Separation of Hydrocarbons from Refinery Effluents Using PTFE Membrane by Membrane Distillation

Jafar hamidzadeh*, Mouzafar isobauve

* Department of chemistry, Faculty of basic sciences, Islamic azad university, Gorgan branch, Gorgan, Iran
Jafar.hamidzadeh@yahoo.com, Cordin@index.ru

Abstract: Separation is one of the most important steps in a chemical process so that a major part of energyis used for separation, concentration and purification. Fro the same reason, considerable work has been done to improve traditional processes and develop the savings technologies in regarding energy usage. Because of complexity and high cost of current processes, membrane separation technology has been recently examined as a good alternative. Membrane distillation (MD) has been taken into consideration as a new membrane distillation process enables to separate particles as tiny and petite as 0.1-7nm This process functions in low temperature between 30-90ºC that needs little source of energy besides high economic benefit. In membrane distillation (MD) process a hydrophobic membrane is utilized in contact with an input food solution. The base is on vapor-liquid equilibrium. In this paper, while describing membrane distillation, the parameters influencing MD as well as the laboratory system used were studied.
[hamidzadeh J, Isobauve M. **Separation of Hydrocarbons from Refinery Effluents Using PTFE Membrane by Membrane Distillation**. *Life Sci J* 2013;10(6s):178-184] (ISSN:1097-8135). http://www.lifesciencesite.com. 28

Keywords: Membrane distillation nanometer particles, Vapor - liquid equilibrium, Flexibility, Azeotrope solution

Introduction:

Membrane distillation (MD) is a new process that as a separation process with low cost and high efficiency is considered nowadays an appropriate alternative for conventional distillation process due to its low selectivity and high operating costs. MD is a thermally driven separation process, which was known in 1960s. A porous hydrophobic membrane is used in MD. The used membrane in MD is made of a material such as polyvinyl fluoride (PTFE). Due to hydrophobic effect, water cannot wet this membrane spontaneously. The polymer also has characteristics such as high thermal stability against heat, high chemical resistance against hydrocarbons and oxidizing environments, which are used to build this membrane (1, 2). The membrane contains pores 0.3 μm in diameter. Its porosity and thickness are respectively as 80% and 85-95 μm . The process works in temperatures between 30-90 Cº. Due to the low demand for energy in the process, extra energy of other processes as well as earth and solar energies can be used (1). Membrane separation process is taken into consideration because of its proper flexibility and efficiency (6).

2-mechanism of membrane distillation:

The MD process is standing on vapor-liquid equilibrium and penetration of hypobaric membrane. In this process, at first the liquid around warm food is evaporated then vapor passes through membrane and the penetrated vapor is condensated in the other side of membrane (8).

Input food contacts with the membrane in tempreture30-90ºC. Because of discrepancy between vapor pressure in either side of membrane resulting from temperature difference, the vapor penetration takes place from hydrophobic membrane (9). The MD process holds certain advantages including (3 and 4):

- Full and 100% recovery percentage (gross product)
- No need for additives or solvents in the process
- Usable for Azeotrope solution

3. Effective parameters in process of MD

3-1: food temperature

By increasing food temperature, according to Antoine's equation, partial vapor pressure enhances consequently and leads to maximization of diffusion flux (3and 4).

$$(1\ Logp^{sat} = A - \frac{B}{T + C}$$

Where

p^{sat} :vapor pressure (Pa)

T= temperature (k)

C, B, A= component-specific constants

3-2: food concentration:

If the food contains volatile compounds , increased concentration of food makes diffusing flux raises (2 and 3) and if non-volatile compounds it has any increase causes decrease of diffusion flux (9 and 10).

3-3: food pace:

As the food pace raises it makes heat transfer coefficient develops and thickness of the boundary layer reduces which in turn diffusion flux enhances (7).

4: Test system:

In this system a 10Lit food container used.

To have better mixing and adjusting intensity of food flow, a bypass flow after pump outlet inside food tank is predicted. The rate of this flow back significantly influences on food temperature. Pressures were recorded by an aneroid sphygmomanometers.

The food was entered a membrane module to use intersection flow and enhances membrane turbulence. Food temperature also was measured by a mercury thermometer placed into the container. In order to control the food temperature more accurately a thermostat with maximum operating temperature 90ºC was installed.

Since food flow permanently rotates into the system, we presume that the food temperature throughout the system and on membrane surface is equals to the container temperature. The flow intensity was examined via timer method. Consequently, to perform the experiment a PTFE hydrophobic membrane applied.

The samples of flow from membrane were freezed till -30C then collected. The characteristics of used membrane are presented in Table (1).

Table 1: membrane characteristics of PTFE

(μm) Pore size	Porosity	thickness (μm)	material
0.3	80%	85-95	Polytetrafluoroethylene (PTFE)

In obtained wastewater the total amount of hydrocarbon either in the food or in the product was measured using Formacs device. Since the wastewater concentrations are fixed the experiments were carried out in three levels considering temperature, pressure, and flow intensity (pace of food) factors.

5-method and conditions:

The experiments were performed through PTFE membrane and using …. and L9, Taguchi method of experimental design. In this design the experiment of three factors of temperature, pressure, and flow intensity in three different levels (9 different experiment) were assessed.

5-1: temperature (T):

To test the effect of temperature on the system function the temperature was ranged between 25 to 75ºC. For doing prepared wastewater experiments temperature was adjusted at 35, 50 and 70ºC. According to path of flow back to the food tank and the food mixing it was impossible to lessen temperature less than 25ºC. and because of inconsistency in temperature and rapid decline at temperature higher than 80-90ºC as well as evaluating system productivity at average temperatures it was chosen to be 75ºC.

5-2: pressure (p):

Evaluating the effect of pressure, other test factors related to wastewater were kept constant though the pressure was changing from 10 to 80 psi and 40, 60,and 80psi pressures were determined finally.

5-3: intensity of flow (Q):

The experiments are different in 10-50ml/s food flow intensity which performed in three 20,30, and 40ml/s levels. In intensities lower than 15ml/s three was no chance of continuous flow and in higher than 50ml/s it leads to experimental failure.

Designing of performed experiments are presented in following table.

Table 2: planning experiments to perform on wastewater

(ml/s) Flow intensity	(^{0}C) temperature	(psi) pressure	Test no.
20	35	40	1
30	50	40	2
40	75	40	3
30	35	60	4
40	50	60	5
20	75	60	6
40	35	80	7
20	50	80	8
30	75	80	9

In prepared sample wastewater some hydrocarbons were found that contribute to decrease of surface tension of samples and consequently cause to pressure resistance fall in hydrophobic membrane. This in turn will make the food to pass from membrane in lesser pressure differences.

As a result of such impurities into the wastewater sample the vapor pressure decreases and the available flux at 25C temperature and 80psi are insufficient for required analyzes. As experiments prolong transfer route of the product is blocked because of freezing. To improve the conditions, the low temperature 25ºC was maximized up to 35ºC.

6-Experiments results:

In Table (3) the obtained results for performed experiments for the rate of flux and hydrocarbons are reported using PTFE membrane.

Table 3: results from sample wastewater obtained from PTFE membrane

(mg/l) hydrocarbon		(kg/m^2h) Product flux		Intensity of flow	Temperature	pressure	o.
Series2	1 series	2 series	1 series				
16.2	18.5	3.962	4.245	20	35	40	1
23.6	26.7	8.415	7.643	30	50	40	2
50.7	47.8	13.915	12.612	40	75	40	3
12.9	16.1	3.843	4.382	30	35	60	4
21	23.1	7.428	6.975	40	50	60	5
35.3	37.4	7.283	7.645	20	75	60	6
9.6	13.3	3.722	4.735	40	35	80	7
12.2	10.9	2.531	2.012	20	50	80	8
34.8	35.7	7.597	8.855	30	75	80	9

The product flux for membrane PTFE in time span 210min will decrease due to clogging of the membrane pores in a way that in 210min we experience the least product flux. According to diagrams in Fig. (2) Temperature puts the highest impact on the product flux related to vapor pressure behavior based on temperature.

$$SS = \sum_{i=1}^{K_A} \left(\frac{A_i}{n A_i} \right)^2 - \frac{T^2}{N}$$

SS= sum of squares for each parameter
Ai= sum of observations in
level i factor
K_A: number of parameter A levels
T=sum of observations
N= number of observation
n_{Ai}= number of observation in level i factor A [Q]
P= percentage of each parameter portion

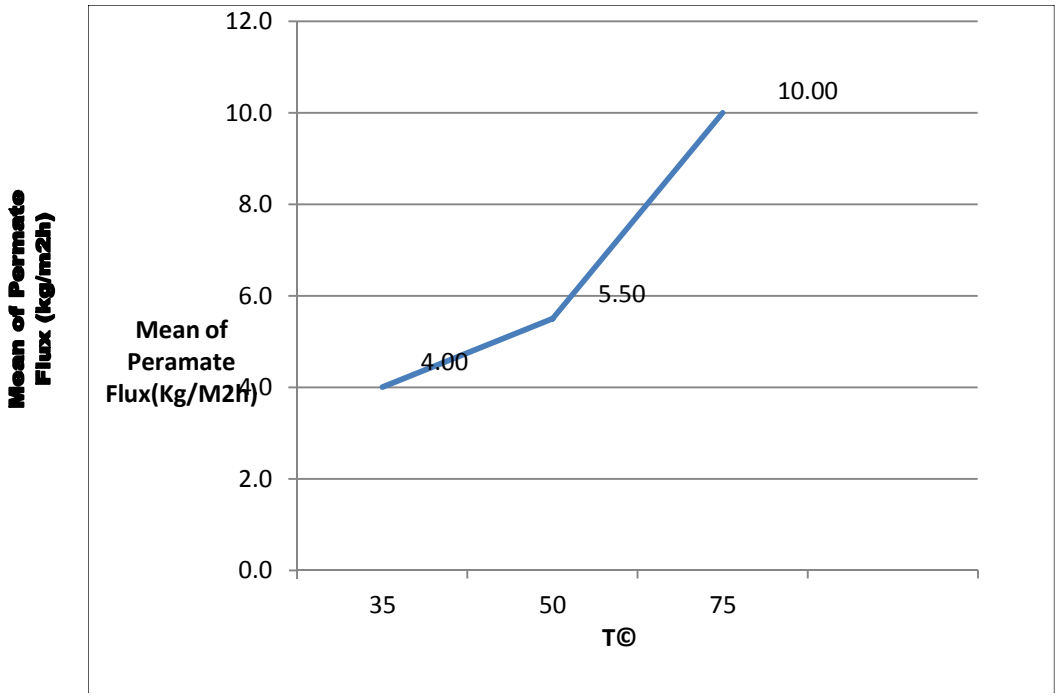
Table (4): obtained results for mean of peramate flux

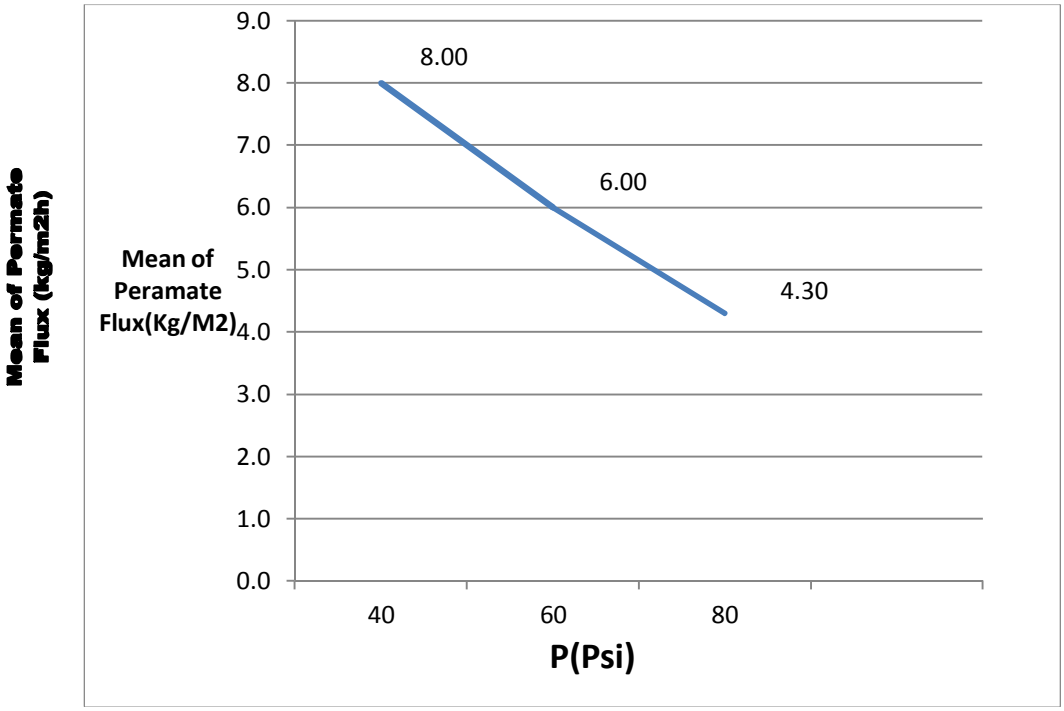
P(%)	SS	factor
25.58	43.72	pressure
57.07	96.22	tempreture
20.05	39.77	Intensity of flow

According to diagrams in Fig.(1) it could be said that all three pressure, temperature and flow intensity influenced the rate mean of peramate flux in the product . This means at pressures greater than this value, its impact on the product flux is less due to concentration polarization effect and reduced membrane repercussion rate.

Table (5): obtained results for level of hydrocarbon

P(%)	SS	factor
14.86	368.19	Pressure
84.7	2345.16	tempreture
3.44	92.21	Intensity of flow


Mean of Permate Flux (kg/m2h)
Mean of Peramate Flux(Kg/M2h)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
10.00
5.50
4.00
35
50
75
T©


Mean of Permate Flux (kg/m2h)
Mean of Peramate Flux(Kg/M2)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.00
6.00
4.30
40
60
80
P(Psi)

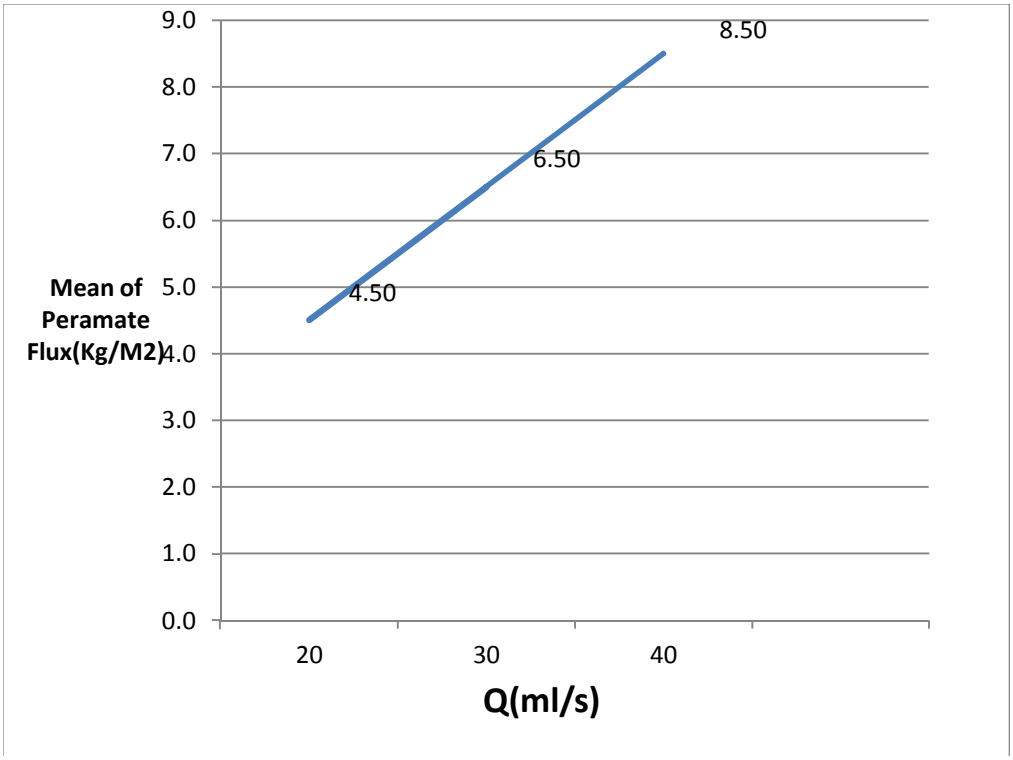
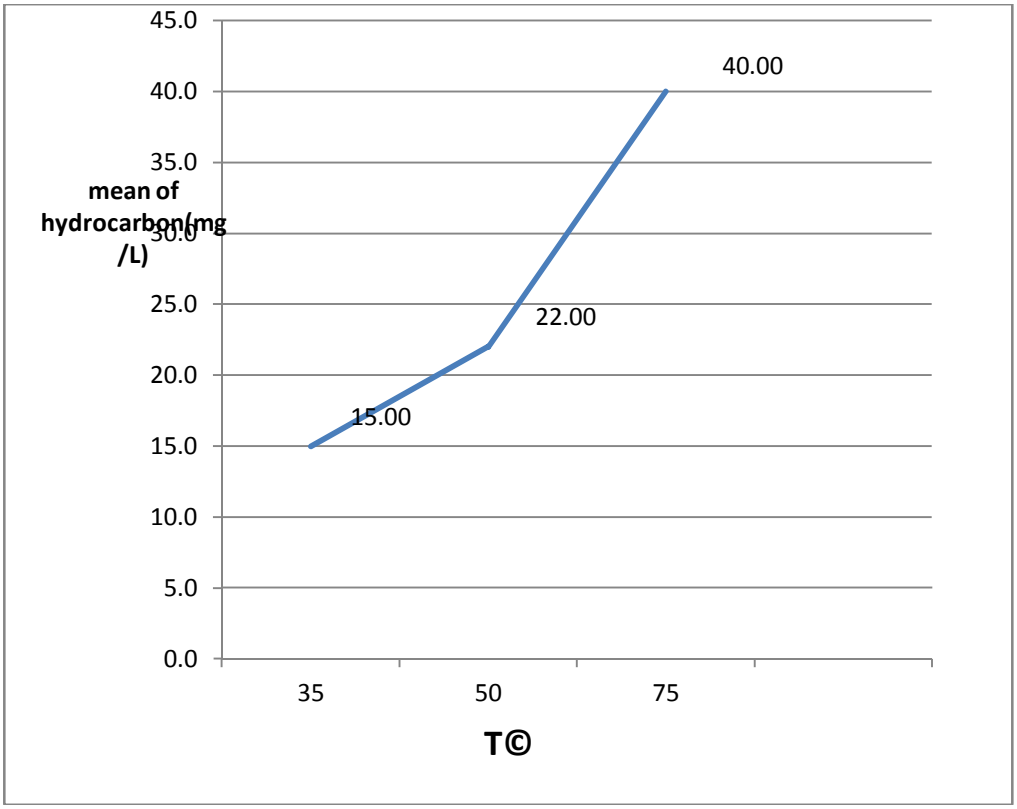
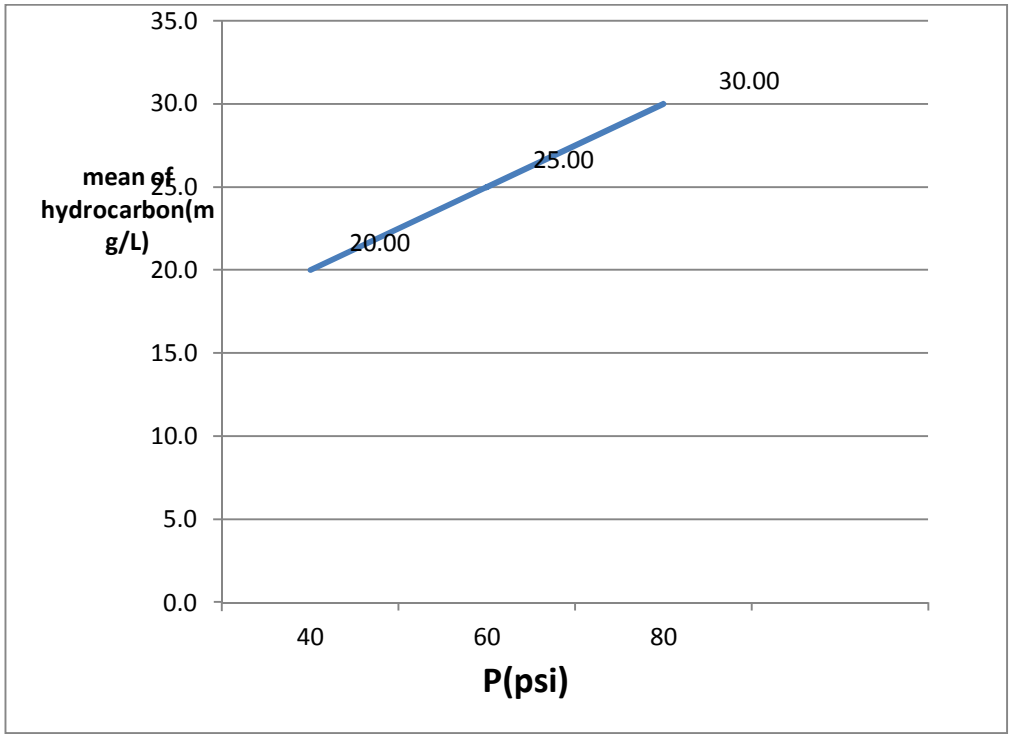


Fig.(1): diagrams related to the effect of each factor on rate of mean of peramate flux using PTFE membrane





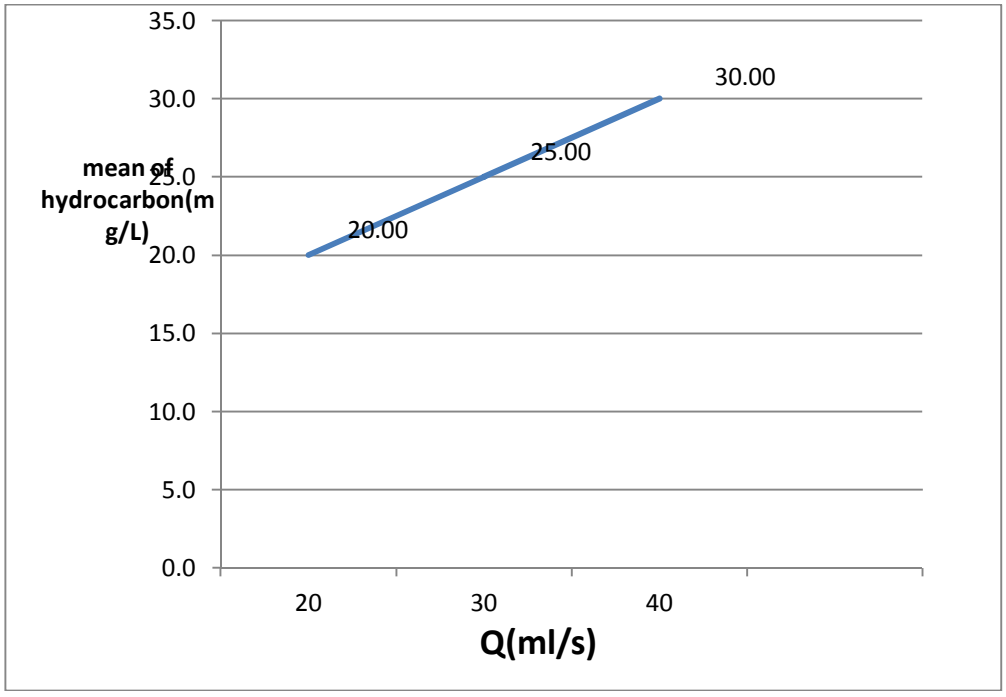


Fig.(2): diagrams related to the effect of each factor on rate of hydrocarbon using PVDF membrane

According to diagrams in Fig.(2) it could be said that all three pressure, temperature and flow intensity influenced the rate of available hydrocarbon in the product . More their amount increase the rate of hydrocarbon enhances more. Also, based on the Table (5) it is possible to say that the temperature has the highest effect on level of hydrocarbon.

7-Conclusion:

1. Factors including temperature, pressure and the flow rate are important in this process so that with increased temperature and flow rate, the penetration flux of the product increases.
2. In the PVDF membrane, the pressure factor affects the flux penetration rate at a certain point, and after that the pressure effect declines.
3. All three factors of temperature, pressure and flow rate influence the product quality, as with increasing temperature, pressure and flow rate, the hydrocarbon values increase in the product.
4. As the temperature increases, the evaporation rate of hydrocarbons increases. The same factor causes the wetting of the membrane surface as an oily layer on the membrane surface.
5. With increased testing time, the product flux reduces due to fouling of the membrane pores.
6. By elongation of the testing time, the diffusion flux rate reduces due to fouling of the membrane pores.

3/17/2013

Reference:

1-J. Wagner, "Membrane Filtration Hand book", 2nd Edition, Revision 2, osmonics, PTFE 8-15, 2001.
2-M. Cooke, C.poole, I.D. Wilson, "Encyclopedia of separation science, Academic press, PTFE. 459-567, 2000.
3-S.P. Nunes, K.V. Peinemann, "Membrane Technology in the chemical industried", wiley, PTFE. 134-139, 2001.
4-M. Cheryan, N. Rajagopalan, "Membrane Processing of oily stereams wastwater treatment and waste reduction." Journal of membrane science, volume 151, PTFE. 13-28, 1998.
5-Mohamad ali. Safari; "Water seporation from petrochemcal waste water by vocuum membrane distillation," 2008.
6- Jalal . BarzinT Majid Esmaili; " Membrane Fouling and Regeneration Methods "17 – 50(2005).
7- Barzin J . and Sadatnia b . (2007) " Theoretical phase diagram calculation and membrane morphology evalution for water/solvent/polyethersulfone systems" , polymer , 48,1620-1631.
8- A.M. alklaibi, NoamLiar ; Transport analysis of air-gap membrane distillation"; Journal of membrane Science 255 (2005).
9- Phattaranawik J, Leiknes T, Pronk W, " Mass transfer studies in flat – sheet membrane contactor with ozonation", Journal of Membrane Science , Volume 247,pp. 153-167,(2005).
10- Siavash Madaeni ; " Membranes and Membrane Processes " 12-60 (2002).