THE STUDY OF MASS TRANSFER COEFFICIENT IN MEMBRANE SEPARATION FOR PRODUCED WATER

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ABSTRACT

In this paper, membrane filtration of produced water is studied in terms of its mass transfer coefficient. This filtration process is incorporated to improve the existing OSPAR method in removing dissolved oil. During membrane filtration, concentration nearer to the membrane is higher than the concentration of bulk solution and thus a concentration profile develops. Studying the mass transfer coefficient (MTC) which drives the concentration difference can help us in understanding the phenomena of fouling in membrane. Two models i.e. combined solution diffusion/film theory model (Murthy and Gupta, 1997) and film theory model are compared and the most suitable model to predict the MTC is selected. From the experimental results, it was found that film theory (FT) model is suitable to calculate MTC for produced water samples in our experimental set-up. The models are found to be suitable only at a certain range of differential pressure.

Keywords: Cross-flow membrane filtration, produced water, mass transfer coefficient.

INTRODUCTION

Produced water is the water that is being extracted from the subsurface during oil and gas production. During early production, the water may be insignificant. However, for old oil well, a sizeable amount of water will be produced (Mondal and Wickramasinghe 2008). It originates from water that is trapped in permeable sedimentary rocks within the well bore. It includes water that has been injected into the formation to maintain reservoir pressure and any chemicals added during the production/treatment processes. Disposal of such waste water can be problematic in environmental terms due to high salinity and oil content.

Produced water needs to be separated from the oil during the production and also before their discharge (Arnold and Stewart, 1999). Currently, most of the oil producing countries has their own regulation for disposal of this water. Most of them use dispersed oil concentration as their monitoring parameter. In oil and gas terms, dispersed oil means oil in produced water which is in the form of small droplets, and may range from sub-microns to hundreds of microns. Large amount of dispersed oil is harmful to the environment, as they can agglomerates together to form a thin film on the surface of the water and prevents oxygen dissolving into the sea thus

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threatening the marine life forms in the ocean (Stephenson, 1992). Another type of oil is termed dissolved oil–such as BETX (benzene, ethyl-benzene, toluene and xylene), NPD (napthalene, phenanthren, dibenzothiophene) and/ or some of the PAHs (polyaromatic hydrocarbons) that are partially soluble and can be present in dissolved form in water.

Several countries adopt the standard of so-called OSPAR to regulate the produced water quality before their discharge. For Shell Global Standard, their dispersed oil limit in produced water disposal is listed in Table 1 below:

Table 1
Shell Global Standard for dispersed oil limit

Shell Global Standard	*Pollutant Parameter*	*Onshore*	*Offshore*
Daily maximum	Oil and grease	40mg/L	70mg/L
Monthly average	Oil and grease	15mg/L	30mg/L

Until now, most of the oil and gas operators are following OSPAR method in monitoring their discharge. However, an issue arises in OSPAR method on monitoring of produced water disposal due to limitation in the instrumental analytical technique used. OSPAR stated a limit in dispersed oil parameter; but with the current analytical method (GC-FID), the total of dissolved oil and dispersed oil are given. Therefore, the readings will be higher than the actual.

With membrane filtration incorporated in the analytical method, membrane could separate both the dispersed and dissolved oil allowing the measurement of dispersed oil to be more accurate. This will increase the efficiency in the work of monitoring the discharge limits of dispersed oil through discharging produced water. During the membrane filtration treatment, oil will be deposited on the membrane surface, thus creating a gel layer, and concentration polarization. By studying the mass transfer coefficient (MTC), fouling phenomena can be well understood. As it is closely related to the hydrodynamic properties thus studying the MTC could aid us in optimizing the filtration process by reducing the gel layer.

In hydrodynamics, the mass transfer coefficient value can be calculated from Sherwood relations, which are represented as:

$$Sh = kd_h D = a\ Re^b\ Sc^c$$

$$Re = \rho v d_h / \eta$$

$$Sc = \eta / \rho D$$

Where d_h is the hydraulic diameter of the system, D is the diffusion coefficient, Re is the Reynolds number, Sc is the Schmidt number and a, b, and c are adjustable parameters which are determined from experiment. With different operating conditions, a, b and c will be different. From recent review, there are at least 27 different mass transfer coefficients for turbulent flow of Newtonian fluids in pipes or flat ducts (van den Berg, 1989). These MTCs available are mostly derives from its initial application for fluid flow in non-porous smooth duct and adapted from heat transfer analogy (Gekas, 1987) thus this has been criticized because in reality, membrane surface is porous and not smooth. In this paper, MTC models using film model theory and solution diffusion/film theory model (Murthy, 1997) are highlighted because it is derived from the diffusion phenomena of particles in membrane system and not from Sherwood

relation. The two models are compared using linear regression method and the best MTC that works in a certain working pressure is determined. Note that Spiegler-Kedem/film theory model in Murthy and Gupta's work is not being used in our work as this is a non-linear model and is not applicable here.

BACKGROUND

Film Theory Model

In membrane separation process, particles being rejected by the membrane will build up near the membrane surface thus forming concentration profile (Noble and Stern, 1999). Concentration at the membrane surface will be higher and decays exponentially back to bulk concentration when away from the membrane wall (Figure 1).
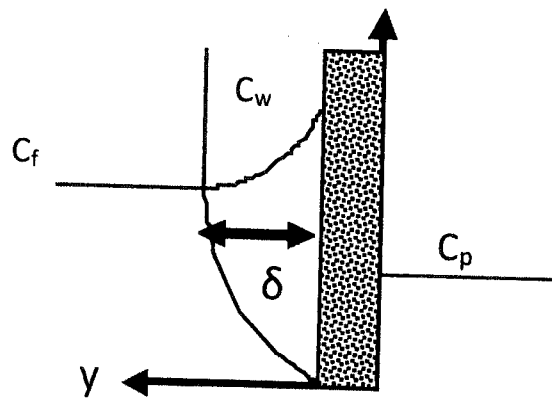

Figure 1: Concentration Profile Develops at the Boundary Layer δ

Some of the particles near the wall will diffuse back to the bulk/feed until equilibrium is formed (Song, 1998). This steady state relationship is represented by the equation below.

$$JC = JC_p + D\frac{dC}{dx}$$

(1)

At the boundary conditions: when $x = \delta$; $C = C_f$ and when $x = 0$; $C = C_w$

Integrating equation (1) with the boundary conditions we have

$$\frac{C_w - C_p}{C_f - C_p} = \exp(\frac{J\delta}{D})$$

(2)

When there are complete rejection, Cp is equal to 0, and rearranging we have

$$J = \frac{D}{\delta}\ln(\frac{C_w}{C_f})$$

(3)

Where $\frac{D}{\delta}$ is equal to mass transfer coefficient (MTC) and can be replaced by k.

Expanding (3) with k incorporated, we have a linear equation

$$J = k \ln C_w - k \ln C_f \tag{4}$$

Where

Component of y-axis, $y = J$

Slope of equation, $m = -k$

Intercept at y-axis, $c = k \ln C_w$

From experiment, we will be able to estimate k value by plotting J vs. ln (C_f).

Combined Solution Diffusion/Film Theory model

An alternative method to estimate the mass transfer coefficient is by using the model derived by Murthy and Gupta from combining solution-diffusion and film model theory (Pusch, 1977). First of all, observed rejection coefficient and true rejection coefficient are defined as below:

$$\text{Observed rejection coefficient, } R_o = \frac{C_f - C_p}{C_f} \tag{5}$$

$$\text{True rejection coefficient, } R = \frac{C_w - C_p}{C_w} \tag{6}$$

Rearranging the rejection coefficient with expression (2) will yield

$$\frac{R_o}{1 - R_o} = (\frac{R}{1 - R}) \exp(\frac{-J}{k}) \tag{7}$$

Expression 7 needs to be modified to find the MTC value. The solution-diffusion model can be combined with (6) to give:

$$\frac{1}{R} = 1 + (D\frac{K}{\delta})(\frac{1}{J}) \tag{8}$$

Where $D\frac{K}{\delta}$ is considered as a single parameter namely solute transport parameter. Rearranging (8), we have

$$\frac{R}{1 - R} = J /(D\frac{K}{\delta}) \tag{9}$$

Substituting (9) into (7) yields,

$$\frac{R_o}{1 - R_o} = \left[\frac{J}{\left(D\frac{K}{\delta}\right)} \right] \exp(\frac{-J}{k}) \tag{10}$$

(10) can be rearranged into linear form as

$$\ln(\frac{R_o}{1-R_o}) - \ln J = \left(-\frac{1}{k}\right)J - \ln\left(\frac{DK}{\delta}\right) \tag{11}$$

Where

Component y-axis, $y = \ln(\frac{R_o}{1-R_o}) - \ln J$

Slope of equation, $m = -1/k$

Intercept at y-axis, $c = -\ln\left(\frac{DK}{\delta}\right)$

From the same experiment, we will be able to estimate k value by plotting $\ln(\frac{R_o}{1-R_o}) - \ln J$ vs. J.

EXPERIMENTAL METHOD

The experiments were performed using cross-flow membrane filtration system from Sartorius with Sartocon Slice Cassette containing Polyethersulfone (PESU) 50kD MWCO membrane. The membrane cassette is in vertical position and the in-flow direction is anti-gravity, from bottom to top. Fig 2 showed the flow diagram of the membrane system used. The filtration was operated at optimum trans-membrane pressure (TMP) which is 2.75bar for 3 differential pressures (DP) which are 0.5bar, 1bar and 1.5bar. TMP is the driving pressure across the membrane. However, by changing the DP, the flow rate in the cross-flow direction is altered. Initially the weight of 12 empty cylinders was measured and recorded. The raw water and distilled water were weighed separately. During the filtration, 100ml of permeate were collected in each of the 12 cylinders with the time recorded. The time recorded is for the calculation of permeate flow rate and the flux. Feed concentration changes with volume change. Therefore the feed volume was measured for each 100ml of permeate taken so that feed concentration can be determined.
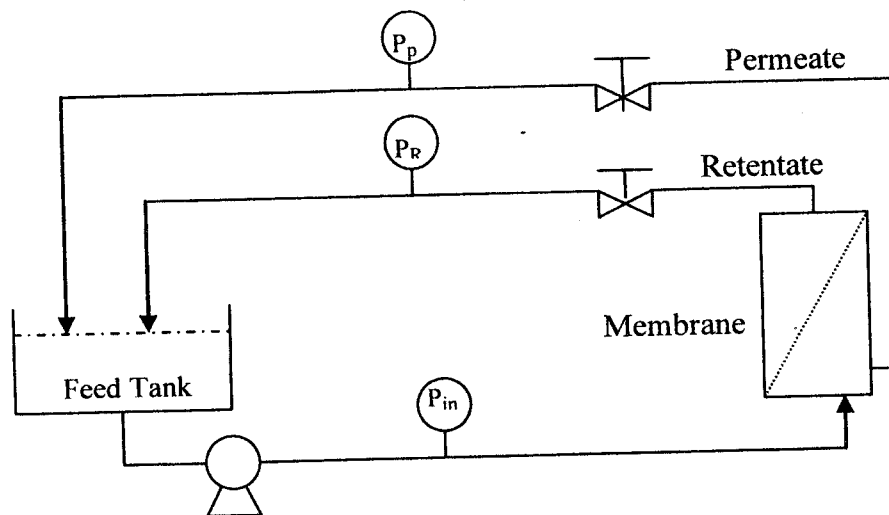

Figure 2: Experimental Set-up for Cross-flow Membrane Filtration

CALCULATIONS

DP = Feed Pressure -- Outlet Pressure

Weight of 100ml water (A) = Weight of Beaker with 100ml water − Weight of Beaker

Weight of 100ml feed water (B) = Weight of Beaker with 100ml feed water − Weight of Beaker

Initial Feed concentration g/ml = (B-A)/100

Weight of permeate (C) = weight of cylinder with 100ml permeate − weight of cylinder

Permeate concentration g/ml = (C-A)/100

Flux = Flow rate calculated/Effective area of membrane

RESULTS AND DISCUSSIONS

From the data, 6 graphs are plotted according to the linear form of Solution-diffusion/film theory model (S-D) and Film theory (FT) model as shown in Figure 3 to 8. From the slope of the graphs, the MTCs or k values can be calculated using (11) and (4) accordingly. MTCs for their respective DPs are summarized in Table 2 below:

Table 2
MTCs for Solution-diffusion Model and Film Theory Model for 50kD Membrane

MTC	DP 0.5	R^2	DP 1.0	R^2	DP 1.5	R^2
S-D	8.69E-06	0.7232	-6.25E-06	0.2725	9.78E-06	0.1038
FT	2.00E-04	0.9635	2.00E-05	0.3778	8.00E-06	0.0535

From Table 2, the coefficient determination, R^2, represents the per cent of the data that is closest to the line of best fit (Box and Hunter, 2006). From the R^2 values, both the models are seen to represent the data at a certain range of operating differential pressure (DP) i.e. DP 0.5. For both models, the R^2 for DP 1.5 and DP 1.0 are very small thus the MTCs
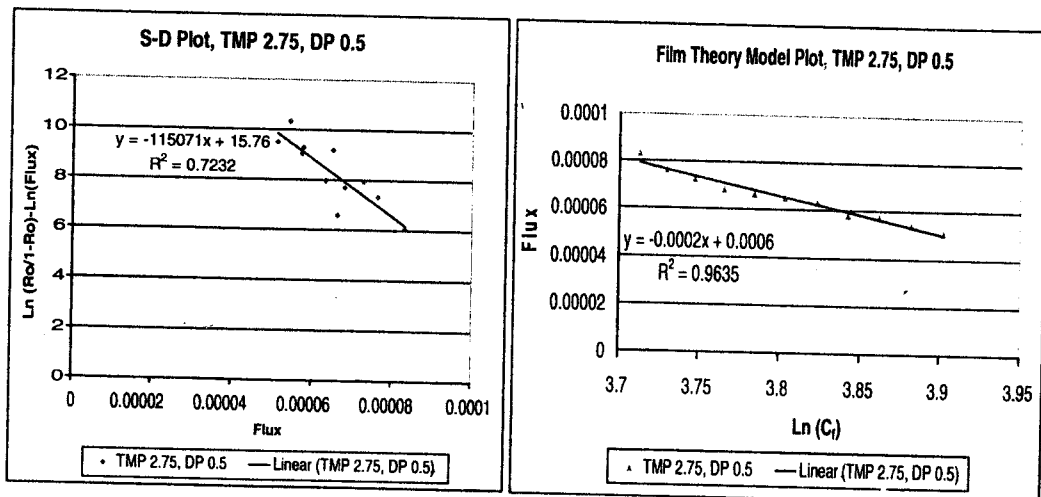

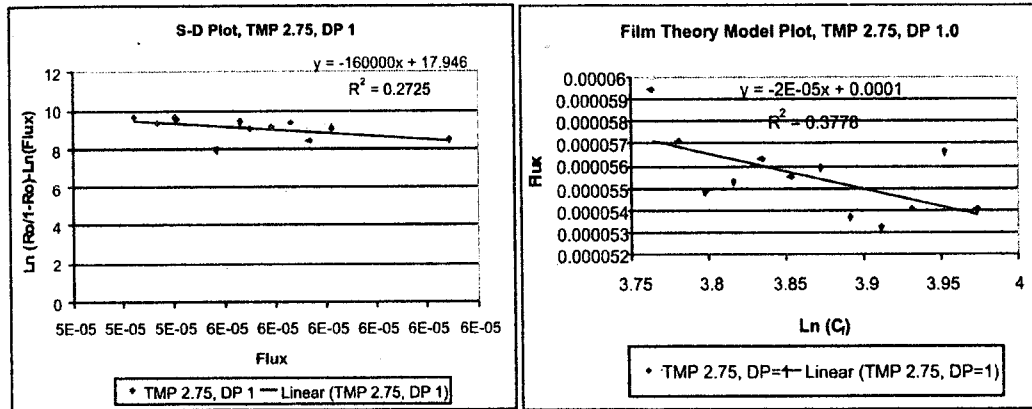**Figure 3 & 4:** S-D Model Plot and FT Model Plot for DP 0.5

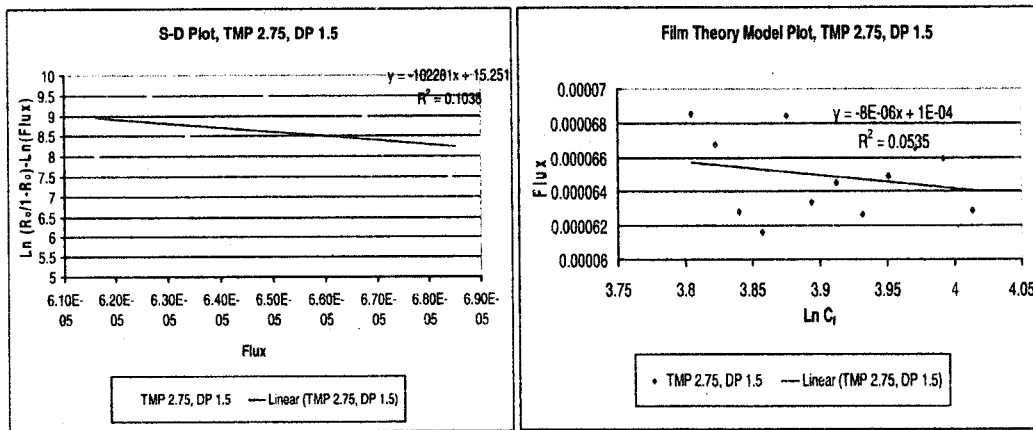**Figure 5 & 6:** S-D Model Plot and FT Model Plot for DP 1.0

Figure 7&8: S-D Model Plot and FT Model Plot for DP 1.5

estimated from the models at these DP do not represent the MTC in the experiment. However, R^2 for FT model operating at DP 0.5 has the highest value i.e. 0.9635 which means 96.4% of the experimental data fits well with the model. Therefore the MTC from FT model operating at DP 0.5 is a reliable value and is the best estimated mass transfer coefficient for our membrane system.

Also from Table 2, the MTC values corresponding to various DP for S-D model change a little but the MTC values for F-T model changes largely with varying DP. From this we can see that DP is a significant factor for F-T model but not the S-D model. This is because the concentration of solute in the produced water is very small e.g. 0.04g/mL, thus the permeate concentration is assumed to be negligible. This fits the assumption made by FT model which states that there are no solute in permeate flux. Whereas concentration plays a significant role in S-D model and predicts the MTC for higher feed concentration.

The same experiment is repeated with 100kD MWCO membrane and the results are shown in Figure 9 to 14.
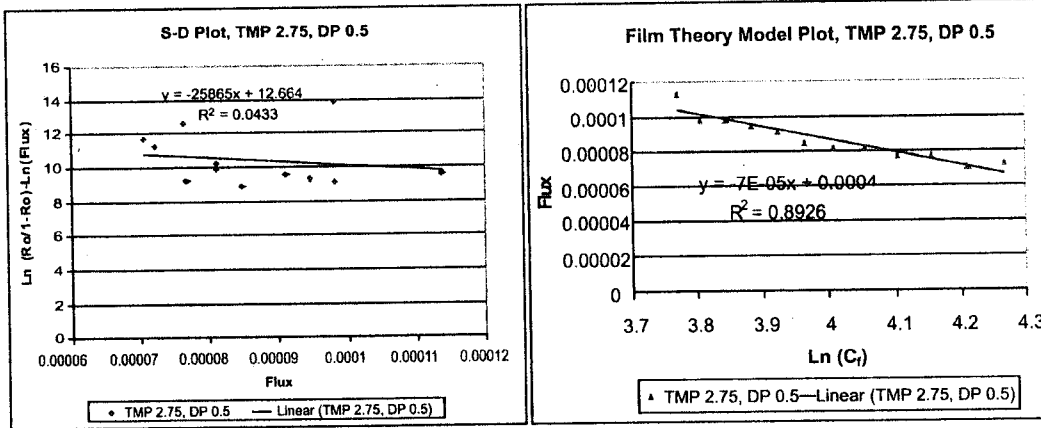
S-D Plot, TMP 2.75, DP 0.5

$y = -25865x + 12.664$
$R^2 = 0.0433$

Ln (Ro/1-Ro)-Ln(Flux)

Flux

• TMP 2.75, DP 0.5 —— Linear (TMP 2.75, DP 0.5)

Film Theory Model Plot, TMP 2.75, DP 0.5

Flux

$y = -7E-05x + 0.0004$
$R^2 = 0.8926$

Ln (C_f)

▲ TMP 2.75, DP 0.5—Linear (TMP 2.75, DP 0.5)

Figure 9 & 10: S-D Model Plot and FT Model Plot for DP 0.5

S-D Plot, TMP 2.75, DP 1

$y = -32803x + 13.017$
$R^2 = 0.0445$

Ln (Ro/1-Ro)-Ln(Flux)

Flux

• TMP 2.75, DP 1 —— Linear (TMP 2.75, DP 1)

Film Theory Model Plot, TMP 2.75, DP 1.0

$y = -8E-05x + 0.0004$
$R^2 = 0.5465$

Flux

Ln (C_f)

• TMP 2.75, DP=1 —— Linear (TMP 2.75, DP=1)
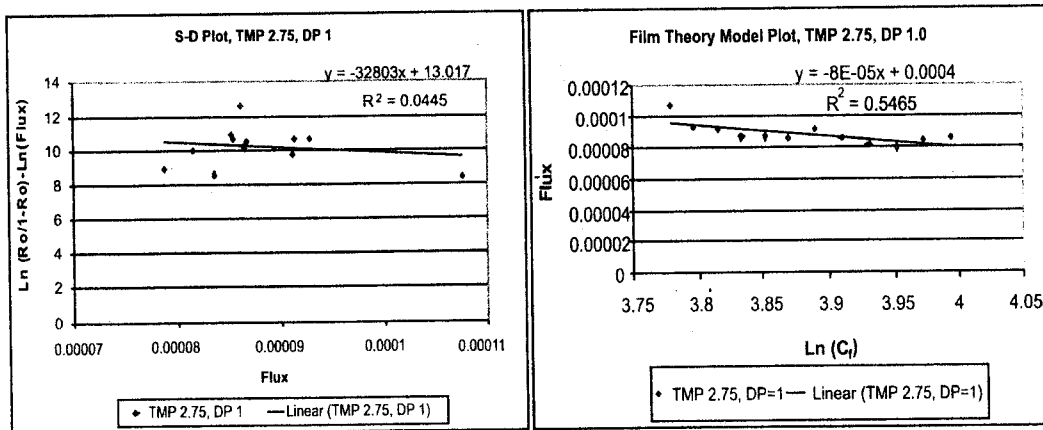
Figure 11 & 12: S-D Model Plot and FT Model Plot for DP 1.0

S-D Plot, TMP 2.75, DP 1.5

$y = -245264x + 27.976$
$R^2 = 0.056$

Ln (R_o/1-R_o)-Ln(Flux)

Flux

■ TMP 2.75, DP 1.5 —— Linear (TMP 2.75, DP 1.5)

Film Theory Model Plot, TMP 2.75, DP 1.5

$y = -1E-05x + 0.0001$
$R^2 = 0.2927$

Flux

Ln C_f

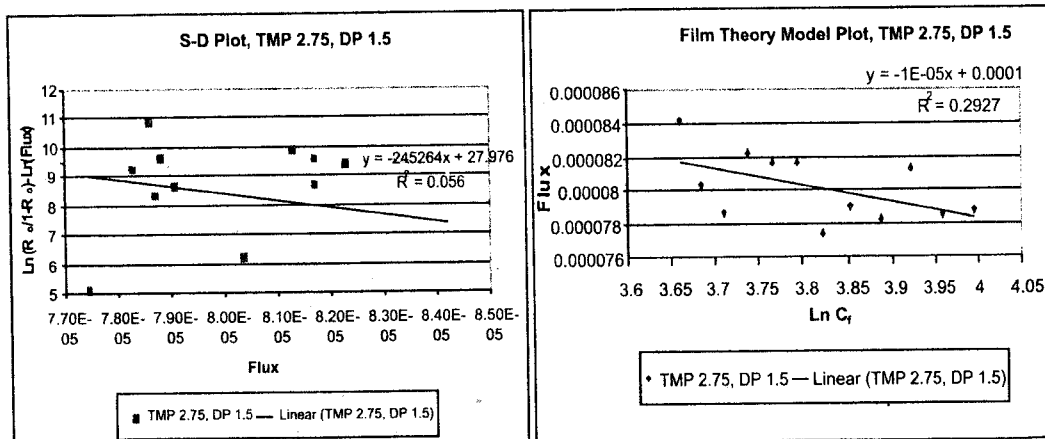• TMP 2.75, DP 1.5 —— Linear (TMP 2.75, DP 1.5)

Figure 13 & 14: S-D Model Plot and FT Model Plot for DP 1.5

The MTC values estimated from the models are summarized in Table 3.

Table 3
MTCs for Solution-diffusion Model and Film Theory Model for 100kD Membrane

MTC	DP 0.5	R^2	DP 1.0	R^2	DP 1.5	R^2
S-D	3.87E-05	0.0433	3.05E-05	0.0445	4.08E-06	0.056
FT	7.00E-05	0.8926	8.00E-05	0.5465	1.00E-05	0.2927

From the two experiments using different type of membrane, the results show consistency that the FT model fits well with our experimental data but only at lower DP range i.e. DP 0.5. As the differential pressure (DP) increases, the model could not be used to predict our MTC value.

Another experiment on finding the optimum TMP was done and the results are shown in Figure 15. When operating at DP 0.5 at TMP 2.75 we have the highest permeate flux which is preferred. From the fitting results (R^2), the MTC derived from the models also shows that for DP 0.5 is more reliable. Combining the two results, optimization of our system is possible by operating at DP 0.5 and using the MTC estimated from F-T model for DP 0.5.
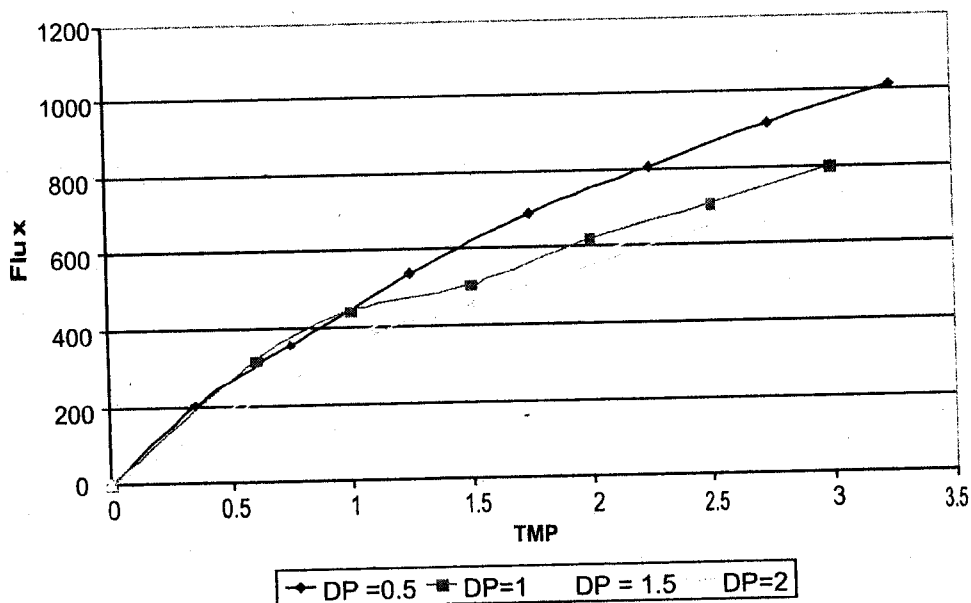
Optimum TMP

Figure 15: Permeate Flux vs. TMP Graph Using Produced Water

CONCLUSION

For membrane filtration of produced water, their MTCs for various DP were calculated using two models i.e. S-D model and FT model. From the results, film theory model is more suitable to be used to calculate MTC for our produced water samples. Further work for optimization

will be done using the MTC value from DP 0.5 with TMP 2.75 as these operating parameters fits well for the model and gives the highest permeate flux.

ACKNOWLEDGEMENT

GLOSSARY

C_f	Feed Concentration
C_w	Membrane Wall Concentration
ä	Boundary layer
J	Flux
k	Mass Transfer Coefficient
D	Diffusivity
R_o	Observed Rejection
DP	Differential Pressure
TMP	Trans-membrane Pressure

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