Estimation of Concentration Polarization Using the Combined Film theory/ Spiegler-Kedem Model and Empirical Correlation

Taha Yaseen Khalaf
Biomedical Engineering Dept/ Al-Khwarizmi Engineering College / University Of Baghdad
Email: Tahayaseen@ymail.com

Abstract

At a given operating pressure and in a given apparatus, concentration polarization results in an increase in the effective osmotic pressure of the feed solution on the membrane surface, a consequent decrease in the effective pressure \( \Delta P \) for fluid flow across the membrane, and progressive changes in the mass transfer coefficient, product rate, and solute separation along the length of the membrane in the direction of feed flow. The problem then is to predict the effect of concentration polarization on solute separation and on predict rate, under specified experimental condition. In the present work, the reverse osmosis experiments were conducted in a spiral wound model to get separation data using a NaCl-water system up to 2500 ppm and cellulose acetate membrane.

The purpose of this paper is to predict and analyze the concentration polarization using a combined film theory model and empirical correlation. Therefore, the results of the experiments show that the concentration polarization affected when using different models.

1. Introduction

Membrane separation such as reverse osmosis, ultra filtration and others are recently developed separation techniques. As compared with other separation methods, membrane processes possess many advantages such as no phase change, simple equipment, low energy consumption and ease of operation. As a result they have a great tendency to be used in industry as well as in scientific and technological circles.

The main task in designing reverse osmosis devices is selecting the optimum hydraulic parameters to reduce the power consumption of the system and extend the life of the membrane, thus lowering production cost. For the optimization of hydraulic parameters, concentration polarization which seriously affects the performance of the separation system, is one of the important control factors influencing the system design. It could be reduced to a certain extend by some appropriate measures, but complete elimination of this phenomenon is impossible in any practical operating system[1).

Figure 1 illustrate the mass transfer system in reverse osmosis for a membrane under steady state conditions[2]. When the solution flows through the system parallel to the membrane surface at a given rate, both the solute and solvent are forced to pass through the membrane owing to the action of the pressure difference. The solvent can pass through the membrane completely, but most of the solute accumulates at the surface due to the rejection caused by the membrane. Thus a concentration gradient is built between the membrane surface and bulk solution, which makes the solute diffuse back towards the bulk solution. The higher the concentration of solute at the membrane surface, the lower the permeation rate of the solvent. This unfavorable phenomenon is called "concentration polarization" [3-5].

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The starting point for our mathematical description of RO/NF separations is the solution–diffusion model. The model assumes that the permeation driving force is the gradient in chemical potential of the solute (Wijmans and Baker, 1995). When the transport equation is expressed in terms of solvent flux (J), it is given as
\[ J_v = A(\Delta P - \sigma \Delta \pi) \]  

Where A is the solvent permeability through the membrane, \( \Delta P \) is the applied pressure, \( \Delta \pi \) is the osmotic pressure difference between the membrane surfaces and \( \sigma \) is the reflection coefficient. The reflection coefficient represents the intrinsic salt rejection by the membrane, but when intrinsic salt rejection is over a 0.98, which is typical for reverse osmosis separations, \( \sigma \) may be assumed equal to unity (Bhattacharjee et al., 2001). When intrinsic salt rejection is significantly less than 0.98 (i.e., nanofiltration), the reflection coefficient should be used to more accurately predict the resultant trans-membrane osmotic pressure (Murthy and Gupta, 1997)[ 6 ].

Equation (1) serves as the starting point for the design of most modern RO/NF separations. The rejection of ionic species results in an elevated salt concentration near the membrane surface creating a local concentrated layer (CP), this layer quickly reaches a steady state, and the transverse solute flux through the CP layer is constant[ 6,7 ]. The solvent flux (J) may then be determined by the following one-dimensional, steady-state mass balance across the CP layer:

\[ J_v C_p = J_v C - \left[ D \frac{dC_s}{dx} \right] \]  

Where, \( J_v \) is the permeate flux through the membrane, \( C_p \) is the permeate solute concentration, \( C \) is the solute concentration in the boundary layer and \( D \) is the solute diffusion coefficient in water[ 8 ].

Integrating the one dimensional (transverse) convection-diffusion mass balance from the membrane surface out to a finite mass boundary (film) layer thickness, \( \delta \), yields the relationship between concentration polarization and permeate flux. The result is,

\[ CP = \frac{C_m - C_p}{C_b - C_p} = \exp \left( \frac{J_v \delta}{D} \right) \]  

where \( C_m \) is concentration at the membrane surface, or channel wall, for the rejected salt, \( C_b \) and \( J_v \) are the bulk solute concentration and the permeate water flux through the membrane respectively, and \( \frac{D}{\delta} = \text{mass transfer coefficient}(k) \) [ 9 ].

2. Theory

Several theoretical models have been proposed for estimating concentration polarization. The models are based on the solution of the diffusion-convection differential equations, using appropriate boundary conditions and simplifying assumption. The most commonly accepted CP models are film theory, Spiegler-Kedem and solution-diffusion models(Sablani et al.,2001, Murthy and Gupta, 1997). The alternative approach to calculate CP is to develop correlations for estimating the mass transfer coefficient [10].The development of a generalized mass transfer correlation begins with the assessment of previous work.

3. Combined solution-Diffusion / film model

Equation (5) shows that CP is strongly dependant on two parameters, \( J_v \) and \( k \). Therefore it can be expressed in terms of the membrane rejection fractions(\( R_{obs} \) and \( R_r \), thus, the concentration polarization expression takes the form[ 11 ]:

\[ \frac{1 - R_{obs}}{R_{obs}} = \frac{1 - R_r \exp \left( \frac{J_v \delta}{k} \right)}{R_r} \]  

The solute transport according to the simple solution-diffusion model is given below[8,12],

\[ J_s = C_p J_v = P_s(C_m - C_p) \]  

Where \( P_s \) is the overall permeability coefficient, which characterizes solute transport through the membrane. Combining
equations (6) and (7), the unknown parameters \( C_m \) and \( R_e \) can be eliminated, giving:

\[
\frac{R_e}{1 - R_e} = \left[ \frac{J_o}{P_s} \right] \exp\left( -\frac{J_o}{k} \right)
\]

4. Combined Spiegler-Kedem/film theory model

A concentration on both sides of membrane causes diffusive transport. When high concentration differences between the reject and the permeate exit, Spiegler and Kedem used the above equation and obtained the following expression of the rejection rate of the solute related to permeation flux:

\[
R = \frac{\sigma (1 - F)}{(1 - \sigma F)}
\]

\[
F = \exp\left( -\frac{J_o (1 - F)}{P_s} \right)
\]

\[
\frac{R_e}{1 - R_e} = \frac{\sigma}{1 - \sigma} \left[ 1 - \exp\left( -\frac{J_o (1 - \sigma)}{P_s} \right) \right] \exp\left( -\frac{J_o}{k} \right)
\]

Where \( R \) is the rejection. According to Eq. (9), the rejection increases with increasing the water flux. The Parameters \( \sigma \) and \( P_s \) can be determined from the experimental data of rejection as a function of flux using best-fit method [13].

5. Empirical correlation of mass transfer coefficient

Generalized correlations of mass transfer for developed flow (in both laminar and turbulent regions) suggest that the Sherwood number (Sh) is related to the Reynolds number (Re), Schmidt number (Sc) and the flow geometry in the form (Cussler, 1997) [8]:

\[
Sh = a (Re)^\alpha (Sc)^\beta \left( \frac{d_h}{L} \right)^\gamma
\]

\[
Sh = \frac{kd_h}{D} = a \left( \frac{d_h \mu}{\nu} \right)^\alpha \left( \frac{\nu}{D} \right)^\beta \left( \frac{d_h}{L} \right)^\gamma
\]

Where \( d_h \) is the hydraulic diameter, \( \mu \) is the flow velocity, \( \nu \) is the kinematic viscosity, \( D \) is the solute diffusivity in water, \( L \) is the length of the tube channel and \( \alpha \) is a numerical constant characterizing the flow channel geometry. The values of constants \( \alpha \) and \( \beta , \gamma \) are parameters, experimentally.

For laminar flow in a thin rectangular channel, the mass transfer coefficient (k) may be related to the Sherwood number (Sh) through the following equation [4]:

\[
Sh = \frac{kd_h}{D} = \frac{1.62 d_h \mu}{\nu} \left( \frac{\nu}{D} \right)^{1/2} \left( \frac{d_h}{L} \right)^{1/2}
\]

For turbulent flow, the mass transfer coefficient (k) may be related to the Sherwood number (Sh) through the following equation (Dittus and Boelter relation) [12]:

\[
Sh = \frac{kd_h}{D} = 0.2487 \left( \frac{d_h \mu}{\nu} \right)^{0.7604} \left( \frac{\nu}{D} \right)^{0.932}
\]

The diffusivity and kinematic viscosity data for the NaCl-water system are taken from the reference [15].

6. Experimental Work

Pilot scale experiments were performed using a custom made pilot scale membrane tester (Berkefeld Filter commercial) which holds a spiral wound membrane module with 20.1 cm (8 inch) nominal diameter and 101.6 cm (40 inch) effective length. The experiment was performed using commercially available pilot scale RO membrane ROGA-HR manufactured by Koch Membrane Systems, Inc., (USA). ROGA-HR is the type high rejection Cellulose Acetate (CA) RO membrane element for brackish water desalination.

The trans-membrane pressure and volumetric flow rate were adjusted using the concentration (reject) outlet valve. The pressure was varied between 15 bar and 35 bar. The experiments were carried out with NaCl-water solution, the feed temperature is constant and feed concentration varied from 725 ppm – 2500 ppm.

7. Results and Discussion
Experimental data were obtained at various feed concentration and transmembrane pressure. Under a fixed set of conditions, \( J_v \) and \( R_o \) were measured. These data were curve fitting using Levenberg-Marquardt [14] nonlinear regression technique to obtain the values of the parameters for the Eqs. (8) and (11). Table 1 shows that the membrane parameters and mass transfer coefficient for the three models (Combined solution-Diffusion / film, Combined Spiegel-Kedem/film theory and Empirical correlation), which shows that the parameters for Eq.(8) are relatively constant and the \( k \) values for the same equation differ markedly. The most important observation is that the \( k \) values estimated from Eq.(8) shows a negligible variation with feed flow rate , as observed early by a simple graphical method as shown clearly in figures (1) and (2), thus the true concentration polarization values cannot be pridect from this model.

| Table (1) Parameters and mass transfer coefficients estimated from the combined film theory/solution diffusion (CFSD) model, the combined film theory/Spiegler-Kedem (CFSK) model and the empirical correlation by a nonlinear parameter estimation program for the NaCl-water system. |
|---|---|---|---|---|---|
| S.no. | Feed rate, \( (m^2/hr) \) | Feed conc., ppm | CFSD model | CFSK model | Empir. Correla. |
| | \( P_f \times 10^5 \) | \( k \times 10^4 \) | \( k \times 10^4 \) | \( k \times 10^4 \) |
| 1 | 20.833 | 725 | 2.145 | 18.06701 | 0.9874 | 2.0037 | 33.298 | 32.431 |
| 2 | 25.833 | 725 | 2.148 | 18.18968 | 0.9856 | 2.0918 | 41.466 | 41.849 |
| 3 | 29.444 | 725 | 2.148 | 18.19046 | 0.9842 | 2.0820 | 47.285 | 47.053 |
| 4 | 31.944 | 725 | 2.148 | 18.19046 | 0.9830 | 2.0739 | 53.267 | 53.562 |
| 5 | 33.888 | 725 | 2.113 | 20.0787 | 0.9822 | 2.0681 | 58.088 | 58.759 |
| 6 | 20.833 | 925 | 2.293 | 19.06532 | 0.9917 | 2.5096 | 33.072 | 34.198 |
| 7 | 25.833 | 925 | 2.317 | 19.20387 | 0.9897 | 2.5007 | 42.265 | 42.731 |
| 8 | 29.444 | 925 | 2.317 | 19.20395 | 0.9883 | 2.4935 | 47.908 | 48.045 |
The values of concentration polarization as a function of feed flow rate at a constant temperature are presented in Figs. (4) and (5). This figures showed that CP decreased with increase in flow rate. The increase in feed flow rate reduces CP values due to increase in turbulence near the membrane. At a constant temperature, the properties of the fluid are not change. Since remaining the effect of feed flow rate on concentration polarization is only.

Permeation flux is an important parameter in the design. Flux is affected by several factors such as feed pressure, operating temperature, feed velocity and/or composition. As shown in Fig. 6, flux decreased with increasing recovery rate. While recovery was increasing, feed stream concentration increased. If the membrane plant was operated at a recovery of 50%, the feed stream concentration was doubled. At high concentration factors, the negative effect of concentration polarization on membrane performance can be so serious that the flux is decreased. Deposition of solute on the surface of membranes can change the separation characteristics and the high concentration of solute at the membrane interface increases the risks of change in composition of the membrane material due to chemical attack.

As recovery rate rises, the salt concentration in the feed stream increases, which causes an increase in the driving force for salt flow or salt passage. Higher salt concentration levels in the feed stream increase the osmotic pressure, which reduce the net pressure driving force and therefore permeate flow. As shown in Fig. 7, conductivity rejection was decreased with increasing recovery rate.
8. Conclusions
For determination of scaling of the propensity of the fouling species in water, it is essential to evaluate the concentration polarization level near membrane surface under the given experimental condition such as flow rate, pressure and feed concentration. The proposed mass transfer and the CP obtained from the combined film theory/ Spiegler-Kedem (CFSK) model gave good agreement with the empirical correlation against the combined film theory/solution diffusion (CFSD) model. The results show that even though the parameters of the Spiegler-Kedem model and the solution-diffusion model are constant over the operating conditions for our experimental data, the k values differ considerably. The reason for this may be the presence of a reflection coefficient in the Spiegler-Kedem model. Finally, at a constant temperature the effect of flow shows much influence on permeate concentration and the accumulate solute (CP) at the membrane shows some effect on the recovery and rejection.

9. Nomenclature
A  Solvent permeability
C  Solute concentration in the boundary layer
C_b  Feed concentration
C_m  Membrane surface concentration
C_p  Permeate concentration
D  Solute diffusivity coefficient in water
J_v  Permeate water flux
k  mass transfer coefficient
ΔP  Trans-membrane pressure difference
P_m  Solute permeability coefficient for SK model
P_s  Overall permeability coefficient
R_o  Observed rejection (1−C_p/C_b) (dimensionless)
R_r  Real rejection (1−C_m/C_p) (dimensionless)
Sh  Sherwood number
Re  Reynolds number
Sc  Schmidt number
d_H  Hydraulic diameter
u  Flow velocity
ν  Kinematics viscosity
D  Solute diffusivity
L  Length of the tube channel
α, β, γ  Parameter experimentally
δ  Film thickness
π  Osmotic pressure
σ  Reflection coefficient, 0 for no rejection, 1 for total rejection

10. References
[8] Dharmesh S. Bhanushali, " Solvent-Resistant Nanofiltration Membranes:
