

## Effect of feed temperature on concentration polarization and efficiency of reverse osmosis systems

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### Abstract

*The objective of the present study was to investigate the effect of temperature in order to improve the efficiency of the RO desalination process, and analyze the concentration polarization in spiral wound salinity water membrane elements. In this study the commercial reverse osmosis membrane (cellulose acetate) have been used to treat medium concentrated (NaCl) salt solutions up to 1200 ppm. The results of the experiments show that the polymer membrane is very sensitive to changes in the feed temperature, and the concentration polarization variation with increase in flow rate and with decrease in temperature. The nonlinear equation obtained is solved numerically using the Marquardt method to determine various parameters. The  $k$  values estimated from the model show a marked variation that may be attributed to the presence of reflection coefficient in the Spiegler-Kedem model. It is suggested that the combined Spiegler- Kedem/film theory model may be the best method for establishing the mass transfer correlation for a given membrane of reverse osmosis and nanofiltration.*

### 1. Introduction

Many mechanistic and mathematical models have been proposed to describe reverse osmosis membranes. Some of these descriptions rely on relatively simple concepts while others are far more complex and require sophisticated solution techniques. Models that adequately describe the performance of RO membranes are very important since these are needed in the design of RO processes. Models that predict separation characteristics also minimize the number of experiments that must be performed to describe a particular system. Excellent reviews of membrane transport models and mechanisms include Jonsson [1], Soltanieh and Gill [2], Mazid [3], Pusch [4],

Dickson [5] Rautenbach and Albrecht[6], and Bhattacharyya and Williams [7].

Reverse osmosis models can be divided into three types: irreversible thermodynamics models (such as Kedem - Katchalsky and Spiegler - Kedem models) [8-10]; nonporous or homogeneous membrane models (such as the solution-diffusion, solution - diffusion-imperfection, and extended solution-diffusion models)[11-13]; and pore models (such as the finely-porous, preferential sorption capillary flow, and surface force-pore flow models). Charged RO membranes theories can be used to describe nanofiltration membranes, which are often negatively charged ; these models (such as

Donnan exclusion and extended Nernst-Planck models) include electrostatic effects. The transport models focus on the top thin skin of asymmetric membranes or the top thin skin layer of composite membranes since these determine fluxes and selectivity's of most membranes (Bhattacharyya and Williams[7]). Also, most of the membrane models assume equilibrium (or near equilibrium) or steady state conditions in the membrane.

A fundamental difference exists between the assumptions of the homogeneous and porous membrane models. The homogeneous models assume that the membrane is nonporous; that is, transport takes place between the interstitial spaces of the polymer chains or polymer nodules, usually by diffusion. The porous models assume that transport takes place through pores that run the length of the membrane barrier layer; as a result, transport can occur by both diffusion and convection through the pores. While both conceptual models have had some success in predicting RO separations, the question of whether a RO membrane is truly homogeneous (no pores) or porous is still a point of debate. No technique is currently available to definitively answer this question. The objective of the present study was to analyze

and model concentration polarization in spiral-wound membrane elements. In particular we evaluated the influence of feed temperature, feed salinity and flow rate on permeate flow and CP. Membrane parameters were estimated using an analytical osmotic pressure model for medium salinity applications.

## 2. Irreversible Thermodynamics Models

Some of the earliest RO membrane models were based on the principles of irreversible thermodynamics; Soltanien and Gill [2] and Baranowski [14] provide excellent discussions of the development and applicability of these models. Irreversible thermodynamics models assume the membrane is not far from equilibrium and so fluxes can be described by phenomenological relationships [1,2,5,15 and 16]. One of the early models was that derived by Kedem and Katchalsky [1,7 and 17]. They assumed that solvent and the solute fluxes were linked by a coupling coefficient called the Staverman reflection coefficient.

$$J_V = L_p(\Delta P - \sigma \Delta \pi) \quad 1$$

$$J_A = \omega \Delta \pi + (1 - \sigma) \times C \times J_V \quad 2$$

Where  $L_p$ ,  $\omega$  and  $\sigma$ , defined as the Staverman reflection coefficient

$$\sigma = \left( \frac{\Delta P}{\Delta \pi} \right)_{J_V=0}, \text{ are functions of the}$$

phenomenological coefficients and  $C$  is the logarithmic mean solute concentration in the membrane. The inherent disadvantage of this model is that the phenomenological coefficients were concentration dependent. To avoid this dependence, the Spiegler-Kedem (1966) was developed which also considered the convective coupling aspects of the solute transport.

## 3. Spiegler-Kedem (SK) model

Most of previous works regarding the development of membrane transport model were either based on non-equilibrium approaches or some mechanistic approaches relative to diffusion of solutes through membrane-pore. In this study the different solute-membrane parameters are estimated using Spiegler-Kadem (SK) model [9, 18 and 19]. This model, based on irreversible thermodynamics is combined with film theory

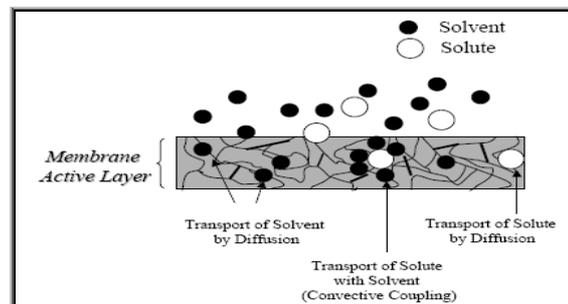
to facilitate parameter estimation, which will be subsequently used for simulation purpose. Based on the film theory, the observed rejection ( $R_o$ ), real rejection ( $R_r$ ), volumetric flux ( $J_V$ ) and mass transfer coefficient ( $k$ ) can be correlated by the following expression [20]:

$$\ln\left(\frac{1-R_o}{R_o}\right) = \ln\left(\frac{1-R_r}{R_r}\right) + \frac{J_V}{k} \quad 3$$

The Spiegler-Kedem model assumes that the solute flux is a combination of diffusion and convection (Kedem, Gilron et al, 2001 and Burghoff [21]). Figure 1, depicts the physical interpretation of the Spiegler - Kedem analysis [18].

The relevant equation for the Spiegler-Kedem model is:

$$J_A = P_S \left( \frac{dC}{dx} \right) + (1 - \sigma) C J_V \quad 4$$



**Figure (1)** Physical Interpretation of the Spiegler-Kedem model for solute transport

The relevant equation for the Spiegler-Kedem model is:

$$J_A = P_S \left( \frac{dC}{dx} \right) + (1 - \sigma) C J_V \quad 4$$

Putting,  $J_A = C_p J_V$

$$P_S \left( \frac{dC}{dx} \right) + [(1 - \sigma) C - C_p] J_V = 0 \quad 5$$

Integrating Eq. 4 with boundary condition as,

$$x = 0, \quad C = C_p \quad 5a$$

And

$$x = \Delta x, \quad C = C_m \quad \text{5b}$$

$$\int_{C_p}^{C_m} \frac{dC}{(1-\sigma)C - C_p} + \int_b^{\Delta x} \frac{J_v dx}{P_s} = 0 \quad \text{6}$$

which on integration gives:

$$\frac{C_p - C_m(1-\sigma)}{\sigma C_p} = \exp\left[-\frac{J_v(1-\sigma)}{P_m}\right] \quad \text{7}$$

where  $P_m = P_s / \Delta x$ . In terms of  $R_r$ , Eq. 7 can be written as:

$$\frac{1}{1-R_r} = \frac{1}{1-\sigma} - \frac{\sigma}{1-\sigma} \exp\left[-\frac{J_v(1-\sigma)}{P_m}\right] \quad \text{8}$$

Substituting Eq. 3 in Eq. 8 to eliminate  $R_r$  will result,

In the above equation, the unknown parameters are as follows:

$$\frac{R_o}{1-R_o} = \frac{\sigma}{1-\sigma} \left[ 1 - \exp\left\{-\frac{J_v(1-\sigma)}{P_m}\right\} \right] \exp\left(\frac{-J}{k}\right) \quad \text{9}$$

$$a'_1 = \frac{\sigma}{1-\sigma}, \quad a'_2 = \frac{1-\sigma}{P_m} \quad \text{and} \quad \text{10}$$

$$a'_3 = \frac{1}{k}$$

$$\frac{R_o}{1-R_o} = a'_1 [1 - \exp\{-J_v a'_2\}] \exp(-J_v a'_3) \quad \text{11}$$

Where  $R_o$  is the rejection coefficient,  $\sigma$  is the reflection coefficient, which represents the rejection capability of a membrane (i.e.,  $\sigma = 0$  means no rejection and  $\sigma = 1$  100% rejection), and  $P_m$  is the overall permeability of the membrane. Using a nonlinear parameter estimation method and the data of observed rejection ( $R_o$ ) and the solvent flux ( $J_v$ ) taken at a given pressure, feed rate and concentration, the membrane

parameters  $\sigma$ ,  $P_m$  and  $k$  can be estimated, simultaneously [22].

The Spiegler-Kedem model has found wide use for the description and analysis of RO membrane separations. While irreversible thermodynamics can describe RO membrane transport, a major disadvantage of these models is the treatment of the membrane as a "black box" (Dickson [5]); that is, these models provide no insight into the transport mechanisms of the membrane. As a result, irreversible thermodynamics models are not very useful for optimizing separations based on membrane structure and properties. These models also do not adequately describe water flux for some solute systems; in particular, some dilute organics (with  $\pi_F = \pi_P = 0$ ) have substantially lower water fluxes than those described by Eq. 1.

#### 4. Experimental Work

Pilot scale experiments were performed using a custom made pilot scale membrane tester (Berkefeld Filter, Fig. 2) 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

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 a NaCl-water solution and the feed temperature varied from 20°C to 35°C.

Finally, the experimental data is fitted using the Spiegler – Kedem model in order to calculate the reflection coefficient ( $\sigma$ ) and the permeability of salt ( $P_m$ ).



Figure (2) Pilot plant RO unit (Berkefeld Filter).

## 5. Results and Discussion

- *Effect of feed temperature and pressure on permeate flux*

The results in figure 3a and 3b show the effect of pressure on the pure solvent and saline solvent that transport through the cellulose acetate membrane. Two observations can be made from the figures that, the solvent flux increases in a linear fashion with the applied

pressure and this occurred both in presence and absence of solute as shown in figure 3a and 3b. Also, the Permeate flux increases as temperature increases because ion diffusivity increases more rapidly than the viscosity of water decreases with increasing temperature and due to an increase in pore size of the polymeric membrane with temperature. Finally, the Figure 3a, 3b and Table 1 shows the Permeate flux is essentially based on actual net driving forces and sensitive to variation in the feed temperature.

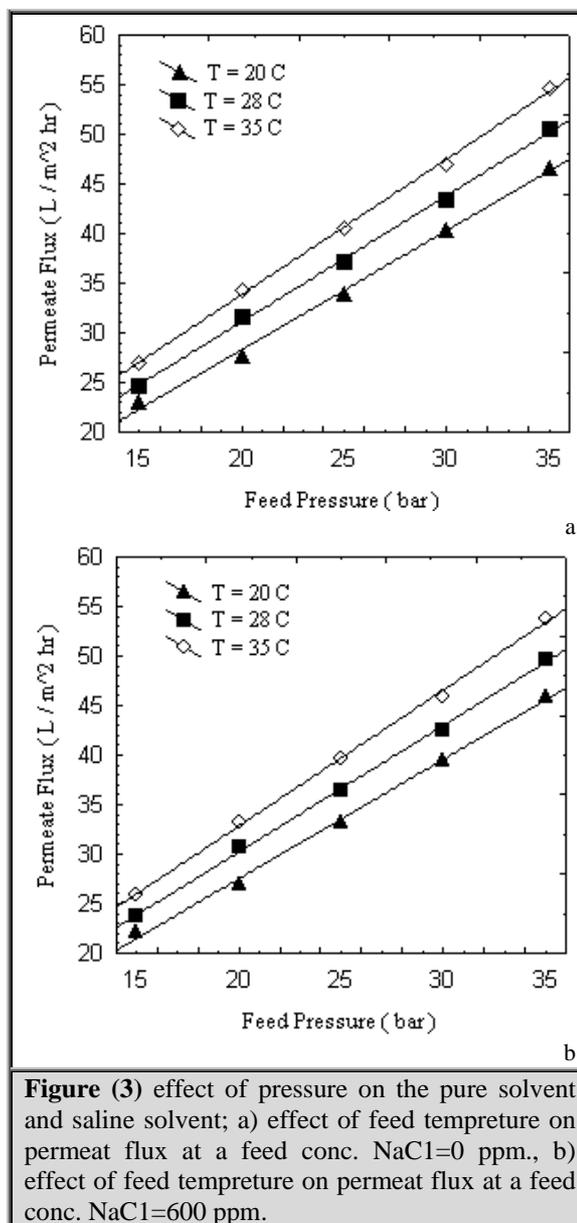


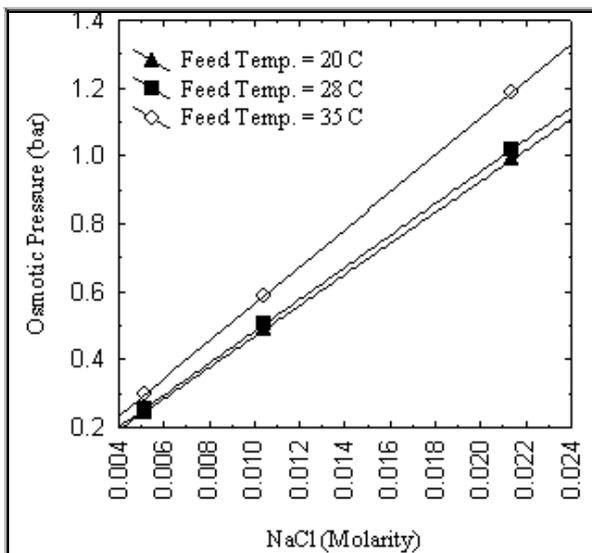
Figure (3) effect of pressure on the pure solvent and saline solvent; a) effect of feed temperature on permeate flux at a feed conc. NaCl=0 ppm., b) effect of feed temperature on permeate flux at a feed conc. NaCl=600 ppm.

- *Effect of feed concentration and feed flow rate on osmotic pressure and permeate flux*

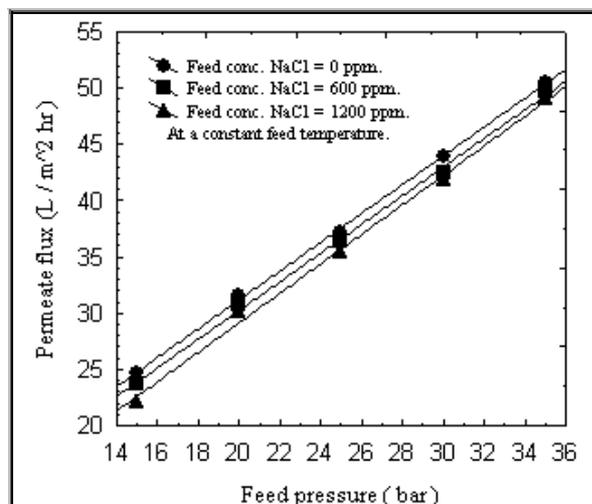
Fig. 4 shows the variation of osmotic pressure with the salt molarity at feed temperature 20, 28 and 35 °C. It's clear that the osmotic pressure increase linearly when the feed concentration was increased due to the supersaturation phenomena for the sodium ion at the high temperature. But, in fig. 5 when the feed concentration was increased at a constant temperature, the permeate flux decreased due to enhanced solute build-up at the membrane surface.

**Table (1)** Effect of feed temperature on permeates flux.

Feed Conc . ppm	Feed temperature, °C					
	20		28		35	
	Transmembran e pressure, bar	Permeate flux,L/m 2 hr	Transmembran e pressure, bar	Permeate flux,L/m 2 hr	Transmembran e pressure, bar	Permeate flux,L/m 2 hr
0	14.65	22.983	14.65	24.648	14.65	26.984
0	19.65	27.642	19.65	31.607	19.65	34.249
0	24.65	33.966	24.65	37.234	24.65	40.509
0	29.65	40.297	29.65	43.320	29.65	46.905
0	34.65	46.615	34.65	50.532	34.65	54.717
600	14.141	22.151	14.129	23.734	14.115	25.949
600	19.138	26.898	19.113	30.696	19.084	33.227
600	24.128	33.227	24.108	36.392	24.087	39.556
600	29.118	39.556	29.102	42.500	29.081	45.981
600	34.120	45.886	34.102	49.715	34.081	53.797



**Figure (4)** Effecte of feed conc.NaCl on Osmotic pressure at different feed temperature.



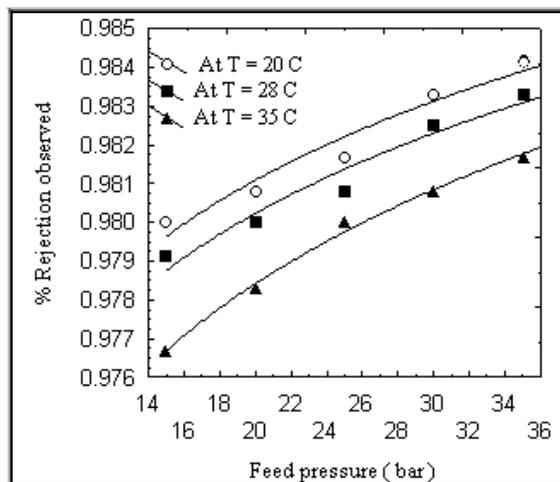
**Figure (5)** Effecte of feed conc.NaCl on Osmotic pressure at different feed pressure value.

- *Effect of feed pressure on salt rejection observed*

Fig. 5 shows the rejection observed of NaCl for studied membrane with different pressure and tempreture. It is clear that the rejection observed increases with increasing pressure and decreasing temperature for the membrane investigated.

- *Effect of feed temperature on the mass transfer coefficient, k, and the membrane permeability*

The experimental results were fitted using a combined Spiegler–Kedem/film theory model [Eq. 11]. Using a nonlinear parameter



**Figure (6)** Effecte of feed pressure at different feed pressure value permeat flux at variable feed temperature.

estimation method and experimental data on observed rejection and the solvent flux at a given pressure, feed rate and salt

concentration, the membrane parameters reflection coefficient ( $\sigma$ ), membrane permeability ( $P_m$ ) and mass transfer coefficient ( $k$ ) were estimated simultaneously. The modeling studies showed that the mass transfer coefficient was very sensitive to the feed salt concentration as well as the feed temperature. The mass transfer coefficient,  $k$ , and the membrane permeability,  $P_m$ , increased with an decrease in feed salt concentration, and an increase in feed temperature (Table 2). This supports experimental results that suggest that increased resistance to the solvent flux (i.e., pure water) across the membrane is due to increased concentration polarization at the membrane surface.

The product fluxes ( $J_v$ ) of the permeate and the observed solute rejections ( $Ro$ ) were plotted against the applied pressure for different feed flow rates and feed concentrations. The Levenberg-Marquardt method [22], a nonlinear parameter estimation method, was used to solve Eqs. (11). The data supplied are  $Ro$  vs.  $J_v$  taken at different operating pressures keeping feed rate and feed concentration constant for each set of data. The parameters estimated from Eqs. (11) are shown in Table 2, which shows that the membrane parameters are reasonably constant over the operating conditions. Although the membrane parameters of Eq. (11) is relatively constant, the  $k$  values differ markedly. The most important observation is that the  $k$  values estimated from Eq. (11) varied with feed rate, which is what one would expect theoretically. The difference in  $k$  values is obviously because of the presence of a reflection coefficient,  $\sigma$ , in Eq. (11).

• *Effect of feed flow rate and feed temperature on concentration polarization*

The values of concentration polarization as a function of flow rate at temperature 20, 28 and 35 C<sup>o</sup> are presented in figure 7. This figure showed that CP decreased with increase in flow rate and increased with decrease in temperature. The increase in feed flow rate reduces CP value due to increase in turbulence near the membrane resulting in decrease in the boundary layer thickness and solute concentration. But, In fig. 8 the concentration polarization was decreased with the increase in

feed temperature due to the change in density and viscosity of the solution.

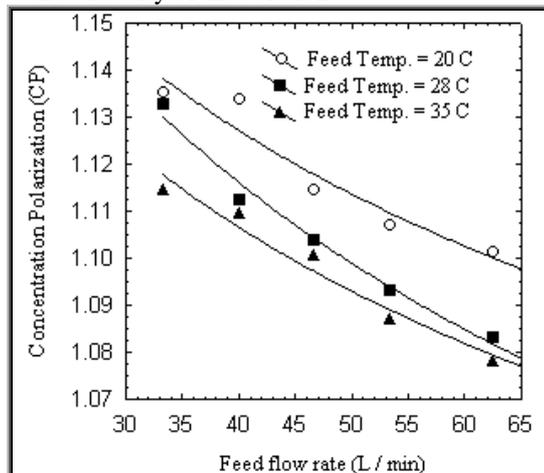


Figure (7) Effecte of feed flow rate on concentration polariztion.

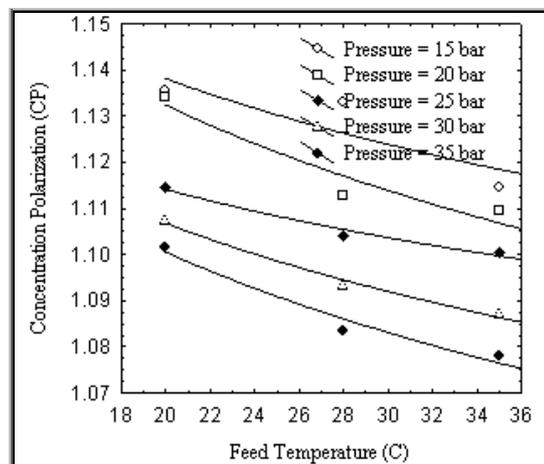


Figure (8) effect of feed temperture on concentration polariztion.

**Conclusion**

For determination of the scaling propensity of the fouling species in the water, it is essential to evaluate the concentration polarization level near membrane surface under the given experimental conditions such as flow rate, pressure and temperature of the feed solution. At the high feed flow rate, the CP was decreased, while at the high feed temperature, the CP decreased by a small rapidly. In general, the effect of Temperature on the efficiency of the RO membrane has been investigated through the experiments. Still there are many ways to improve the experiments by using another module, another method for calculations and establish the validity of the theoretical methodes for the test.

**Table (2)** Parameters estimated from the combined film theory/Spiegler-Kedem model by a nonlinear parameter estimation program for the NaCl – water system for three temperatures.

Temp. C	Feed flow rate ( L / min )	$P_m \times 10^5$ ( cm / s )	s	k x 10 <sup>3</sup> ( cm / s )
20	33.33	8.3270	0.99012165	50.2664
20	40.00	8.2078	0.98927842	61.0277
20	46.66	8.0878	0.98807416	86.9187
20	53.33	8.0084	0.987480422	109.91426
20	62.50	7.9461	0.987181229	127.86088
28	33.33	9.4084	0.989474229	54.866673
28	40.00	9.1864	0.987771682	82.297753
28	46.66	9.0829	0.987054914	104.591569
28	53.33	8.9725	0.986343258	142.186833
28	62.50	8.8859	0.98599019	175.346309
35	33.33	10.9732	0.988135242	63.155235
35	40.00	10.7788	0.986835086	84.480865
35	46.66	10.6361	0.985982722	107.898144
35	53.33	10.502	0.985190424	144.133756
35	62.50	10.4016	0.984650124	186.532363

### Nomenclature

$a'_1$ ,  $a'_2$  and  $a'_3$  model parameter of the SK models  
A pure water permeability coefficient (L/  $m^2$  hr bar)  
C logarithmic average of solute concentration across membrane (Kg  $m^{-3}$ )  
 $C_b$  feed concentration (Kg  $m^{-3}$ )  
 $C_m$  membrane surface concentration (Kg  $m^{-3}$ )  
 $C_p$  permeate concentration (Kg  $m^{-3}$ )  
 $J_A$  solute flux through membrane (kgm<sup>-2</sup> s<sup>-1</sup>)  
 $J_v$  volumetric flux (m<sup>3</sup> m<sup>-2</sup> s<sup>-1</sup>)  
k mass transfer coefficient (m s<sup>-1</sup>)  
 $\Delta P$  trans-membrane pressure difference (bar)  
 $P_m$  solute permeability coefficient for SK model (m s<sup>-1</sup>)  
 $P_s$  local solute permeability in the membrane (m<sup>2</sup> s<sup>-1</sup>)  
 $R_o$  observed rejection ( $1 - C_p / C_b$ ) (dimensionless)  
 $R_r$  real rejection ( $1 - C_m / C_p$ ) (dimensionless)  
TMP trans-membrane pressure

$\Delta x$  membrane thickness (m)  
 $\delta$  film thickness (m)  
 $\pi$  osmotic pressure (bar)  
 $\sigma$  reflection coefficient, 0 for no rejection, 1 for total rejection

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#### الخلاصة:-

إن هدف هذا البحث هو لدراسة مدى تأثير تغير درجة الحرارة للمياه الداخلة على كفاءة عملية التنافذ العكسي وعمل المنظومة وكذلك لتحليل ظاهرة تركيز الاستقطاب (concentration polarization) التي تحدث في أغشية التنافذ العكسي من نوع (Spiral wound) والمصنع من مادة السليلوز اسيتيت مع استخدام المحلول القياسي (NaCl-water) لغرض الاختبار بتركيز تصل إلى 1200 ppm. إن النتائج التجريبية التي تم الحصول عليها تبين إن الغشاء البوليمري ذات حساسية جدا عالية لدرجة الحرارة وان ظاهرة تركيز الاستقطاب تقل بزيادة معدل الجريان وبزيادة درجة الحرارة.

إن المعادلة الغير خطية التي وضعت حلت بإحدى أساليب الطرق العددية مستخدمين طريقة (Marquardt) لحساب المتغيرات ولإيجاد معامل انتقال الكتلة مستخدمين بذلك الموديل الرياضي (Spiegler–Kedem / film) علما أن هذا الموديل ناجح التطبيق لعملية التنافذ العكسي ولعملية (Nanofiltration).

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