Reverse Osmosis Polyamide Thin Film Nanocomposite Membranes for Water Desalination: A Study

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Abstract: *Reverse osmosis (RO) desalination is one of the well-known technologies for water purification. Since its development, many studies have been devoted to improve this technique. Nanostructured reverse osmosis membrane is expected to play an important role in water desalination. The main objective of this study is to highlight the most important achievements in reverse osmosis membrane technology.*

Keywords: *Thin Film Nanocomposite (TFN); Reverse Osmosis (RO); Desalination; Nanoparticles (NPs).*

1. INTRODUCTION

Lack of clean water resources is a grand issue in modern society [1,2]. Water desalination represents a real solution to produce clean water for human consumption and industrial sectors [3]. Because of its high efficiency, reverse osmosis (RO) is considered as the most important desalination technology [4,5]. Thin film nanocomposite membrane has become a frequently selected RO membrane [6].This membrane is prepared by interfacial polymerization (IP) process and incorporation of nanoparticles into polyamide (PA) active layer with the aim of improving membrane characteristics including the hydrophilicity and surface charge. The term TFN membrane was first introduced by Hoek and his coworkers in 2007 [7]. In their work, they used zeolite NaA nanoparticles as filler in PA active layer during interfacial polymerization between m-phenylenediamine (MPD) and trimesoyl Chloride (TMC). Remarkable enhancement in water flux was achieved by embedding zeolite NaA nanoparticle without sacrificing membrane separation efficiency. This improvement was ascribed to hydrophilic property of zeolite nanoparticles which facilitate water solubilization and diffusion through the membrane.

Table 1 summarized the performance of RO TFN membrane that studied in research publications. Next section is presented the recent scientific and technological advances in the development of nanocomposite membranes for water treatment.

2. PERMEABILITY AND SELECTIVITY

Embedding hydrophilic nanoparticles into the polyamide layer of the composite membrane lead to significant enhancement in the membrane performance including water flux and salt rejection. As it mentioned earlier, zeolite NaA is the first nanomaterial that has been used to improve membrane water flux due to its superior hydrophilicity, high negative surface charge, and internal pores which facilitate water adsorption across the membrane [7].

Lind and his coworkers [9] investigated the effect of nanoparticles size on membrane performance using different size of zeolite nanoparticles. Smaller nanoparticles produced higher water flux due to its large pores, on the other hand larger nanoparticles produce better surface properties. This study suggested that nanoparticles size is an important factor needs to be considered while fabricating PA nanocomposite membrane.

In addition to zeolite, different nanomaterials have been used to modify membrane performance; all mentioned in table 1.

Table1. *Summary of thin-film nanocomposite membranes*

Nanofiller	PA Layer monomers	Substrate	performance of TFN	Ref.
Zeolite NaA	MPD-TMC	PSU	Water flux increased from $2.5*10^{12}$ to $3.9*10^{12}$ mPa^{-1} s^{-1} without compromising salt rejection (94%) by increasing concentration of nanoparticles from 0 t0 0.4 wt%.	[7]
Zeolite NaA AaA	MPD:TEA-TMC	PSU	Both AgA-TFN and NaA-TFN membranes exhibited higher water flux than that of TFC membrane. No change in salt rejection was observed. Less accumulation of bacterial cells on AgA-FTN and NaA-TFN membranes compared to TFC membrane	[8]
Different Sized Zeolite	MPD:TEA:SLS:IPA-TMC	PSU	Changes in interfacial polymerization chemistry can be used to tune PA TFN membrane properties. Smaller zeolite NPs produced greater improvement in membrane performance than that of bigger zeolite NPs.	[9]
Silica	MPD-TMC	PSU	By increasing silica concentration, more thermally membrane produced. Excellent water flux was observed for TFN membrane containing 1-2 wt%.	[10]
MWCNTs	MPD-TMC	PSU	Both water flux and salt rejection decreased from 18 to 12 L/m hr and 98 to 92.2 wt%, respectively, by increasing concentration of MWCNTs from 0 to 1wt%. MWCNTs enhanced chlorine resistance of TFN membrane.	[11]
Zeolite LTA	MPD-TMC-post Treatment	PSU	Post treatment with NaOCl, $Na_2S_2O_5$, and $NaHCO_3$ resulted in very high salt rejection 99.4 wt% and high water flux 42 L/m2. Defects and molecular sieving largely control transport through zeolite-TFN membranes.	[12]
F-Silica	MPD-TMC	PSU	The water flux increased by increasing concentration of NPs from 0 to 0.4wt% with little decrease in salt rejection. Thermally stable membrane produced.	[13]
F-MWCNTs	MPD-TMC	PSU	Water permeability increased from 25 to 70 L/m²h by increasing concentration of NPs from 0 to 0.1 wt% while NaCl rejection dramatically decreased. Rough and hydrophilic membrane produced.	[14]
Metal alkokxide	MPD: SLS-TMC	PSU	Three different type of Metal-alkokxide (PhTES, BTESE, TTIP) used to prepared TFNs, all three type show superior performance in term of permeability. TTIP and BTESE led to little decrease in salt rejection while TTIP did not affect the rejection.	[15]
Zeolite NaX	MPD-TMC	PES	Concentration of MPD and TMC significantly affect membrane performance. The membrane of high concentration of TMC (0.15% w/v) and MPD (3% w/v) has the highest water flux 50 L/m² hr, but lowest salt rejection (94%). Zeolite NPs increased membrane hydrophilicity.	[16]
iLSMM	MPD-TMC	PSU	Different concentration of MPD, different curing time, and different concentration of NPs (0-0.25) used in preparation of twelve TFN membranes. Water flux ranging from 21 t0 42 l/m²hr and salt rejection from 86 to 97	[17]

			%. Present of iLSMM enhanced antifouling properties of TFB membranes.	
MCM-41	MPD-TMC	PSU	Water flux increased from 28 to 46 L/m² hr by increasing concentration of NPs from 0 to 0.1 wt% while NaCl rejection almost remain constant (79 wt%). Porous structure of NPs plays important roles in creating short path for water molecules.	[18]
APQZ	MPD-TMC	PSU	The resulting membrane has good mechanical stability when tested under 10 bar. Water flux increased from 16 to 40 L/m²hr by increasing concentration of NP from o to 0.1 wt%.	[19]
Zwitterion-CNT	MPD-TMC	PES	Water flux increased from 11.85 to 48 L/m² hr using 20% NPs, under 350 PSI. salt rejection decreased little bit.	[20]
Carboxylic MWNTs	MPD-TMC	PES	The resulting membrane has good mechanical properties. Charged NPs prevent formation of biofouling layer on membrane surface. Water flux increased to 21 40 L/m²hr under 100 PSI. Applying electrical potential to the membrane does not change its transport properties.	[21]
Zeolite (Silicate-1)	MPD-TMC	PSU	The resultant membrane has outstanding chemical stability in comparison with NaX-Zeolite mixed membrane. Water flux of silicate-zeolite (65 L/m² hr at 0.05wt%) is higher than that of NaX (35 L/m² hr at 0.1 wt%) due to larger pores size and higher water diffusion rate of silicate zeolite. Both membrane have good salt rejection.	[22]
Zeolite NaA	MPD-TMC	PSU	Good water flux achieved (46.5 L/m² hr) by adding NPs in organic phase. high salt rejection (97%) by adding NPS in aqueous phase.	[23]
Aminated Zeolite	MPD:PES:TEA-TMC	PSU	Adding PES and TEA to MPD-nanoparticle solution increased water flux from 23.2 to 37.8 L/m² hr without compromising salt rejection (98%). The membrane showed good chlorine resistance.	[24]
Zeolite A	MPD-TMC	PSU	The resultant membrane exhibited superior interfacial properties and separation performance including high water flux, observed salt rejection and enhanced resistance to irreversible flux decline due to physical compaction	[25]
Mesoporous silica	MPD-TMC	PSU	Water flux increased from 19 to 53 L/m² hr. salt rejection remain constant 97%	[26]
HBP-g-silica	MPD: aPES-TMC	PSU	Water flux increased from 22.1 to 34.4 L/m² hr while the salt rejection decreased from 98 to 97.7%. The membrane showed better chlorine resistance.	[27]
Aluminosilicate CNTs	MPD-TMC	PSU	Water flux increased from 13 to 23 L/m² hr under low pressure while salt rejection almost remained constant 97.5%.	[28]
F-MWCNTs	MPD-TMC	PSU	Water flux increased from 14.86 to 28.05 L/m² hr while salt rejection slightly deceased to 90%. The membrane showed better antifouling and antioxidant properties.	[29]
HNTs	MPD-TMC	PSU	Water flux increased from 18 to 36.1 L/m² hr while salt rejection decreased 94 to 93 %. The membrane has enhanced fouling properties.	[30]
OA-silica	MPD-TMC	PSU	The OA modified-silica PA membrane produced higher salt rejection (98%) in	[31]

			comparison to unmodified silica PA membrane (95 %) while maintain its high water flux around 49 L/m² hr.	
Clay	MPD-TMC	PSU	The water flux increased from 36.6 to 51 L/m² hr by adding 0.1 wt% NPs without compromising salt rejection (around 99%). Modified membrane exhibited significant antifouling properties.	[32]
Graphene-TiO$_2$	MPD-TMC	PSU	Both water flux and salt rejection increased from 34 to 51 L/m² hr and 97 to 99% by adding 0.02wt% NPs. Antifouling properties and anti-chlorine resistance were enhanced.	[33]
HN$_2$-TNTs	MPD-TMC	PSU	Both water flux and salt rejection increased from 19 to 36 L/m² hr and 94 to 96% by adding 0.05wt% NPs. Antifouling properties and anti-chlorine resistance were enhanced. Modified membrane exhibited significantly mitigate BSA fouling and achieved good water flux recovery after simple rinsing.	[34]
Graphene Oxide	MPD-TMC	PSU	The water flux increased from 1.8 to 22 L/m² hr by increasing NPs concentration to 0.20 wt% (working under 217 psi). NaCl rejection almost remain constant (above 80%). Modified TFN exhibited excellent anti-fouling properties against BSA and HA	[35]
Al-ZnO	MPD-TMC	PSU	Water flux increased from 26 to 32 L/m² hr by increasing NPs concentrations to 0.5 wt%. salt rejection decreased little bit then return to its original value 98%.	[36]
MCM-48	MPD-TMC	PSU	The NPs embedded first in organic phase: water flux increased from 34 to 40 L/m² hr (salt rejection remain constant 95%). Second in aqueous phase water flux increased from 24 to 68 L/m² hr (salt rejection decreased from 97 t0 80 %).	[37]
Graphene Oxide	MPD-TMC	PSU	Water flux increased from 39 to 60 L/m² hr by increasing NPs concentrations to 0.015wt% while salt rejection decreased from 95.5 to 93 %. Working pressure 300 psi	[38]

Another significant enhancement in membrane water flux was accomplished by Yin and his coworkers [18] upon incorporating of MCM-41 silica nanoparticles. The enhanced water flux was ascribed to high hydrophilicity of the embedded nanoparticles and the pores in the nanoparticles that provided additional channels for water to pass through.

3. CHLORINE RESISTANCE

It has been pointed out that the polyamide RO membranes have weak resistance to chlorine. When the PA membrane contacts with chlorine, N-H in the amide bond (-NHCO-) is chlorinated and then hydrolyzed in water. Finally, the amine is changed into a quinoid structure and decomposed, causing failure in membrane performance [13]. Park et al [11] used acid functionalized MWCNTs to enhance PA membrane anti-chlorine properties. When MWCNTs were embedded into the PA layer, the membrane exhibited improved chlorine resistance. This can be ascribed to the reaction between hydroxylic groups in CNTs and amine groups in polyamide layer.

Because amide bonds are the main target of chlorine attack, introducing additional amide bonds or amino groups to the membrane seems to be a reasonable strategy to protect PA cross-linking structure. So, Chun et al [27] introduced polyamide modified silica NPs into the polyamide layer. Results showed that the modified composite membrane demonstrated better chlorine resistance. This ascribed to introduction of extra amide groups to membrane surface which mitigate the hydrogen-chlorine interaction at the PA structure.

4. ORGANIC AND MICROBIOLOGICAL FOULING

Membrane fouling is defined as the deposition of undesired substance on membrane surfaces causing membrane performance failure. Organic fouling of composite membranes is the primary cause for the declination in membrane performance [39]. Hence, many studies are focused on fabricating a membrane with better anti-fouling properties.

Kim and his coworkers [40] showed that the membrane hydrophilicity is related to fouling stability. In other words, increasing the membrane hydrophilicity resulted in a membrane with good antifouling properties. Rana et al [41] showed that introducing negatively charge nanoparticles to membrane surface could improve membrane antifouling properties by generating electrostatic repulsion force between membrane surface and negative foulants.

5. CONCLUSION

Reverse osmosis membrane technology witnessed a tremendous development in recent years. Although Incorporating of nanoparticles in membrane PA layer resulted in a membrane with significantly improved characteristic including water flux, salt rejection, and antifouling properties, several challenges are still need to be addressed such as relationship between water flux and salt rejection, effect of particle size on defecting membrane rejection barrier, and improve nanoparticle dispersion in membrane.

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