Influence of N-Butanol Composition on Membrane Performance in Coagulation Bath for Membrane Distillation

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Abstract. Membrane Distillation is one of the extensively used desalination technologies for the utilization of the waste heat in the industries. The membranes used in for membrane distillation have to be hydrophobic in nature so as to permeate only vapour through the membrane pores. In this background, there is a necessity to develop membranes with better hydrophobicity and mechanical strength for overall performance. In this paper, we discuss the preparation of polyvinylidene fluoride homopolymer by phase inversion technique using N - methyl pyrrolidone as solvent. Water and n – butanol in varying compositions by weight percent from 0 to 100% is used as non-solvent. Contact angle and permeate flux were measured for the synthesized membranes. The results indicated that the membranes made of PVDF immersed in 100 % n - butanol coagulation solution shows good hydrophobic behaviour and also achieved higher permeate flux compared to the other membranes reported in literature.

Keywords. Water recovery; Hydrophobic; PVDF; Membrane distillation; Phase inversion;

1. Introduction

The major global concern is the clean water shortage and the potable water accessibility and these issues affecting many parts of the world. The seawater contributes most of the world water which is salty for the purposes like drinking or usage in industries. So, there are pressing needs for substitute desalination and technologies in waste water management to meet the increasing demands of portable water with reasonable and consistent water sources [1]. Brackish desalination offers a cost-effective option for the availability of high-quality water compared with desalination by seawater [2]. Reverse osmosis (RO) was considered one of the most promising innovations for rising drinking water sources amongst the variety of methods suggested for desalination. Nevertheless, in many situations the recovery of the water is below 55% [3]. In view of these considerations, membrane distillation (MD) proven to be one of the potential technology in addressing the applications of purification of water like desalting highly saline waters with a broad range including seawater [4,5]. The hydrostatic pressure experienced in MD is lower than that used in pressure-driven membrane processes like reverse osmosis (RO) [6]. MD is a separation mechanism in which a stream of hot feed is passed over a hydrophobic microporous membrane. More appropriate membranes such as hydrophobic membranes made of polypropylene (PP), polyethylene (PE), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) have become available in MD processes [7]. The difference in temperature between the two sides of the membrane results in a difference in vapor pressure which causes water to evaporate from the hot side and to pass through the pores to the cold side [8].
MD typically employs four basic configurations; those include the vacuum membrane distillation (VMD), direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), and air gap membrane distillation (AGMD) [9]. In addition, all the previous techniques follow the same principle; contact the feed water with the membrane’s hot side, which allows the water vapor to diffuse through the membrane pores, but not through the solution. The study based on Direct Contact Membrane Distillation (DCMD) utilise hot saline and cold streams contact directly on both sides of the membrane with a temperature driving force where results in a vapour pressure differential produced between them to permit vapour transfer through the membrane where water is permeated as flux through a hydrophobic membrane [10,11]. Evidently, the mass transfer is followed by the transfer through the membrane of the corresponding latent heat and the conductive heat leak. The transport mechanism from the feed solution to the permeate flux can be divided into three stages. Since the membrane is hydrophobic, fluid cannot penetrate the pores of the membrane, hence the first stage is the evaporation of the volatile components at the hotter side of the membrane interface. The second stage is the transmission of vapour through the membrane microporous system. The final stage is the condensation of vapour at the interface of the cold membrane [2]. The main advantages are: Due to its simple design, DCMD is widely used and it can offer a higher permeate flux rate in contrast with other configurations of MD [12]. The porous membrane’s hydrophilic property will prevent penetration of the aqueous solution into the pores of the membrane. Higher hydrophobicity and larger membrane pores with high permeate flux under high rejection are therefore expected to occur. Several authors studied the outcome of individual PVDF membranes for their hydrophobic behaviour, excellent chemical resistance, high thermal resistance [13–15] as well as good membrane forming characteristics. Membrane preparation mechanism using phase inversion technique influences the membrane formation by affecting inter-diffusion of solvent and non-solvent. The composition of the coagulation bath and also the polymer dope solutions influence the solvent exchange rate of the mechanism. In many studies, dual coagulation bath, non-solvents singly and to our best of our understanding, there are no reported literatures based on membranes using mixed coagulation bath based on water and n-butanol systems. In this work our approach is to study the behaviour of the PVDF membranes for membrane distillation applications which are casted in various coagulation bath conditions to achieve hydrophobic condition using PVDF as polymer, NMP as solvent in different coagulation bath conditions from 0% to 100% water –butanol without using pore forming agent. The PVDF membranes synthesized were characterized for their porosity, water contact angle; permeate flux and liquid entry pressure measurement.

2. Materials and Methods

2.1. Materials
Polyvinylidene fluoride (PVDF) polymer with a molecular weight range of 40,0000 g/mol, N-methyl-2-pyrrolidone (NMP) (anhydrous 99.9%) solvent, were purchased from Tech Inc., Chennai, India and coagulation bath solvent n-butanol (99.9% purity) was purchased from Sisco Research Laboratories Private Limited, India. Without further purification of these chemicals, the experiments were conducted.

2.2. Membrane Preparation
Membranes were fabricated by phase inversion technique. The polymer casting solution was prepared by dissolving the suitable amount of PVDF in NMP solvent by vigorous stirring using a mechanical stirrer. By trial and error method, the concentration of PVDF was optimized to 16 wt%. The polymer was added fractionally into the solvent at 35°C until the whole volume has been dissolved to form a dope and stirred mechanically for about 12 hours. The dope solution was further subjected to degassing to remove air bubbles. The degassed dope solution was then casted manually on a polyester support glass plate of 0.2 mm thickness at room temperature and immediately immersed into the coagulation bath. The coagulation bath conditions used in the present studies namely MB membrane code where the wt% of n-butanol and water varied. Then further the membranes were rinsed in water coagulation bath. The membranes of various coagulation bath compositions are shown in Table 1. The membranes were kept in the coagulation bath for atleast 6 hours for the formation of nascent membranes and proper removal of solvent.

| Membrane | PVDF Polymer Concentration wt. % | NMP Solvent Concentration wt. % | Coagulation bath conditions |
|----------|---------------------------------|---------------------------------|-----------------------------|
| MB 1     | 16                              | 84                              | n-butanol: water (100:0)    |
| MB 2     | 16                              | 84                              | n-butanol: water (75:25)    |
2.3. Membrane Characterization

2.3.1. Membrane Porosity

For the measurement of porosity, the membranes were wetted for at least 24 hours. The wet weight of the membrane samples was measured and dried in the oven for a minimum of 2 days and dry weight was measured. The experiments were repeated thrice for concordant values. The membrane porosity was calculated using the following formula:

$$
\varepsilon_m = \frac{(M_{\text{wet}} - M_{\text{dry}})/\rho_w}{(M_d/\rho_m) + (M_w - M_d)/\rho_w} \times 100%
$$

Where, $M_{\text{wet}}$ is the weight of the wet membrane and $M_{\text{dry}}$ is the weight of the dry membrane, $\rho_w$ and $\rho_m$ are the density of water and the membrane respectively.

2.3.2. Contact angle

The contact angle was measured for the fabricated membranes to check for the hydrophobic characteristics for the membrane distillation application. The membranes were dried under ambient conditions for 24 hours. Contact angle was measured using Tech Inc Economy model which enables measurement based on image analysis. A droplet of water transferred using a syringe on the X-Y table manually. The droplet is focussed by adjusting the movement and the image was captured using Autocad software.

2.3.3 Permeate flux and Liquid entry pressure measurement

For the Permeate flux measurement, the membranes prior itself wetted in pure water for 24 hours and measured using a membrane test cell in Fig. 1. The test cell consists of a membrane module with an effective area of 0.0125 m². An operating pump is connected from feed tank to the membrane module unit with a pressure gauge (PG-1) with a gauge pressure of 0 to 1.0 kg/cm². The performance of fabricated membranes was estimated using the membrane test cell by performing flux study experiments. With regard to the time taken to extract permeated water, the permeate flux was measured. The experiments of all membranes were carried out at constant gauge pressure of 0.8 kg/cm². The permeate flux was calculated from the following equation:

$$
J = \frac{A}{V} \times t
$$

Where, $J$ is the permeate flux in L/m²h, $A$ is the effective area of the membrane in m², $V$ is the volume collected in litres and $t$ is the volume collection time in hours.

| Membrane | Type | Temperature | Description |
|----------|------|-------------|-------------|
| MB 3     | n-butanol: water (50:50) | 16 | 84 |
| MB 4     | n-butanol: water (25:75) | 16 | 84 |
| MB 5     | n-butanol: water (0:100) | 16 | 84 |

In this work, Distilled water is used as rinsing bath after the coagulation bath conditions.
Fig. 1. Schematic diagram of membrane module set up

The minimum trans-membrane pressure required for the feed solution to penetrate the large pore size is known as LEP. For the measurement, the same membrane module is used. The membranes are fixed in the module and fasten the bolts. The feed pump which is connected at the inlet is operated with a minimum operating pressure. At first no permeate flow is observed and the reject from the module is recirculated back to the feed tank. The pressure slowly increased in steps of 0.1 kg/cm² until the first droplets of the permeate are noted. This corresponds to the liquid entry pressure or wetted pressure of the membranes.

3. Results and Discussions

3.1 Porosity measurement

The porosity values for the membranes for different coagulation bath conditions were indicated in Fig. 2. From the Figure, it is seen clearly that the porosity value for the membrane MB5 seems higher compared with the other membranes which were immersed in various coagulation bath conditions. This attributes that the coagulation bath conditions that affects the phenomenon of phase inversion and therefore the pores are formed. This may be because of the altered interactions between the polymer of the membrane and the medium of coagulation [16].
3.2 Contact angle measurement
The contact angle measurement for different coagulation bath conditions is shown in Fig. 4. The membrane MB1 shows lesser water wettability than other membranes. The contact angle of the membrane which is immersed in 100 % n-butanol is higher and considered to be more hydrophobic as compared with the other membrane MB2 to MB4. This also corresponds to the surface porosity of the membranes, where it is significantly higher [17]. The membrane MB5 displayed lower porosity, but greater absorption of water. The contact angle measurements may also illustrate this inference. The contact angle measurement is depicted in Fig. 5.

3.3 Permeate flux and Liquid entry pressure measurement
The permeate flux measurement was studied for the membranes. The flux was found to increase in the membrane MB5 compared to other membranes from MB1-MB4. This is due the higher pore formation and good hydrophobicity. The highest permeate flux for MB1 was 2016 L/m²h and it is significantly reduced for MB5 which is 4.8 L/m²h. This finding shows that the permeability is closely related to the coagulation bath pore formation [16].
The liquid entry pressure increases for the membrane M1 was 0.3 kg/cm², as it results in less wettability compared to the other membranes M2, M3, M4, M4 which is around 0.2 to 0.1 kg/cm². This attributes to the higher hydrophobic behaviour.

4. Conclusion:

In this paper, Polyvinylidene fluoride (PVDF) membranes were fabricated using phase inversion technique (immersion precipitation) with dual coagulation bath conditions, that is once it is immerse in (n-butanol – water) bath and it is then rinsed in second bath (water). The contact angle of the synthesised membranes increased with increasing percentage of n-butanol signifying the hydrophobic nature of the membranes. On varying ratios of n-butanol, the porosity also increased which also corresponds to the contact angle. The permeate flux which significantly high for the higher ratio n-butanol as well as the liquid entry pressure. From our experiments, we have inferred that when the coagulation bath conditions can act an important role in defining the membrane characteristics and hydrophobicity. Therefore the membranes can be tailored for the applications of membrane distillation.
References

[1] M. Kummu, J.H.A. Guillaume, H. De Moel, S. Eisner, M. Flörke, M. Porkka, S. Siebert, T.I.E. Veldkamp, P.J. Ward, The world’s road to water scarcity: Shortage and stress in the 20th century and pathways towards sustainability, Scientific Reports. 6 (2016) 1–16. https://doi.org/10.1038/srep38495.

[2] P. Termpiyakul, R. Jiraratananon, S. Srisurichan, Heat and mass transfer characteristics of a direct contact membrane distillation process for desalination, Desalination. 177 (2005) 133–141. https://doi.org/10.1016/j.desal.2004.11.019.

[3] D. Qu, J. Wang, B. Fan, Z. Luan, D. Hou, Study on concentrating primary reverse osmosis retentate by direct contact membrane distillation, Desalination. 247 (2009) 540–550. https://doi.org/10.1016/j.desal.2008.08.004.

[4] M.S. El-Bourawi, Z. Ding, R. Ma, M. Khayet, A framework for better understanding membrane distillation separation process, Journal of Membrane Science. 285 (2006) 4–29. https://doi.org/10.1016/j.memsci.2006.08.002.

[5] A. Alkhudhiri, N. Hilal, Membrane distillation-Principles, applications, configurations, design, and implementation, Elsevier Inc., 2018. https://doi.org/10.1016/B978-0-12-815818-0.00003-5.

[6] M. Bhadra, S. Roy, S. Mitra, Flux enhancement in direct contact membrane distillation by implementing carbon nanotube immobilized PTFE membrane, Separation and Purification Technology. 161 (2016) 136–143. https://doi.org/10.1016/j.seppur.2016.01.046.

[7] K.W. Lawson, D.R. Lloyd, Membrane distillation, 124 (1997) 1–25.

[8] A.A. Kiss, O.M. Kattan Readi, An industrial perspective on membrane distillation processes, Journal of Chemical Technology and Biotechnology. 93 (2018) 2047–2055. https://doi.org/10.1002/jctb.5674.

[9] E. Curcio, E. Drioli, Membrane distillation and related operations - A review, Separation and Purification Reviews. 34 (2005) 35–86. https://doi.org/10.1081/SPM-200054951.

[10] J. Wang, B. Fan, Z. Luan, D. Qu, X. Peng, D. Hou, Integration of direct contact membrane distillation and recirculating cooling water system for pure water production, Journal of Cleaner Production. 16 (2008) 1847–1855. https://doi.org/10.1016/j.jclepro.2007.12.004.

[11] H.C. Duong, P. Cooper, B. Nelemans, T.Y. Cath, L.D. Nghiem, Optimising thermal efficiency of direct contact membrane distillation by brine recycling for small-scale seawater desalination, Desalination. 374 (2015) 1–9. https://doi.org/10.1016/j.desal.2015.07.009.

[12] B.B. Ashoor, S. Mansour, A. Giwa, V. Dufour, S.W. Hasan, Principles and applications of direct contact membrane distillation (DCMD): A comprehensive review, Desalination. 398 (2016) 222–246. https://doi.org/10.1016/j.desal.2016.07.043.

[13] Q. Sun, Z. Yang, C. Hu, C. Li, G. Yan, Z. Wang, Facile preparation of superhydrophobic PVDF microporous membranes with excellent anti-fouling ability for vacuum membrane distillation, Journal of Membrane Science. 605 (2020) 1–13. https://doi.org/10.1016/j.memsci.2020.118106.

[14] A. Politano, G. Di Profio, E. Fontananova, V. Sanna, A. Cupolillo, E. Curcio, Overcoming temperature polarization in membrane distillation by thermoplasmonic effects activated by Ag nanofilms in polymeric membranes, Desalination. (2019) 192–199. https://doi.org/10.1016/j.desal.2018.03.006.

[15] N.M. Mokhtar, W.J. Lau, B.C. Ng, A.F. Ismail, D. Veerasamy, Preparation and characterization of PVDF membranes incorporated with different additives for dyeing solution treatment using membrane distillation, Desalination and Water Treatment. 56 (2015) 1999–2012. https://doi.org/10.1007/19443994.2014.959063.

[16] M.B. Thürmer, P. Poletto, M. Marcolin, J. Duarte, M. Zeni, Effect of non-solvents used in the coagulation bath on morphology of PVDF membranes, Materials Research. 15 (2012) 884–890. https://doi.org/10.1590/S1516-1439201200500115.

[17] Q. Li, Z.L. Xu, M. Liu, Preparation and characterization of PVDF microporous membrane with highly hydrophobic surface, Polymers for Advanced Technologies. 22 (2011) 520–531. https://doi.org/10.1002/pat.1549.