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New approach for Spiegler-Kedem model in order to decrease the permeate volumetric flux error

M. Hadian

Department of water and environmental engineering, Shahid Beheshti University, Tehran, Iran,
email: m_hadian1986@yahoo.com (M. Hadian)

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ABSTRACT

In this paper, a new approach has been presented and verified to estimate Spiegler-Kedem model parameters. In this study, in addition to concentration polarization phenomenon, the distinguish between reflection coefficient and solute-solution coupling coefficient has been considered and a direct relationship between them introduced by considering some assumptions within the main framework of the model whereby the predicted fluxes error decreased in comparison to results estimated without considering the distinguish of the parameters. Finally, a self-fit method has been introduced using the new relationship to estimate the model parameters simultaneously so that in some tests, more accurate predictions have been obtained.

Keywords: Nanofiltration; Spiegler-Kedem model; Decreasing the permeate flux error

1. Introduction

Nanofiltration membrane (NF) are being used for many applications of desalination [1,2], food and pharmaceutical processes [3,4]. Modelling such processes successfully not only helps save time and money in developmental step of a given process by optimizing scale formation on equipment, but can also assists in selecting good input variables such as applied pressure and temperature. Many models are defined and applied to predict permeate volumetric flux and rejection and divided into mechanism-dependent-transport and mechanism-independent-transport models [5,6]. The first models rely on some physical parameters describing complex phenomena that cause solute and solvent to transport through membrane. An example of these models that are largely used to predict the permeate flux are models based on Nernst-Plank equation like Donnan-steric-pore model [7]. These models describe mass transfer processes in terms of effective membrane charge density, porosity ratio and effective membrane thickness. Although many investigators successfully applied these models for prediction of desalination processes, the models didn't give an accurate prediction in some applications done at very high concentration of salt such as desalination of seawater and desalination in chlor-alkali industry, since the models have based on dilute solution assumption [8,9]. The second models like Kedem-Katchalsky (KK) model based on irreversible thermodynamics treat membrane as a black box and are applied to estimate a dilute solution [10,11]. KK model is a good alternative for models relied on describing complex phenomena and is used for systems that are not far from equilibrium. KK model has been developed by introducing Spiegler-Kedem (SK) model [12]. Although SK model is able to estimate well the permeate flux and the rejection for different salt mixtures [13], its prediction overestimated at very high concentration of electrolyte solutions for the permeate flux, and now it is a challenging work for investigators [14]. Hence this paper introduces a new approach for the SK model to avoid overestimating the model prediction.

The SK model has two following equations

$$J_v = L_p\left(\Delta p - \sigma_1 \Delta\pi\right) \cdot \Delta\pi = \upsilon RT\left(C_b - C_p\right)\exp\left(\frac{J_v}{k}\right) \tag{1}$$

$$J_s = P_m \frac{dc}{dx} + \left(1 - \sigma_2\right) C_m J_v \tag{2}$$

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*Corresponding author.

For better estimation, considering concentration polarization effect has been suggested [15] hence using Eq. (2) and combining that with the film theory [16] yield

$$\frac{R_0}{1-R_0}=\frac{\sigma_2}{1-\sigma_2}\left(1-\exp\left(\frac{-\left(1-\sigma_2\right)J_v}{P_s=\dfrac{P_m}{\Delta x}}\right)\right)\exp\left(\frac{-J_v}{k}\right) \tag{3}$$

where J_v is total permeate volumetric flux; p and π are applied and osmosis pressure; σ_1 and σ_2 are reflection coefficient and solute-solution coupling coefficient respectively; k is mass transfer coefficient; R_0 is observed rejection coefficient; J_s is total solute flux; P_m is local solute permeability in the membrane; C_b, C_p, C_m are concentrations in feed side, permeate side and through the membrane respectively. Hydraulic permeability of the membrane (L_p) is an experimental parameter related to feature of membrane and solvent, and can experimentally be obtained by laboratory tests [14–17] or theoretically estimated by a best-fit method. Bowen et al. [18] estimated L_p using the first model equation (Eq. (1)) and considered the concentration polarization phenomenon just for the first equation while it should be considered for both the equations. Beside they assumed that σ_1 and σ_2 are equal while those parameters should separately be estimated. In some studies, only parameters of Eq. (3) were estimated [19–23] while for achieving full capacity of the model especially at very high concentrations, both the model equations [Eqs. (1) and (3)] should be considered. For this purpose, it is better to estimate all parameters simultaneously because except of (L_p) that can be estimated in laboratory tests, SK model has four parameters which k is common in its equations.

2. Theory

The SK model relies on the irreversible thermodynamics which considers membrane as a black box, but I subdivide it into two small black boxes and assume that one of those sections is perfect and another is not and rewrite model equations for them. According to the SK model when membrane is perfect, $\sigma_1 = \sigma_2 = 1$ and when it is quite not, $\sigma_1 = \sigma_2 = 0$, hence it can be written

$$J_{v1}=L_{p1}\left(\Delta p-\Delta\pi\right) \tag{4}$$

$$J_{v2}=L_{p2}\left(\Delta p\right) \tag{5}$$

$$J_v=J_{v1}+J_{v2} \tag{6}$$

$$J_v=(L_{p1}+L_{p2})\left(\Delta p-\frac{L_{p1}}{L_{p1}+L_{p2}}\Delta\pi\right) \tag{7}$$

According to Eqs. (7) and (1), it can be written

$$L_p=L_{p1}+L_{p2},\sigma_1=\frac{L_{p1}}{L_{p1}+L_{p2}} \tag{8}$$

According to the SK model the solute flux is divided into diffusional and convective term [Eq. (2)], for convective term the below equations can be written

$$J_{Scon}=J_{Scon1}+J_{Scon2} \tag{9}$$

$$\left(1-\sigma_2\right)C_mJ_v=\left(1-\sigma_{21}\right)C_{m1}J_{v1}+\left(1-\sigma_{22}\right)C_{m2}J_{v2} \tag{10}$$

where J_{scon} is convective solute flux, C_{m1} and C_{m2} are concentrations of the first and the second section respectively, it is assumed that concentration throughout the membrane is equal ($C_{m1} = C_{m2} = C_m$) because of solute diffusion that exists between the two sections [24].

Using Eqs. (6) and (10) yield

$$\sigma_2=\frac{J_{v1}}{J_v}=\frac{L_{p1}\left(\Delta p-\Delta\pi\right)}{L_p\left(\Delta p-\sigma_1\Delta\pi\right)} \tag{11}$$

Using Eqs. (8) and (11) yield

$$\sigma_1=\frac{\sigma_2\Delta p}{\sigma_2\Delta\pi+\left(\Delta p-\Delta\pi\right)} \tag{12}$$

Using the Eqs. (12) and (1) yield

$$J_v=L_p\left(\Delta p-\frac{\sigma_2\Delta p}{\sigma_2\Delta\pi+\left(\Delta p-\Delta\pi\right)}\Delta\pi\right) \tag{13}$$

Using Eq. (13), a new definition for σ_2 is obtained

$$\sigma_2=\frac{\sum_{i=1}^{n}\dfrac{\left(\Delta p_i-\dfrac{J_{vi}}{L_p}\right)\left(\Delta p_i-\Delta\pi_i\right)}{\dfrac{J_{vi}}{L_p}\Delta\pi_i}}{n} \tag{14}$$

where n is number of iteration of experimental tests done by various pressures with a same initial feed concentration and L_p has already been estimated (see, e.g. [14–17]). s_2 is estimated by Eqs. (14) and (3) so that the both equations should simultaneously be considered. For this purpose, the below equation can be used

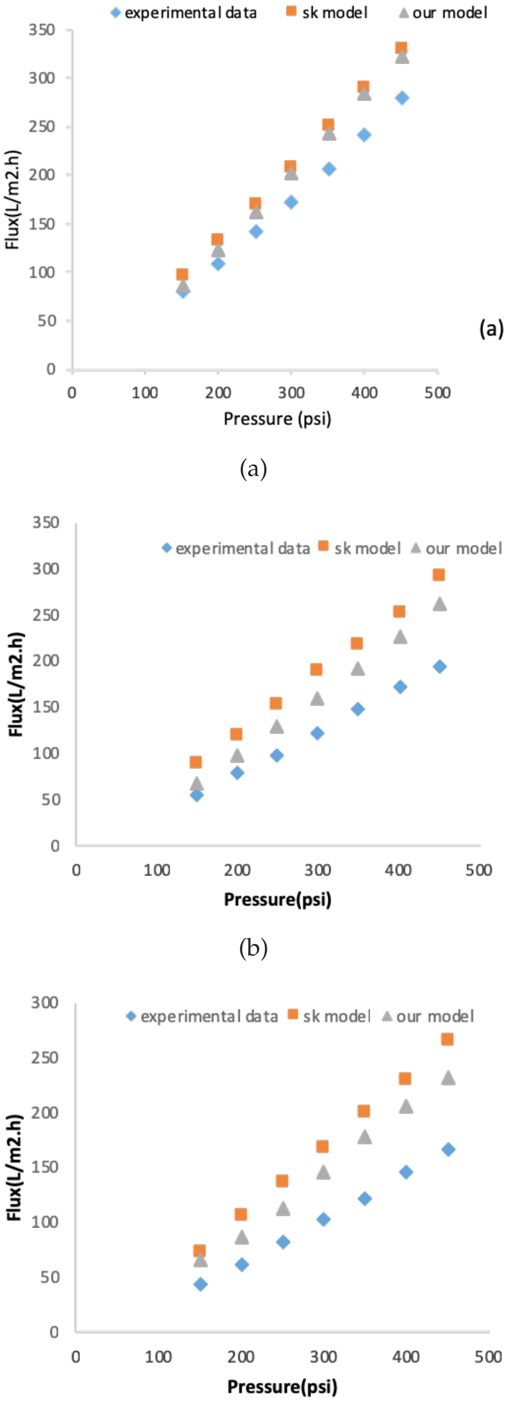
$$\left|\frac{\sigma_{2fit}-\sigma_2}{\sigma_{2fit}}\right|<0.01 \tag{15}$$

s_{2fit}, k, and P_s are estimated by Eq. (3). σ_2 is determined by Eq. (14) using k that has already been estimated by Eq. (3). If Eq. (15) isn't satisfied, σ_{2fit} (determined σ_2) should be substituted in Eq. (3) and other parameters of Eq. (3) should again be estimated and σ_2 should again be determined using Eq. (14). This procedure should be repeated until Eq. (15) is satisfied.

3. Verification and discussion

This present work introduces a method to reduce the error of estimated permeate flux by considering the distinguish between $\sigma_1$and σ_2, and introducing some assumptions within the main framework of the SK model which does not give any insight into mass transfer [25] and assumes the membrane have not electrical charge [26]. Some authors didn't consider the distinction between σ_1 and σ_2 [18–27], it can be ignored when the feed concentrations are low, but at very high feed concentrations cannot. As can be seen in Fig. 1a at concentration of 0.23 M NaCl, the difference between experimental and predicted flux (when $\sigma_1 = \sigma_2$) is low, but at high concentrations of 0.6 M NaCl and 0.82 M NaCl it is considerable (Figs. 1b and 1c) while by considering my offer this deference decreases [σ_2 has already obtained using Eq. (3), then substituted in Eq. (13)] because at higher concentrations, salt rejection decreases and osmotic pressure gradient increases, consequently σ_1 in Eq. (12) decreases, finally the predicted flux decreases.

In this paper, according to SK model I have subdivided the membrane into two sections and rewritten model equa-

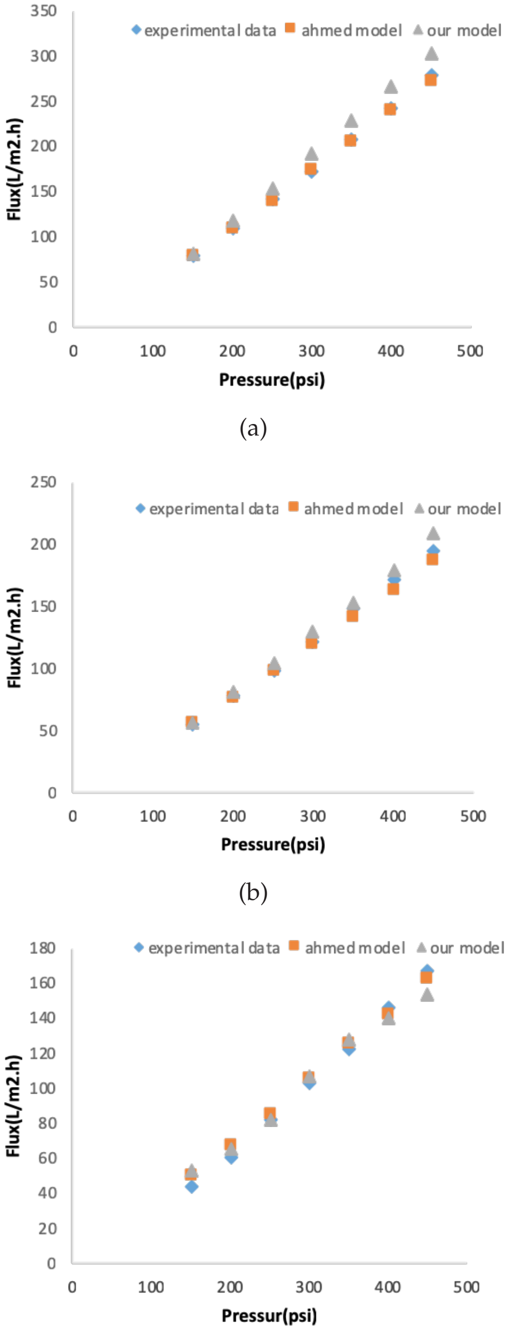


(a)

(b)

(c)

Fig. 1. The comparison between predicted flux by considering (our model) the distinguish between σ_1 and σ_2, and without it (SK model) using Ahmed's data [27] for NF270 a) 0.23M b) 0.6M c) 0.82 M NaCl.



(a)

(b)

(c)

Fig. 2. The comparison between our model and Ahmed's model according to Ahmed's data [27] for NF270 a) 0.23M b) 0.6M c) 0.82 M NaCl.

tions for them and obtained a new equation [Eq. (12)] to introduce a self-fit method to estimate the model parameters whereas Ahmed [27] didn't pay attention to the concept of SK model and introduced electric resistance between salt and membrane as an effective factor for SK model while this factor belongs to mechanistic models like Donnan-steric-pore model. According to Fig. 2 at lower concentrations the Ahmed's modified model is more accurate than my model (Fig. 2a), but at feed concentrations of 0.6 M NaCl and 0.82 M NaCl the differences between two models decrease even in some pressures my model gives better responses (Fig. 2c).

4. Conclusion

This new method has some advantages

1. In my new method, mass transfer coefficient (*k*) has considered in both model equations and all of the model parameters are simultaneously estimated whereby the application of the model has become more simple.
2. In my new method, the estimation of the model parameters depends on input variable like; temperature, applied and osmotic pressure, and experimental parameter of hydraulic permeability of the membrane (L_p), which helps model close to actual conditions and decrease predicted flux error.
3. My new method does not rely on especial mass transfer function like electric resistance exists between feed solution and membrane and there is no deviation from the main concept of the SK model which considers the membrane as a black box, therefore, it can be used to both charged and uncharged feed solutions.
4. My model isn't limited to charged solutions and can help membrane modeling to any natural solutions with different ingredients, because according to the presumption of the model there are no consideration of any especial kind of solution ingredients, and membrane was merely divided into perfect and imperfect sections. Nevertheless, for more verification, more investigations need to be done.

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Symbols

C_b — Feed concentration
C_m — Membrane concentration
C_{m1} — Perfect concentration
C_{m2} — Imperfect concentration
C_p — Permeate concentration
J_s — Total solute flux
J_{scon} — Total convective solute flux
J_{scon1} — Convective solute flux in perfect part
J_{scon2} — Convective solute flux in imperfect part
J_v — Total permeate flux
J_{v1} — Permeate flux in perfect
J_{v2} — Permeate flux in imperfect
k — Mass transfer coefficient
L_p — Hydraulic permeability of the membrane
L_{p1} — Hydraulic permeability of the perfect
L_{p2} — Hydraulic permeability of the imperfect
n — Number of experimental test at a given concentration
P_m — Local solute permeability in the membrane
R — Gas universal constant
R_0 — Observed rejection coefficient
T — Absolute temperature
Δx — Total membrane thickness
ΔP — Applied pressure difference across the membrane
Δp — Osmotic pressure difference across the membrane
σ_1 — Reflection coefficient
σ_2 — Solute and solution coupling coefficient
σ_{21} — Solute and solution coupling coefficient in perfect
σ_{22} — Solute and solution coefficient in imperfect
υ — Van't Hoff factor

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