>.

8 To avoid zeolite agglomeration, surface modification seems to be a possible way to address this issue. Several researchers  
9 have indicated that the modifiers could elevate the nano zeolite and polymer adhesion and dispersibility of zeolite in the  
10 polyamide layer and consequently the membrane performance<sup>35, 243-245</sup>.

11 The priming method is another way to reduce agglomeration and enhance the compatibility of nano zeolites within a polymer  
12 matrix. In this preparation method, the surface coating of the filler particles with a dilute polymer (normally below 10 wt%)  
13 before the addition of the bulk polymer in the matrix phase, is forming suspended particles thus increasing the polymer-filler  
14 adhesion<sup>239, 241, 246</sup>.

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1     *Defects*

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3     Although the incorporation of zeolite nanoparticles in the membrane top layer has yielded extraordinary results, zeolite-based  
4     TFN membranes have technical and economic difficulties in scale-up without defects or small cracks, and practically they  
5     showed functional destruction <sup>39</sup>.

6     Beside zeolite pores all prepared zeolite membranes contain intercrystalline non-zeolite pores. For high quality membranes  
7     with an insignificant degree of pinholes and defects, these non-zeolite pores should be not more than 2 nm <sup>247</sup>.

8     Fabricating ultrathin defect-free composite membranes is required for all membrane applications. In an extremely thin  
9     selective layer, solute-permeable defects are easily generated and can greatly affect the membrane performance <sup>35, 248, 249</sup>.

10    Failure to control the generation of defects during membrane fabrication is a barrier that deteriorates transport properties and  
11    rejection, and is one of the main drawbacks of zeolite membranes <sup>32</sup>.

12    A lack of sufficient interactions and compatibility between nano zeolite and the polymeric layer interrupts the transport  
13    process through zeolite-polymer composite membranes. Therefore, more investigation is needed to achieve a better bonding  
14    between zeolite particles and the polymer. Some studies demonstrate that a high nanoparticle loading during the IP process  
15    causes significant agglomeration and as well as surface defects that might lead to reducing the selectivity of TFN membranes  
16    <sup>211, 250, 251</sup>. Hence, making a defect-free membrane through a good dispersion of nano zeolite particles in a polymer structure  
17    is a challenge that needs to be addressed. Furthermore, the correlation between nanoparticle dispersion quality during the IP  
18    process with possible agglomeration and surface defects requires more study.

1 To have a better pressure stability and higher permeability in RO, a thin zeolite layer well connected to the substrate was  
2 proposed <sup>161</sup>. Lind et al. suggested that defect formation might be caused by the interaction between nano zeolite and active  
3 monomers altering the pore structure of the polyamide layer and decrease polyamide cross-linking degree (if the C/N ratio  
4 decreases the cross-linking degree increases), which provides more evidence for the hypothesis of transport through defects  
5 and molecular-sieving in zeolite thin film nanocomposite membranes <sup>141, 199</sup>.

6 Generally, two methods may allow controlling defect generation in membranes. First, inserting a gutter layer between the  
7 selective layer and the support, made of polydimethylsiloxane (PPMS) or poly[(1-trimethylsilyl)-1-propyne] (PTMSP), may  
8 improve the adhesion among the two phases <sup>252, 253</sup>. The gutter layer is often composed of highly permeable but low selective  
9 materials to restrict the penetration of polymer to the support <sup>254, 255</sup>.

10 Using a protective layer on top of a selective layer of membranes is the second approach that could be a solution for plugging  
11 defects and preventing a reduction of selectivity. Yoo et al. proved that with the assistance of a protective layer, a membrane  
12 with a selective ultrathin layer could be prepared at a large scale without a significant decrease in performance <sup>252</sup>.

13 In an effort to minimize defect formation, researchers suggested using an amine rich solution with MPD monomer <sup>256</sup>. Other  
14 studies suggested polyamide-zeolite nanocomposite preparation via a pre-seeding method, which enables a more uniform  
15 distribution of the NPs on the substrate. In the pre-seeding method, UF supports are immersed in the amine rich solution and  
16 then contacted with an organic suspension consisting of zeolite NPs, hexane, ethanol and a low concentration of TMC (0.01  
17 to 0.05 wt%). This method led to an embedded higher concentration of zeolites in the TFN membranes and an increased water  
18 flux without a considerable decrease in salt rejection <sup>142, 201</sup>.



## 1        **Conclusions and future trends**

2

3        Zeolite nanocomposite membranes have been studied in the last two decades to fabricate high-performance membranes and  
4        overcome the shortcomings of the current TFC membranes for water treatment and desalination. However, developing a  
5        defect-free zeolite nanocomposite membrane is still very challenging to scale-up due to agglomeration and defect formation.  
6        Introducing new methods to control defect formation in zeolite composite membranes would be helpful to conquer these  
7        challenges and commercialize these types of membranes.

8        Although the fabrication of zeolite nanocomposite membranes is not at an early stage, more studies are needed on the stability  
9        and durability of these membranes for long term applications. More investigation in the deposition of zeolite on the support  
10       layer could open new gates to overcome the leaching out problem and environmental concerns about synthesized zeolite  
11       nanoparticles.

12       The interaction between zeolites and polyamide and support layer in membranes deserves more attention and studies are  
13       needed to describe the influence of the substrate on the zeolite TFN membranes. More research needs to give a brighter view  
14       and explore the exact effect of the structured shape, the pore size of different nano zeolites and the addition of cross-linking  
15       agent on the fabrication of the zeolite TFN membranes and their role in enhancing antifouling, boron removal and chlorine  
16       resistance performance. A better understanding of the responsible mechanism for separation through zeolite nanoparticles  
17       with different apertures may help to design absolute selective membranes for individual ions removal applications.  
18       Furthermore, simulation and modeling might help to have a better understanding of mass transport through zeolite membranes.

1 The leading industrial concern of current RO membranes is their sensitivity to chlorination. Despite considerable research  
2 investigated in RO membranes development, the approach to chlorine resistance membrane for the long run industrial use  
3 needs more effort. As de-chlorination is required as pretreatment in the desalination industry, the development of chlorine-  
4 tolerant RO TFN and lowering the cost of desalted water can be the most beneficial way for future industrial needs.  
5 Understanding kinetics of polyamide degradation by chlorine and the interaction of PA layer and chlorine could be helpful to  
6 develop and commercialize cost-effective chlorine resistance membranes.

7 Although some type of nano zeolites reviewed in this paper are not likely applicable in seawater desalination, findings could  
8 help to develop potential directions for researchers to provide a viable alternative for TFC membranes and developing RO  
9 membranes for desalination. Last but not least, boron removal still remains a challenging issue in desalination processes.  
10 Therefore, more research is needed to study boron chemistry in the river water and the seawater, understanding the interactions  
11 between boron and the polyamide layer and developing advanced novel RO membranes to approach the cost-benefit boron  
12 removal strategy from seawater. Research should continue to develop membranes with high flux, low pressure, and enhanced  
13 salt rejection with more resistance to fouling and compaction.

14

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16

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