International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249-8958 (Online), Volume-8 Issue-6, August 2019

Theoretical and Experimental Desalination Using Ultrasound Assisted PVDF Membrane in Direct Contact Membrane Distillation

R. P. Birmod, S. D. Dawande

Abstract: ***Desalination by the direct contact membrane distillation (DCMD) for prepared saline water and Ambazari lake water sample was investigated. The self-prepared ultrasound assisted polyvinylidene fluoride (PVDF) membrane by wet phase inversion method exhibited effects on membrane contact angle, pore size, and porosity and investigated performance of DCMD. Membrane properties are characterized and employed in theoretical model with assumptions for water vapor transport in the transition region. It is observed that similar pattern obtained for permeate flux from experimental results and simulated results for transition region. Effects of operating parameter on permeate flux also simulated and compared with experimental data. For this work mathematical models developed and* simulated in Polymath. *PVDF membrane exhibited its characteristics like contact angle, pore size and flux enhancement may be due to ultrasound assisted polymer solution preparation for membrane casting.***

Index Terms: desalination, hydrophobic membrane, PVDF, membrane distillation, ultrasonication

I. INTRODUCTION

About 70% portion of the Earth's is covered with 97.5 % salt water and remaining in glaciers form water. From whole water present on Earth's surface only 0.3% can be useful for human activity. Water plays vital role in any countries economic development [2]. But agricultural and industrial development of many developing countries causes 70 to 80% water pollution [3]. India is second largest populated country after China contributing 20 % of world population. Population growth of India demands nutritional food along with good quality drinking water, which needs more water. This leads India towards disaster shortly. All Indian water bodies within and near population centers are now grossly polluted with organic and hazardous pollutants released from domestic, industries and natural sources. Other than domestic sewage and industrial wastewater, there is another factor effects on water quality depletion; large number of idol immersion in water bodies due to use of heavy metals during idol sculpturing in the form of paints causes increase of heavy metal level than desirable level. In the membrane separation process membrane plays vital role; to meet demand of membrane characteristics, preparation and application of hydrophobic membrane have become a recent trend in membrane science [4-6]. The hydrophobic characteristic of the membrane is very important for membrane distillation; membrane with low hydrophobicity enhances membrane pore wetting so reduces rejection rate and permeate flux [7]. PVDF membrane came into focous due to excellent chemical and mechanical properties [8]. However, membrane distillation (MD) is not fully accepted at industrial level. MD has different configurations; DCMD is commonly used MD configuration considered in this study. MD works on basic principle of transportation of water vapor from hot side fluid to cold side fluid of membrane due to vapor pressure difference on two sides of membrane. So many attempts have been observed in literature based on three regimes during membrane distillation. In this work we prepared novel ultrasound assisted hydrophobic PVDF membrane with phase inversion method and transition model used to check and correlate experimental and simulated data from model. Numerical iterative technique has been used to solve the set of nonlinear equations of flat sheet DCMD process for desalination. Validity of model is evaluated by comparing with obtained experimental results.

II. MODEL DESCRIPTION

D is a nonisothermal thermally driven process in which vapor molecules transfers from feed solution i.e. hot solution to permeate side, where cold liquid or gas may present to condense vapor molecules transferred through microporous hydrophobic membrane. DCMD represents complex heat transfer mechanism due to simultaneous heat transfer and mass transfer. Due to simultaneous heat transfer and mass transfer; mass transfer shows effect on heat transfer coefficient and its flux in feed and permeate side.

Due to simple configuration of DCMD, most of the modeling approach for MD process has been shown towards DCMD. Whatever models developed till now days depends on measuring the resistance of mass and heat transfer in the MD process. Heat balance is applied to predict membrane interface surface temperature in DCMD.

Revised Manuscript Received on August 30, 2019.

* Correspondence Author

Mr. Ramesh P Birmod*, Department of Chemical Engineering, Laxminarayan Institute of Technology, RTMNU, Nagpur, email id: rbirmod408@gmail.com

Dr. Shrikant D. Dawande, Department of Chemical Engineering, Laxminarayan Institute of Technology, RTMNU, Nagpur, email id: sddawande@gmail.com

After evaporation of water molecule in water vapor from feed solution transfers through membrane pores by mass transfer mechanisms; Knudsen diffusion, Poiseuille flow, molecular diffusion, transition flow and surface diffusion in DCMD.

When there is frequent collision between vapor molecules and membrane pore wall, Knudsen flow occurs and Poisseuille flow occurs, when collision takes place between two water vapor molecules. In molecular diffusion, collision between two water vapor molecules as well as between water vapor molecule and membrane pore wall occurs.

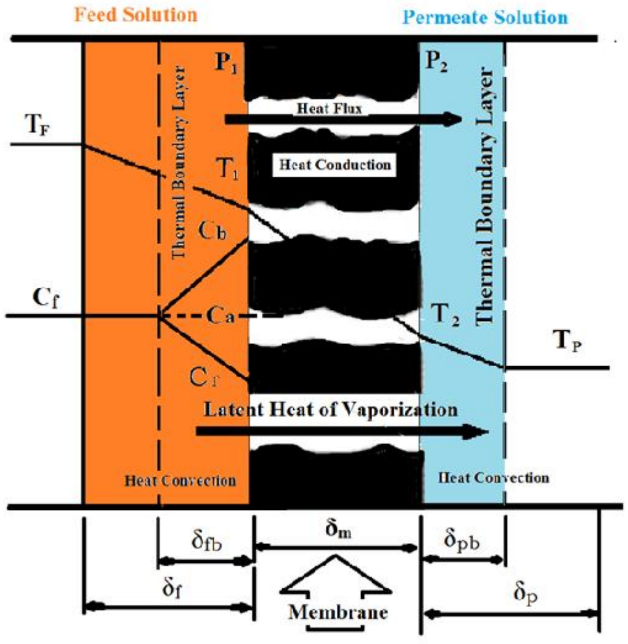

Fig 1 Heat and Mass transfer mechanism in DCMD

Fig. 1 shows the heat and mass transfer mechanism in DCMD.In Fig. 1, T_f and T_1 are the feed side inlet and membrane temperature, and T_2 and T_p are the cold side membrane and Permeate side temperature respectively. P_1 and P_2 are the vapour pressure on the feed and permeate side of the membrane. Due to temperature gradient, when evaporated water vapor travels from feed side (hot solution) to permeate side (cold solution) of membrane with amount of energy which transferred to permeate side during the condensation. The thermal boundary layer developed near the interface of the membrane due to combine effect of sensible heat; energy transferred through membrane matrix itself due to condensation and heat due to evaporation of water vapors, leads to reduction of the transmembrane flux.

$$J = C_m(P_1 - P_2) \qquad (1)$$

Where C_m is the membrane coefficient, J is the permeate flux, and P_1 and P_2 can be calculated from the Antoine equation.

In the DCMD process the feed solution is in direct contact with the membrane and hence there is a boundary layer formation between the feed side solution and membrane interface. As the feed approaches the feed side membrane interface, its temperature drops from T_f to T_1 in this region. The feed heat transfer Q_f equals to the product of film heat transfer coefficient and the temperature difference across the feed side boundary layer, which is calculated as below:

$$h_f(T_f - T_1) = Q_f \qquad (2)$$

The permeate heat transfer Q_p is as below:

$$h_p(T_2 - T_p) = Q_p \qquad (3)$$

Evaporated water vapor molecules energy is enough to transfer through membrane pores to cold side of membrane. During this process heat transfer takes place in two way; one is convection heat transfer from water vapor in feed and conduction heat transfer through membrane pores. So, the heat transfer across the hydrophobic membrane can be represented as:

$$\frac{k_m}{\delta}(T_1 - T_2) + J\Delta H_v = Q_m \qquad (4)$$

And

$$Km = (1 - \text{porosity})\, K_p + \text{porosityX}K_g \qquad (5)$$

Where K_p is the thermal conductivity of the polymer material and K_g is the thermal conductivity of the air in the pores.

Using Nusselt number approach the values of feed side and permeate side heat transfer coefficient are calculated. In this work the Nusselt number which can be used for this regime is as follows.

$$Nu = 0.097\, Re^{0.73} Pr^{0.13} \qquad (6)$$

After the calculation of Nusselt number and heat transfer coefficients for both side of the membrane, effect of operating parameters on membrane distillation performance studied experimentally and validated with this model.

III. MATERIAL AND EXPERIMENTAL

A. Material

PVDF purchased from Sigma Aldrich® Lot #MKBW6180V of average Mw~180,000 by GPC, average Mn~71,000 properties. To dissolve PVDF, N, N-Dimethyl formamide of Emparta® purity≥99.8% from Merck life science private limited, Vikroli, Mumbai was purchased as a solvent. Distilled water was used as non-solvent for wet phase inversion coagulation bath. De-ionized water, NaCl/water and Ambazari lake water have been taken as feed solution. Ambazari lake water sample contains heavy metals fluoride; 1.9091ml/l, lead; 0.0602ml/l, and chromium; 0.05ml/l.

B. Preparation of casting solution

Desired amount of PVDF pellets was poured into the conical flask containing solvent and sonicated for 1 hour at 80 ^{0}C to get homogeneous solution. To maintain the solution temperature bath tub is used. After getting homogeneous solution, the prepared solution kept steady for 24 hours to remove air bubbles. The ratio of pure PVDF and solvent was 15: 85.

C. Membrane preparation

After preparation of PVDF hydrophobic membrane solutions, polypropylene (PP) nonwoven fabric was attached on flat, clean and smooth glass surface. Fabric tightened with tape from both sides and prepared casting solution was poured on attached PP fabric and casted with membrane casting knife (Fig. 1). PP nonwoven fabric of 60 GSM was used to get good mechanical strength. After 15 second exposure to open air the semi-prepared membrane was immersed into the coagulation bath of non-solvent distilled water at 35°C for 30 mins and taken out from distilled water for 15 sec and re-immersed into the coagulation bath and kept as it is for 24 hrs. The completely prepared membrane was water rinsed to remove the residual of solvent then put into the vacuum woven for 30 mins for drying purpose at 60°C. Finally, the dry membrane was preserved in zip-lock bag for subsequent measurement and application.

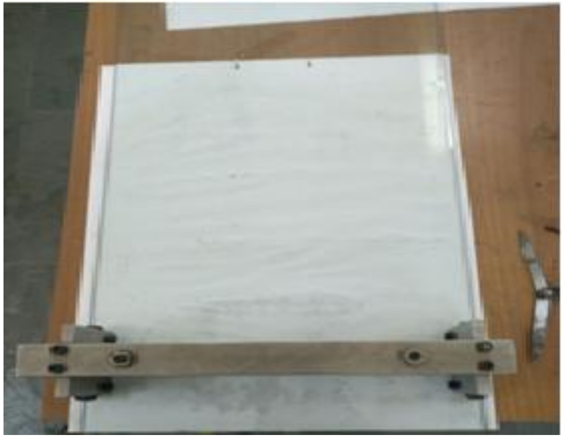

Fig. 2 Membrane casting using casting knife on smooth surface glass

D. *Membrane characterization*

1) Morphology

The field emission scanning electron microscopy (FESEM) was used for surface morphologies of the fabricated membrane. Various image samples were taken of different Au/Pd lightly coated membrane samples. The FESEM imaging was carried out at an accelerating voltage of 20 kV. Figure 4 shows FESEM of ultrasound assisted hydrophobic PVDF membrane. The fabricated membrane and thickness of support was measured using micrometer.

2) Contact angle

The sessile drop method using an optical subsystem integrated with image-processing software was used to measure membrane contact angle (CA). Hydrophobic membrane samples were placed on a platform, and water droplets of 5-8 µL were dropped carefully on the membrane surface and captured the image of the droplet after 60 seconds using real time camera, and the CA was measured. Five images were taken at different places of same membrane sample and the average value is considered as final contact angle.

3) Porosity

The membrane porosity was measured via a gravimetric test. In the gravimetric test measured weight of dry membrane sample of 2 cm × 2 cm and were immersed in ethanol. After immersion, weight of Wetted membrane sample measured. Porosity has been determined using dry and wetted membrane sample weight using following equation [9]:

$$Porosity = \frac{\frac{W_h - W_d}{\rho_w}}{\frac{W_d}{\rho_{PVDF}} + \frac{W_h - W_d}{\rho_w}} \qquad (7)$$

Where,

w_h is the weight of the wet membrane
w_d is the weight of the dry membrane
ρ_w is the kerosene density
ρ_{PVDF} is the polymer density (1.72 g cm-3).

The liquid entry pressure of water (LEPw) and pore size were measured for pure PVDF hydrophobic membrane. The membrane prepared by wet phase inversion was placed in a dead end cell and the cell was filled up with DI water. Pressure was applied by compressed nitrogen in the cell and noted when the first drop of water came from the cell. LEPw was measured thrice using three different membrane sample made from same composition and average result noted as final LEPw.

III. EXPERIMENTATION

Performance study of the altrasound assisted hydrophobic PVDF membrane was investigated with a DCMD setup as shown below. The effective area of membrane module in DCMD was 90cm^2. The feed and permeate channels were used as per module design at both side of membrane module. Feed temperatures varied from 40 to 90 ^{0}C with 10 ^{0}C intervals, and permeate temperature varied from 20 to 30 ^{0}C with 5 ^{0}C intervals. Permeate flow rate was fixed to 9ml/Sec and feed flow rate was ranging from 6, 7, 8 and 9ml/Sec. feed and permeate temperature measured by digital temperature indicators and flow was controlled by flow meters at both feed and permeate side of membrane module. While deionized water was used on the permeate side throughout all the tests, and three different feed solutions were used; DI water, salt water with 6 to 10% concentration, and Ambazari lake water sample, Fig. 2.5 shows the schematic setup of the experiment. Using permeate solution fluxes were determined by runs that lasted for time interval 1h, 2h and 3h. Three evaluation of each condition were exhibited. Variations in fluxes w.r.t. salt concentration in NaCl/water sample have been exhibited with the membrane.

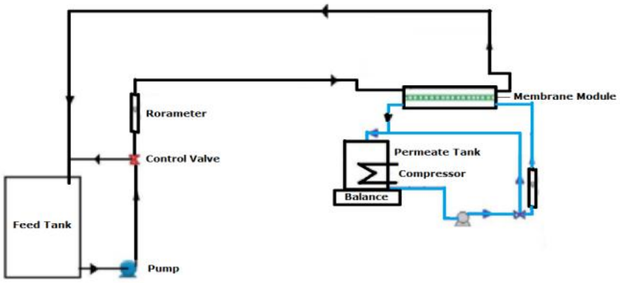

Fig. 3 schematic diagram of DCMD setup

IV. RESULTS AND DISCUSSION

A. Membrane morphology

The precipitation and crystallization will takes place during phase inversion. There is no effect of intermolecular attraction and repulsion on polymer chains. PVDF is a semi-crystalline polymer and it may precipitate either by liquid–liquid demixing and forms cellular morphology, and/or due to crystallization forms particulate-type structures during the phase inversion to produce membranes.

The morphology of the membrane surface is shown in Fig. 4. The FESEM analysis from fig. 4 shows typical microporous surface morphology of pure ultra sound assisted hydrophobic PVDF membrane. The surface of membrane prepared from the 15 wt% PVDF solution. This membrane shows clear void formation of size about 0.5 to 1 µm. Due to diffusion of solvent and non-solvent in polymer solution creates the micro-voids of less number and large size or large number and smaller size depending upon polymer concentration at the membrane surface.

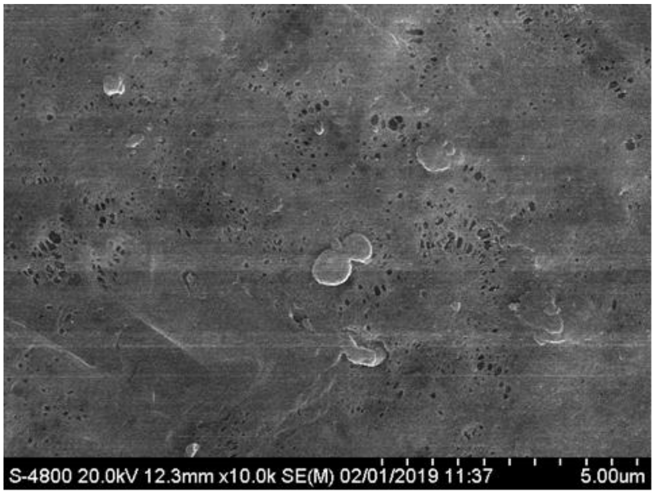

Fig. 4 FESEM image of ultrasound assisted hydrophobic (15%) PVDF membrane

B. Effect of Operating Parameters

The three feed solutions DI water, NaCl-water, and Ambazari lake water were studied The concentration of NaCl-water feed solution was set to 6%, 8%, and 10%. Three different LEPw were measured using three different membrane sample made from same composition and average result noted as final LEPw.

Table 1 Ultra sound assisted PVDF membrane characteristics.

Characteristics	Measures
Thickness	125 µm
Contact Angle	99.5±.56
LEP	199 KPa
Pore Size	0.312 µm
Porosity	75 %

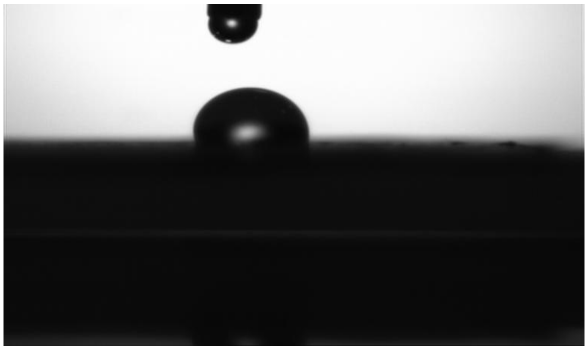

Fig. 5 Contact angle image of ultrasound assisted hydrophobic (15%) PVDF membrane

Feed and permeate solution (DI water) was kept same initially. Permeate temperature, feed and permeate flow rate were constant 20 ^{0}C and 540 ml/min respectively. Effect of feed temperature was investigated on flux experimentally and validated with theoretical model and results shown in figure 6. Optimum feed temperature noted from figure 6 and kept constant to investigate effect of flow rate on flux and results shown in figure 7. Similarly, effect of permeate temperature, permeate flow rate and feed concentration on flux were investigated and noted in figure 7, 8 and figure 8.

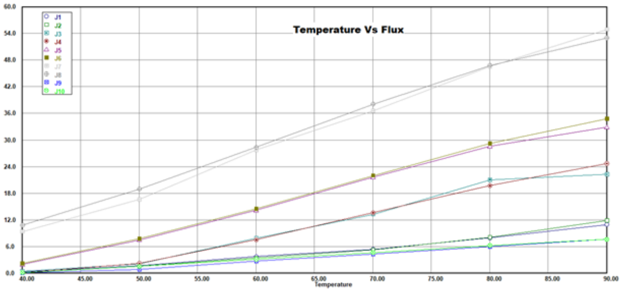

Fig. 6 Effect of feed temperature on flux for DI water, 6%NaCl/Water, 8%NaCl/Water, 10%NaCl/Water and Ambazari Lake water sample

Whereas,

J1, J3, J5, J7, and J9 are permeate fluxs from experimental data for 10gm/l, 8gm/l and 6gm/l NaCl, distilled water and Ambazari lake water sample respectively

J2, J4, J6, J8, and J10 are permeate fluxs from calculated data for 10gm/l, 8gm/l and 6gm/l NaCl, distilled water and Ambazari lake water sample respectively

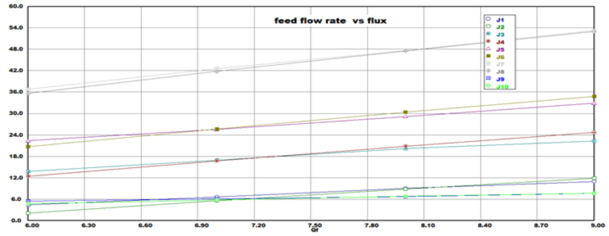

Fig. 7 Effect of feed flow rate on flux for DI water, 6%NaCl/Water, 8%NaCl/Water, 10%NaCl/Water and Ambazari Lake water sample

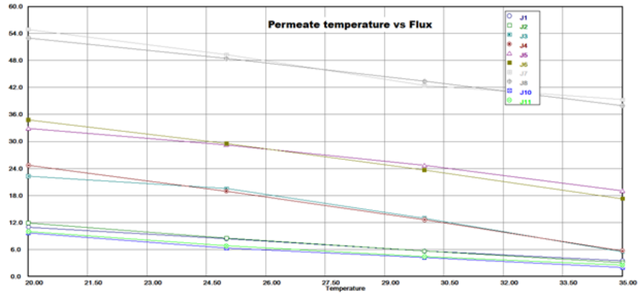

Fig. 8 Effect of permeate temperature on flux for DI water, 6%NaCl/Water, 8%NaCl/Water, 10%NaCl/Water and Ambazari Lake water sample

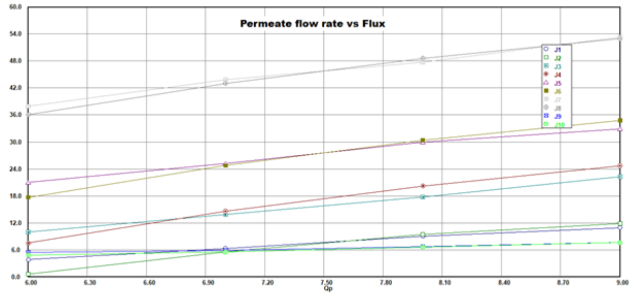

Fig. 9 Effect of permeate flow rate on flux for DI water, 6%NaCl/Water, 8%NaCl/Water, 10%NaCl/Water and Ambazari Lake water sample

When the volumetric flow rate of DI water feed solution was 420 ml/min, and the impact of feed temperature on the flux was investigated. The results were noted that flux increased with increasing feed temperature as shown in Figure 5. Figure 6 showed that influence of volumetric feed flow rate on flux has been investigated and noted that flux increased with increasing volumetric feed flow rate.

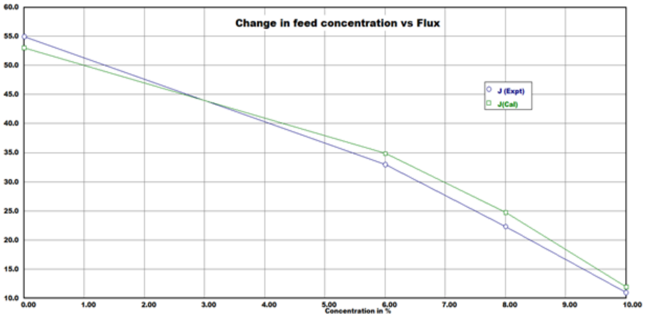

Fig. 10 Effect of feed concentration on flux for salt water

On other hand figure 7 and 8 indicates flux decreases with increasing feed solution concentration and permeate temperature as temperature gradient between feed and permeate solution so driving force affected with increase in feed solution concentration and permeate temperature.

1. Effect of feed and permeate temperature

Figure 6 showed that the influence of feed side temperature on flux, when the feed solutions were DI water, salt water of concentration 6gm/l, 8gm/l and 10gm/l, and Ambazari lake water, permeate temperature was 20 ^{0}C, the feed and permeate solution volumetric flow rate were 540ml/min. figure 6 indicates flux increases with feed solution temperature but it varied with feed solution to solution. The effect of concentration polarization and temperature polarization observed in the variation of flux with feed solution. Highest flux noted with DI water feed solution, then flux decreased to 20% with 10gm/l salt water feed solution and the lowest flux has been noted with Ambazari lake water sample that7.6667kg/m^{2}.h, 13.9394% of DI water and salt water. It may be flux decreased due to salt concentration in DI water. Deposition of NaCl ions on membrane surface is one of the reason to decrease the permeate flux. Various compositions in Ambazari lake water sample which contains TDS and various heavy metals and its deposition on membrane surface influenced to highest flux reduction than other sample.

2. Effect of feed and permeate solution flow rate

Figure 7 and 9 showed that the flux variation with volumetric flow rate of feed solution ranging from 6ml/sec to 9ml/sec, when feed solution temperature was 90 ^{0}C, the permeate temperature was 20 ^{0}C, concentration of salt water was varied from 6 to 10gm/l and permeate volumetric flow rate was varied from 6ml/sec to 9ml/sec.

From the figure 7 and 9, it indicates that flux increased with the increase of volumetric flow rate with all three feed solutions, but the flux curve relatively flat as compare to theoretical model to change in feed temperature; it showed that the influence of volumetric flow rate of feed solution on flux was small. Increase or decrease in feed and permeate flow rate slightly disturb the boundary layer thickness of temperature and concentration in DCMD, because thermal efficiency and heat transfer by conduction were hardly influenced by the feed velocity.

3. Effect of feed solution concentration and permeate temperature

The temperature of the feed solution was 90 ^{0}C, the feed and permeate flow rate was 9ml/sec, permeate temperature was 20 ^{0}C; the influence of the concentration of salt in feed solution on the flux was studied.

Figure 10 shows the increase in concentration of salt in feed solution from 6gm/l to 10gm/l with 2gm intervals, and increase in permeate temperature from 20 ^{0}C to 35 ^{0}C with 5 ^{0}C intervals permeate flux decreased.

Remarkable effect on feed side partial vapor pressure has been noted due to change in feed solution concentration, this vapor pressure difference indicates the greater the feed concentration, the smaller the water vapor partial pressure of feed solution which decreased driving force.

Increase in permeate side temperature was affected temperature gradient of feed and permeate side solution, so it also decreased flux by increasing permeate temperature (Fig 8); it is the effect of temperature polarization. Due to concentration polarization at membrane separation interface flux curve decreased when the concentration of the salt in feed solution increased.

V. CONCLUSION

In this paper self-made ultrasound assisted PVDF flat sheet hydrophobic porous membrane on non-woven PP sheet was used to carry out experimental research on the process of direct contact membrane distillation, focused on the effect of operating parameters like feed and permeate temperature, feed and permeate flow rate, concentration of salt in feed solution on the permeate flux. Use of sonication helped to reduce dope preparation time from 24h to 2h. The results showed that the efficiency of the DCMD process can be increased by increasing the feed solution temperature, volumetric flow rate of the feed solution. Increase in Feed temperature and flow rate was vapor pressure difference across the membrane which enhanced the driving force of membrane distillation. During MD study there are some considerations such as characteristics of feed solution, the material of the membrane and type of membrane module. In present study three types of feed solutions were used and these three feed solution were of different characteristics so, effect of feed solution characteristics has been noted on permeate flux. Membrane material also one of the important factor which effects on permeate flux. Maximum flux was noted for three different feed. It was found that the maximum flux reached 7.67kg/m^2.h for Ambazari lake water sample and validated with theoretical model, which indicates broad aspects of so the membrane distillation for the desalination and waste water treatment.

REFERENCES

1. Karagiannis, C. Ioannis, Soldatos, G. Petros, “Water desalination cost literature: review and assessment,” Desalination, vol. 223, 2008, pp. 448–456.
2. S. Judd, B. Jefferson, “Membranes for Industrial Wastewater Recovery and Re-use‖ Elsevier Advanced Technology,” The Boulevard, Langford Lane, Kidlington, Oxford OX5 lGB, UK, 2003, ISBN 1-8561 7-389-5.
3. D. H. Furukawa, "A Review of Seawater Reverse Osmosis." IDA Desalination Seminar, Cairo, Egypt, September, 1997.
4. E. Drioli, G. Di Profio, E. Curcio, “Progress in membrane crystallization,” Current opinion in chemical engineering, vol. 1, 2012, pp. 178-182.
5. E. Drioli, A. Ali, F. Macedonio, “Membrane distillation: Recent developments and perspectives,” Desalination, vol. 356, 2015, pp. 56-84.
6. C. Zambra, J. Romero, L. Pino, A. Saavedra, J. Sanchez, “Concentration of cranberry juice by osmotic distillation process,” Journal of food engineering, vol. 144, 2015, pp. 58-65.
7. S. Mosadegh-Sedghi, D. Rodrigue, J. Brisson, M. C. Iliuta, “Wetting phenomenon in membrane contactors-Causes and prevention,” Journal of membrane science, vol. 452, 2014 pp. 332-353.
8. L. Guo, Y. Liu, C. Zhang, J. Chen, “Preparation of PVDF-based polymer inclusion membrane using ionic liquid plasticizer and Cyphos IL 104 carrier for Cr (VI) transport,” Journal of membrane science, vol. 372, 2011, pp. 314-321.
9. S. Santoro, I. M. Vidorreta, V. Sebastian, A. Moro, I. M. Coelhoso, C. A. M. Portugal, J. C. Lima, G. Desiderio, G. Lombardo, E. Drioli, R. Mallada, J. G. Crespo, A. Criscuoli, A. Figoli, “A non-invasive optical method for mapping temperature polarization in direct contact membrane distillation,” Journal of Membrane Science, vol. 536, 2017, pp. 156-166.
10. Theoretical and experimental desalination using ultrasound assisted PVDF membrane in direct contact membrane distillation

AUTHORS PROFILE

Mr. Ramesh P. Birmod, M.Tech in Chemical Enginnering (IIT Bombay) and pursuing PhD at Rashtrasant Tukadaji Maharaj Nagpur University, Nagpur. He is working as an Assistant Professor at Laxminarayan Institute of Technology, R. T. M. N. University, Nagpur and has more than eight years teaching experience. He has ranked AIR 230 in GATE 2008. He has published two international research papers and one national research paper.

Dr. Shrikant D. Dawande PhD, ex-Associate Professor at Laxminarayan Institute of Technology, R. T. M. N. University, Nagpur. He has teaching and research experience of more than 30 years and published several national and international research papers in reputed journals. He has produced 5 PhD students and several M.Tech students. He has books related to chemical engineering on his name.