

Composite Membranes for Membrane Distillation Desalination Process

Final Report Submitted to

The New Mexico Water Resources Research Institute (NMWRI)

By

Sai R. Pinappu

Graduate Advisor: Prof. Shuguang Deng

Chemical Engineering Department

New Mexico State University

April 30, 2010

Abstract

Membrane distillation (MD) is an emerging membrane technology for pure water production from saline water, solution concentration, recovery of volatile compounds from aqueous solution and other separation and purification processes. Membrane distillation differs from other membrane technologies in that the driving force for separation is the difference in vapor pressure of volatile compound across the membrane, rather than total pressure. The main difference between membrane distillation and conventional thermal distillation is that membrane distillation could occur at a much lower temperature than conventional thermal distillation. The membranes for membrane distillation are hydrophobic, which allows vapor (but not liquid solution) to pass. The vapor pressure gradient is created by heating the feed solution and cooling/purging the condensate in the permeate side. Therefore membrane distillation enables separation to occur below the normal boiling point of the feed solution and could utilize low-grade alternative energy. For all these to be possible the membrane should have following properties: 1) Low Thermal conductivity and high thermal stability 2) Low Mass transfer resistance 3) Chemically resistant towards different feed solutions and cleaning agents. 4) Membrane should have high porosity 5) Membrane should have high liquid entry pressure for water.

Conventional polymer membranes possess all the properties but the problem with those membranes are 1) Thermally Unstable 2) High Heat losses within the membrane 3) Non uniform pore size distribution due to thermal expansion and contraction during the process.

Above mentioned drawbacks can be rectified by a relatively simple way i.e. by using a composite membrane (hydrophobic + hydrophilic polymers or hydrophobic polymer + hydrophobic in organics) to improve the thermal stability and to curtail the conduction. The top hydrophobic thin layer will be responsible for mass transport in MD process while the top hydrophobic and hydrophilic sub layer will prevent the conductive heat loss through the whole membrane matrix. These composite membranes have prepared by phase inversion method. We have characterized the composite membranes by conventional membrane distillation process.

Table of Contents

1. Introduction	3
2. Experimental	5
3. Results and Discussion	6
4. Conclusions	9
5. References	10

1. Introduction:

Water is one of the prime elements responsible for life on earth perhaps fresh water is the most important natural resource for human survival and it is a human necessity. Food production, industrial productivity, energy production, and the global economy are dependent on availability of water, demand is rapidly approaching the available fresh water supply and hence the global shortage of fresh water demands purification of nontraditional water sources with energy efficient methods of water desalination^{1, 2}. Membrane distillation can be future desalination process since it can use low-grade thermal or solar heat to treat brackish water, remove volatile organic compounds to produce fresh water³.

Membranes distillation is based on the principle of application of thermal gradient between both sides of a hydrophobic membrane that separates hot feed solution from a cooling chamber containing a liquid, gas or vacuum⁴. Depending on the type of configuration used membrane distillation has been named as follows.

Direct contact membrane distillation (DCMD) - In DCMD a cold liquid solution will be allowed to flow through the permeate side of the membranes in order to condense the vapor that has migrated through the membrane pores from the hot feed solution⁴.

Vacuum membrane distillation (VMD) - In VMD feed solution will be on one side of the membrane and a vacuum on the other side of the membrane to create driving force for the vapor to migrate through membrane pores from the hot feed solution⁴.

Air gap membrane distillation (AGMD) - In AGMD only feed solution is in direct contact with the membrane and the Permeate is condensed on a cold surface. There is an air gap situated between the membrane and the cold surface to reduce energy loss by heat conduction through the membrane⁴.

Sweep gas Membrane distillation (SGMD) - In Sweep gas membrane distillation, the vapor at the permeate side of the membrane is removed by sweep gas and subsequently externally condensed⁴.

The main advantages of membrane distillation over other desalination process are⁵

1. Nearly 100 % retention of non-volatile compounds.
2. Low energy consumption.
3. No Extensive pretreatment is necessary as in reverse osmosis.

In spite of these obvious advantages membrane distillation process cannot compete with commercial desalination process such as reverse osmosis since membrane distillation has

1. Lower Flux compared to reverse osmosis process.
2. Membrane wetting (Diminishes the durability of membrane distillation membranes).

A good membrane distillation membrane should exhibit

1. High permeability.
2. Low thermal conductivity.
3. High hydrophobicity.

To obtain high permeability, membrane should be thin and as porous as possible but high hydrophobicity can be achieved by a membrane with small maximum pore size at its surface. In addition the gas entrapped within the membrane pore has lower conductive heat transfer coefficient than the membrane matrix which accounts for conductive heat loss in membrane distillation process. It seems there is a conflict between the requirements of an ideal membrane distillation membrane i.e. high mass transfer and low heat transfer through the membrane. A possible solution is to increase the porosity of the membrane since the air entrapped has low heat transfer coefficient and also increased porosity provides high surface area for evaporation. The idea of hydrophobic/hydrophilic composite membranes may resolve this issue with top hydrophobic thin layer responsible for mass transport, while both top hydrophobic and the hydrophilic sub-layer may prevent the conductive heat loss through the whole membrane matrix⁵.

The membranes that are being used in membrane distillation are actually manufactured for microfiltration and ultra filtration processes but recently much research has been devoted to develop membranes specifically designed for membrane distillation applications. The objectives of the researches were either to increase the membrane durability or to improve the permeation flux. The concept of a mixed-matrix membrane, where a small filler material is dispersed throughout a larger polymeric matrix, has brought new degrees of freedom to the development of advanced membrane materials for numerous separation processes⁶. These novel materials often have improved mechanical, chemical, and thermal stability, as well as enhanced separation, reaction, and sorption capacity⁷⁻¹⁰. Better membranes have been developed for gas separation, pervaporation, ion exchange and fuel cell applications by exploiting zeolite or carbon molecular-sieve particles dispersed within relatively thick membrane films¹¹⁻¹³.

In this research study polysulfone which is widely used in preparing reverse osmosis, ultra filtration and microfiltration membranes has been used as possible hydrophobic polymer membrane matrix and zeolite-4A has been used as hydrophilic material. Polysulfone may not be as hydrophobic as compared to polypropylene, poly(vinylidene fluoride), polytetrafluoroethylene but the ease of processability at the lab scale to make membranes has prompted us to choose polysulfone as membrane matrix.

It is expected that the incorporation of zeolites in polysulfone would preserve or even improve the selectivity of the polymer and simultaneously increase the flux characteristic for polysulfone membranes. In this study, 3-aminopropyltrimethoxysilane (APTMS) was introduced

as a kind of compatibilizer to eliminate the interfacial voids between zeolite and polysulfone. If the interfacial voids could be eliminated completely, the molecular sieving effect of zeolite could be clearly observed.

2. Experimental:

2.1 Materials: Polysulfone (UDEL P-35000), N-methyl-Pyrrolidone (NMP), 3-aminopropyltrimethoxysilane (APTMS), Ethanol, Zeolite 4A.

2.2 Membrane Preparation:

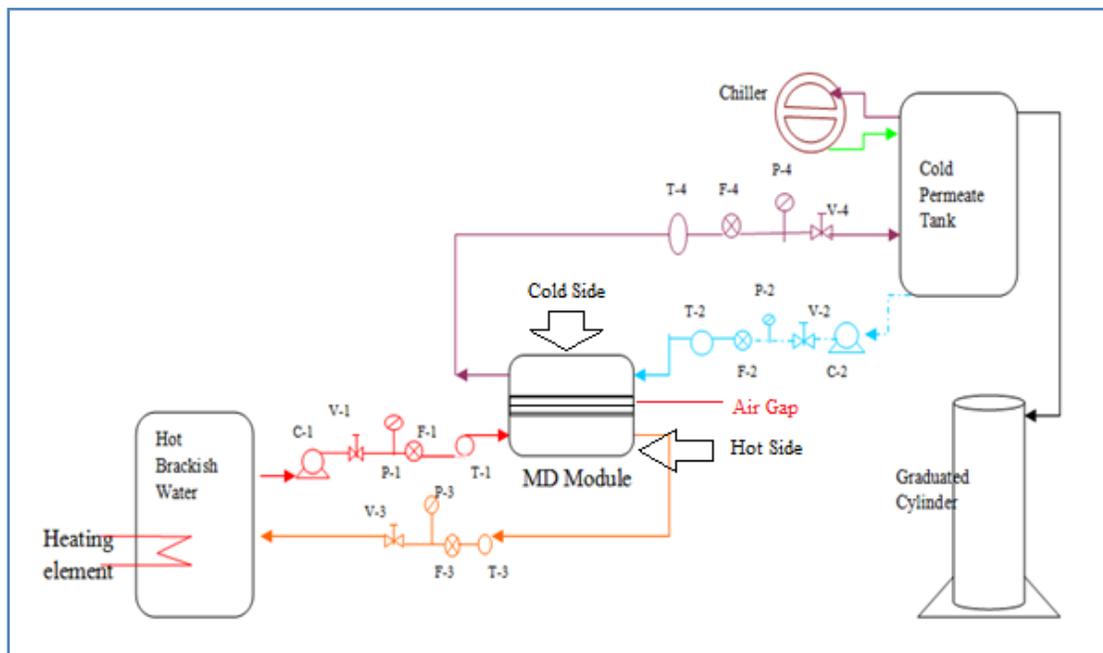
The APTMS was mixed with distilled water and then the zeolite was added. The reacting mixture was then stirred for adequate time. After filtration and thoroughly washing with distilled water to remove unreacted silane, the zeolite was dried at 80°C in vacuum for 2 days. PSF solution with desired PSF weight percent was prepared by dissolving PSF in NMP (90ml) + Ethanol (10ml) solution at room temperature and then desired percentage of zeolite was added to this solution. Preparation conditions and codes for all membranes are provided in Table 1. The homogeneous solutions were cast on a glass plate by using a Sheen micrometer adjustable film applicator with 300 µm thickness after this the entire assembly was immediately immersed into a room temperature de-ionized water. Phase inversion starts immediately forming polymer rich phase region (membranes) and polymer lean phase (Water + NMP) the membranes were kept in the water for 1hr to allow complete phase inversion. Each membrane was washed thoroughly with de-ionized water to remove any residual solvent and allowed to dry at ambient conditions for 48 hrs.

Table 1

Membrane Code	Polymer concentration (wt%)	Zeolite Concentration (wt%)
M1	10	0
M2	12	0
M3	14	0
M4	16	0
M5	12	33.3
M6	12	40
M7	12	50
M8	12	70
M9	12	90
M10	14	33.3
M11	14	40
M12	14	50
M13	14	70
M14	14	90

2.3 Membrane distillation Experiments:

Traditional AGMD experiments were performed on the prepared membranes. In AGMD only feed solution is in direct contact with the membrane. The permeate is condensed on a cold surface. The main advantage of AGMD process is that it is suitable for all DCMD applications alongside removing volatile substances which can wet the membrane at permeate side due to lower surface tension and smaller water contact angle with the membrane since in AGMD permeate is not in direct contact with the membrane the problem of membrane wetting is avoided on the permeate side of the membrane. The only disadvantage of AGMD process is that there will be additional resistance to mass transfer due to the presence of air gap between cold side of the assembly and permeate side of the membrane. The laboratory system used to conduct the AGMD experiments is shown in the following flow diagram.



Schematic Representation of AGMD Setup

3. Results and Discussion:

3.1 Effect of Polymer Concentration on Salt Rejection and Flux:

Pure polysulfone membranes were prepared with different polymer weight percents to know the effect of polymer concentration on the flux and salt rejection. It can be observed in the figure 1 & 2 that as polymer weight percent increases flux decreases but salt rejection increases this may be due to the fact that increasing the polymer concentration in the dope solution leads to a much higher polymer concentration at the interface. This implies that the volume fraction of polymer increases and consequently a lower porosity is obtained.

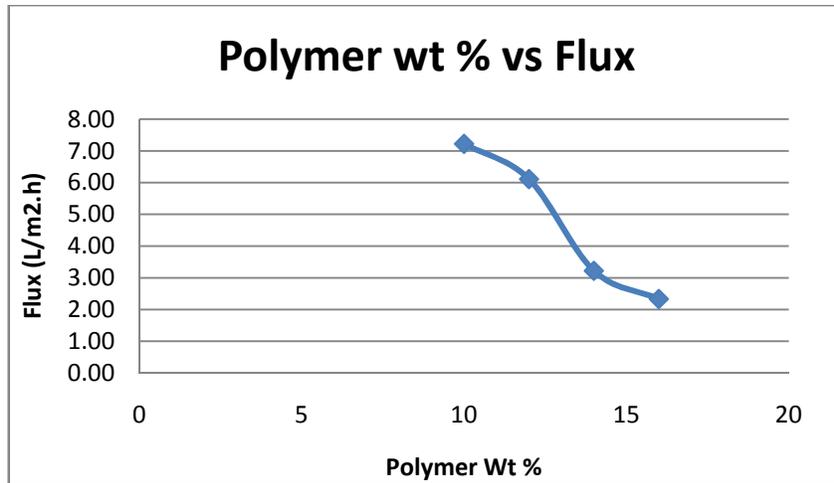


Figure 1: Polymer weight % vs Flux

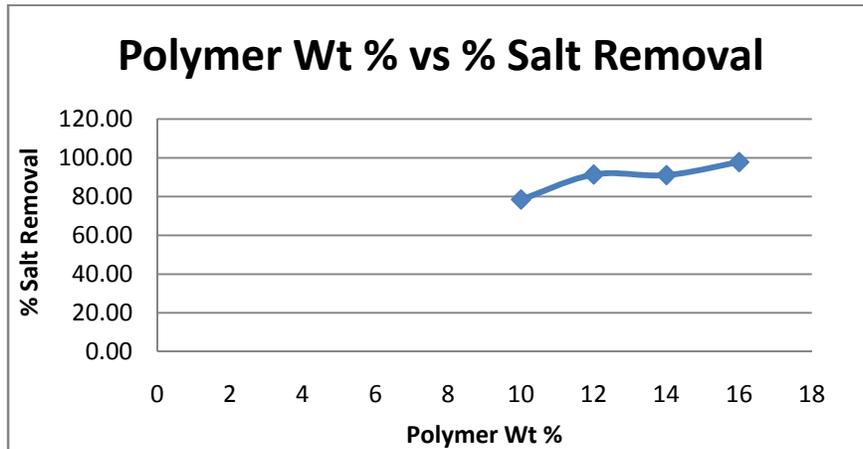


Figure 2: Polymer weight % vs Salt Removal

3.2 Effect of Zeolite Loading on Salt Rejection and Flux:

The effect of addition of zeolite particles, in the 0-90wt% range, to the polymer matrix on the membrane performance was studied in this work. Zeolite used in this work is type 4A. Type 4A zeolites have approximately 4.2 Å pore diameter and the diameters of hydrated sodium and chloride ions are approximately 8-9 Å¹⁴, hence it is expected that type 4A zeolite is a good candidate to separate salt from water by molecular sieving.

Only two polymer concentrations were selected in order to incorporate zeolite since polymer concentrations of 12 and 14 wt% had optimal fluxes and salt rejection. From the following graphs we can see that as we increase the zeolite content salt rejection increases to certain extent and then decreases this may be due to the fact that as the zeolite content in the

membrane increases, the thickness of the zeolite –filled layer also increases and the thickness of the zeolite –free layer decreases. When the zeolite content is low (in between 33.3 wt % to 50 wt %), zeolite –free polymer layer determines the permeation rate of the composite membranes. The affinity of zeolite particles in the zeolite-filled layer may play an important role at moderate zeolite contents (between 33.3 to 50 wt % from the figure 3 and figure 4). At higher zeolite contents that are above 50wt %, the relative thickness of the zeolite –filled layer is higher and it loosens up the structure of the mixed-matrix membranes, controlling the permeation mechanism hence lower salt rejections but higher fluxes. The optimum performance membranes from the below graphs were M6 and M11 membranes.

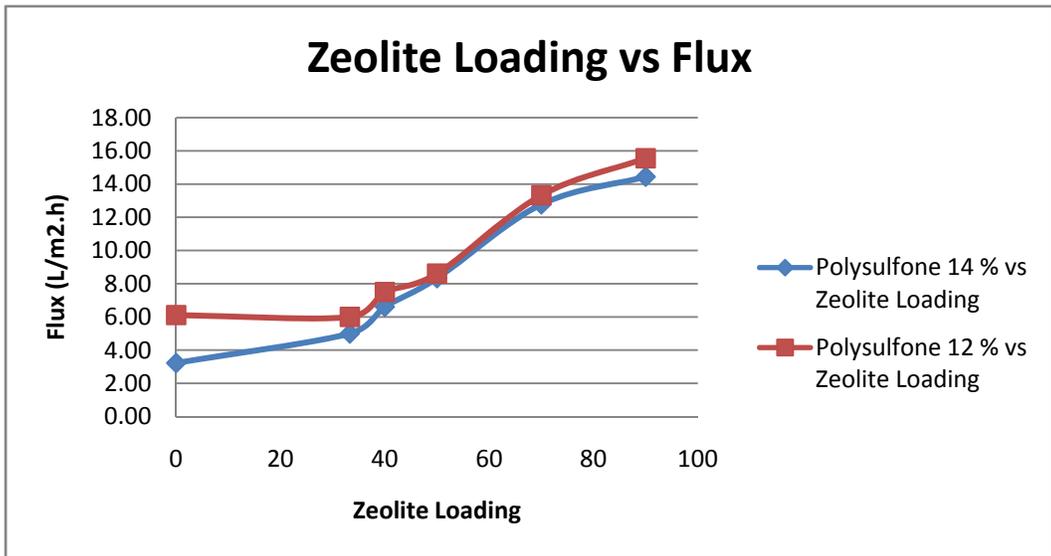


Figure 3: Zeolite loading vs Flux

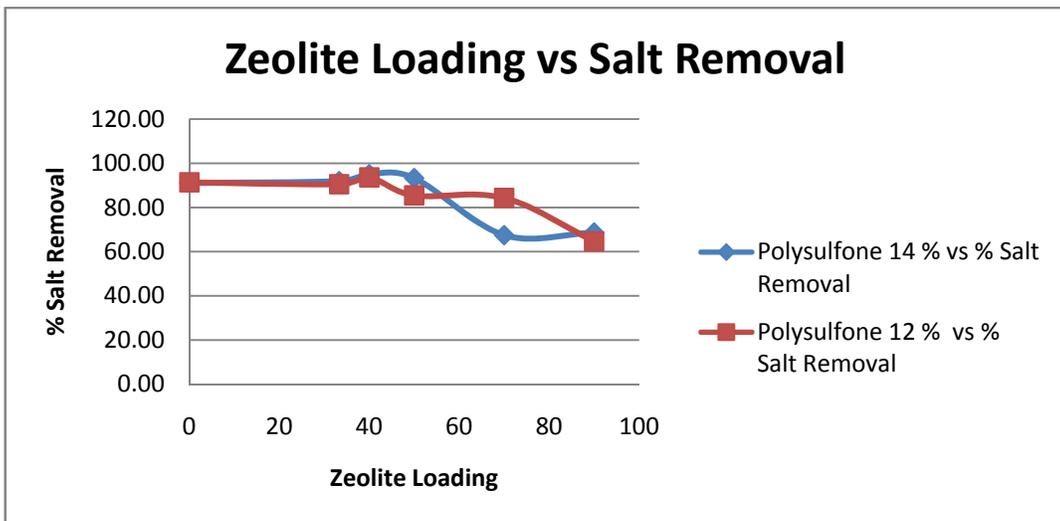


Figure 4: Zeolite loading vs Salt Removal

4. Conclusions

The general conclusions inferred during this study are:

1. Incorporation of zeolites in to the polymer matrix offered an extra degree of freedom that can be used to tailor the permeability and selectivity of the membranes.
2. The addition of zeolite particles affects the membrane performance differently at different zeolite concentrations higher zeolite content gives more fluxes at the expense of selectivity.
3. The optimum membrane performance was obtained at about 40 wt % of zeolite content.

Acknowledgment

Financial support for this research was provided by The New Mexico Water Resources Research Institute (NMWRRI).

References

1. Elimelech, M. "The Global Challenge for Adequate and Safe Water", *Journal of Water Supply: Research and Technology – AQUA*, Volume 55, February 2006, pages 3-10.
2. Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Mariñas, B.J. and Mayes, A.M. "Science and Technology for Water Purification in the Coming Decades", *Nature*, Volume 452, March 2008, pages 301-310 .
3. Cath, T.Y., Childress, A.E., and Elimelech, M. "Forward osmosis: Principles, Applications, and Recent Developments", *Journal of Membrane Science*, Volume 281, September 2006, pages 70-87.
4. Meindersma, G.W, Gujit, C.M, de Hann, A.B. " Desalination and Water recycling by air gap membrane distillation" , *Desalination*, Volume 187, 2006, pages 291-301.
5. Qtaishat, M., Khayet, M., Matsura, T." Novel porous composite hydrophobic/hydrophilic polysulfone membranes for desalination by direct contact membrane distillation", *Journal of Membrane science*, Volume 341, 2009, pages 139-148.
6. Koros, W. J., "Evolving beyond the thermal age of separation processes: membranes can lead the way", *AIChE J.*, 50(10), 2326-2334 (2004).
7. Behera, D., Banthia, A.K., "BisGMA/TiO₂ Organic-Inorganic Hybrid Nanocomposite "Polymer-plastics technology and engineering. Volume 26, 2007 pages 10-12.
8. Holt, J. K.; Park, H. G.; Wang, Y. M.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, " Fast Mass transport through sub-2-Nanometer carbon nanotube", *Science* Volume 312, May 2006 , Pages 1034-1037.
9. Rittigstein, P., Priestley, R.D., Broadbelt, L.J., and Torkelson, J.M., "Model Polymer Nanocomposites with Known Interlayer Spacing Provide Understanding of Confinement Effects in Real Nanocomposites", *Nature Materials*, Volume 6 ,2007, Pages 278-282.
10. Baglio, V. , Arico, A. S. , DiBlasi, A. , Antonucci, P. L. , Nannetti, F. , Tricoli, V. and Antonucci, " Zeolite-based composite membranes for high temperature direct methanol fuel cells". *Journal of applied Electrochemistry*. Volume 35 , page 207
11. Sholl, D. S.; Johnson, J. K., "Making High flux membranes with carbon nanotubes" , *Science* 2006, Volume 312, Pages 1003–1004.
12. Tin PS, Chung TS, Jiang LY, Kulprathipanja S. "Carbon–zeolite composite membranes for gas separation". *Carbon*. 2005 Volume 43, Pages 2025–2027.
13. Won, J. G.; Seo, J. S.; Kim, J. H.; Kim, H. S.; Kang, Y. S.; Kim, S. J.; Kim, Y. M.; Jegal, J. G. *Adv. Mater.* 2005, Volume 17, Page 80.
14. Mary, L., Asim, K., Anna, J., Xiaofei, H., William, H., Yang, Y., Eric, M., " Influence of Zeolite crystal on zeolite-polyamide thin film nanocomposite membranes" *Langmuir*, Volume 25, May 2009, Page 10139-10145.