Comparison of Spiegler–Kedem combined with film theory model and original SK model

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ABSTRACT

In recent days, membrane technology has obtained a special position in water and wastewater treatment, and modeling of such processes seems to be necessary. If the modeling of these processes had not been applied properly, this success would have not been obtained. Researchers should modify traditional models according to the recent needs, and by getting the benefits of modified models, they can get better information to develop the membrane performances through designing appropriate equipment, putting proper input variables such as applied pressures and temperature and cutting down the cost of removal of various salts. It can give key methods to membrane makers to manage membrane processes well. According to the basic concept of Spiegler–Kedem (SK) model, this work shows a way to estimate the parameters of SK model and combined SK model with the film theory (SKCF), and compares SKCF model with SK model, and shows SK model gives better estimations.

Keywords: Nanofiltration; Reverse osmosis; Spiegler–Kedem model; Combined Spiegler–Kedem model with film theory; Modified Spiegler–Kedem model

1. Introduction

Presently, salts are removed from water using various methods like reverse osmosis [1] so that it is the most promising approach to salt removal. It is easy to handle, very moderate in the demand for chemical additives and enables a high extent of water recovery. There are membrane transport models for modeling reverse osmosis processes [2–4]. These models develop not only our knowledge about the membrane processes by introducing some parameters but also help justify mass transfer mechanisms for designing more appropriate membranes. Researchers should have accurate knowledge of original concepts of models and their association with a particular category. Reverse osmosis

process models are divided into mechanistic dependent and mechanistic independent models [5,6]. Spiegler–Kedem (SK) [7] and Speigler–Kedem–Katchalsky (SKK) [8] models belong to mechanistic independent models and don't introduce insight into mass transfer phenomenon [9]. They base on irreversible thermodynamics and despite SKK, SK equations is obtained differentially. Solution diffusion imperfection (SDI) belongs to mechanistic dependent models but in [10] the author has combined SDI with SK to obtain his modified model parameters and asserted that SK model is not able to describe the predicted variation of solute flux with increasing draw concentration in forward osmosis (FO) processes. In addition to reverse osmosis processes SKK had been used to predict the hypothesised

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breakthrough mode in pressure-retarded osmosis (PRO) which would generate, in theory, very high power densities [11]. In addition, SK model is able to estimate well the permeate flux and the rejection for different salt mixtures in reverse osmosis processes [12]. SK model application is still a challenging work for researchers [13]. Mass transfer coefficient k was introduced and combined with SK model (SKCF) [14], however there is a need to rethink the application of the model to obtain a unique k.

The SK model has the following equations:

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

For SKCF model

$$J_v = L_p \left(\Delta p - \sigma_1 \Delta \pi \right), \Delta \pi = \upsilon RT \left(C_b - C_p \right) \exp\left(\frac{J_v}{k} \right) \tag{2}$$

$$J_s = P_m \frac{dc}{dx} + \left(1 - \sigma_2 \right) C_m J_v \tag{3}$$

By integrating Eq. (3) yields:

$$\frac{R_0}{1 - R_0} = \frac{\sigma_2}{1 - \sigma_2} \left(1 - \exp\left(\frac{-\left(1 - \sigma_2\right) J_v}{P_s = \frac{P_m}{\Delta x}} \right) \right) \tag{4}$$

Considering the concentration polarization effect [15] yields:

$$\frac{R_0}{1 - R_0} = \frac{\sigma_2}{1 - \sigma_2} \left(1 - \exp\left(\frac{-\left(1 - \sigma_2\right) J_v}{J_s = \frac{P_m}{\Delta x}} \right) \right) \exp\left(\frac{-J_v}{k} \right) \tag{5}$$

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 the feed side, the permeate side and through the membrane respectively. Hydraulic permeability coefficient L_p can be determined using laboratory methods or theoretical methods [4,13] using the model equations. For SK model, we should estimate L_p and σ_1 Using Eq. (1) and σ_2 and P_s using Eq. (5). Bowen and Welfoot [16] estimated L_p using the first model equation [Eq. (2)] and considered the concentration polarization phenomenon just for the first equation while it should be considered for Eqs. (2) and (5). They assumed that σ_1 and σ_2 are the same while those parameters should separately be estimated especially at high concentrations of salts. In some studies, in SKCF model only parameters of Eq. (5) were estimated [17,18], but both the model equations [Eqs. (2) and (5)] should be considered.

In SKCF mass transfer coefficient k is a common parameter in the equations of the model. As can be seen in Table 1 for the same initial feed concentration with various pressures different mass transfer coefficients k has been obtained, therefore it is necessary to obtain a unique mass transfer coefficient. For this purpose, we should find a way to correlate between Eqs. (2) and (5) and estimate all of the model parameters except L_p which is obtained using laboratory methods and get a unique k. For SKCF using just Eq. (5) by applying three parameters surely gives a better estimation than SK model using just Eq. (4) by applying two parameters (as the numbers of one equation parameters increase the accuracy of the prediction increases) but to meet a unique k we couldn't use just Eq. (5). By introducing a new application for SKCF, we can compare it with SK model and recommend which model gives better estimations.

2. Theory

We can rewrite the first equation of the model as follows:

$$J_{v1} = L_{p1} \left(\Delta p - \Delta \pi \right) \tag{6}$$

$$J_{v2} = L_{p2} \left(\Delta p \right) \tag{7}$$

$$J_v = J_{v1} + J_{v2} \tag{8}$$

$$J_v = \left(L_{v1} + L_{v2} \right) \left(\Delta p - \frac{L_{p1}}{L_{p1} + L_{p2}} \Delta \pi \right) \tag{9}$$

According to Eqs. (9) and (1), it can be written:

$$L_p = L_{p1} + L_{p2}, \sigma_1 = \frac{L_{p1}}{L_{p1} + L_{p2}} \tag{10}$$

$$J_s = J_v C_p \tag{11}$$

$$J_s = J_{s1} + J_{s2} \tag{12}$$

According to the SK model the solute flux is divided into diffusional and convective terms [Eq. (3)], for the convective term the below equations can be written:

$$J_{\text{Sconvective}} = J_{\text{Sconvective1}} + J_{\text{Sconvective2}} \tag{13}$$

$$\left(1 - \sigma_2 \right) C_m J_v = \left(1 - \sigma_{21} \right) C_m J_{v1} + \left(1 - \sigma_{22} \right)$$
$$C_m J_{v2} \sigma_{21} = \sigma_{11} = 1 \text{ and } \sigma_{22} = \sigma_{12} = 0 \tag{14}$$

where $J_{\text{Sconvective}}$ is convective solute flux, C_m is concentration of the membrane,

Using Eqs. (8) and (14) yields:

$$\sigma_2 = \frac{J_{v1}}{J_v} = \frac{L_{p1} \left(\Delta p - \Delta \pi \right)}{L_p \left(\Delta p - \sigma_1 \Delta \pi \right)} \tag{15}$$

Using Eqs. (10) and (15) yields:

$$\sigma_1 = \frac{\sigma_2 \Delta p}{\sigma_2 \Delta \pi + \left(\Delta p - \Delta \pi \right)} \tag{16}$$

Using Eqs. (16) and (1) yields:

$$J_v = L_p \left(\Delta p - \frac{\sigma_2 \Delta p}{\sigma_2 \Delta \pi + (\Delta p - \Delta \pi)} \Delta \pi \right) \tag{17}$$

Using Eq. (17), a new definition for σ_2 is obtained:

$$\sigma_2 = \frac{\sum_{i=1}^{n} \frac{\left(\Delta p_i - \frac{J_{vi}}{L_p} \right)(\Delta p_i - \Delta \pi_i)}{\frac{J_{vi}}{L_p} \Delta \pi_i}}{n} \tag{18}$$

where n is the number of tests done by various pressures with the same initial feed concentration and L_p has already been estimated. σ_2 is estimated by Eqs. (18) and (5) so that both equations should simultaneously be considered. For this purpose, the below equation can be used:

$$\left| \frac{\sigma_{2\text{fit}} - \sigma_2}{\sigma_{2\text{fit}}} \right| < 0.01 \tag{19}$$

where $\sigma_{2\text{fit}}$ k, and P_s are estimated by Eq. (5). σ_2 is determined by Eq. (18) using k that has already been estimated by Eq. (5). If Eq. (19) isn't satisfied, $\sigma_{2\text{fit}}$ (determined σ_2) should be substituted in Eq. (5) and other parameters of Eq. (5) should again be estimated and σ_2 should again be determined using Eq. (18). This procedure should be repeated until Eq. (19) is satisfied. By proceeding with this application, we can get a unique mass transfer coefficient. After this, we are permitted to calculate input variables such as volumetric flux and applied pressure for industrial purposes.

3. Results and discussion

For SK model, we estimate L_p and σ_1 using Eq. (1), and σ_2 and P_s using Eq. (4). We also rewrite equations of the SKCF model and introduce a way to correlate between equations of the model to obtain a unique mass transfer coefficient k by estimating parameters of the model simultaneously and comparing errors of SKCF model with SK model. As can be seen in Table 2, we have obtained a unique mass transfer coefficient k for each concentration using the introduced method, and other parameters of SKCF model are estimated except L_p which obtains using laboratory methods [19]. Mass transfer coefficient is dependent on feed flow rate [17] but at the time of no setting equal feed flow rate for each test (data available in this paper), the variation between k and concentration can be seen [19]. Notwithstanding, in [4,17] k decreases when concentrations increase

As can be seen in Fig. 1a–c at concentration of 0.23, 0.6, and 0.82 M NaCl in all tests SK model shows better estimations than SKCF model. This is because in SK model parameters of the model (L_p and σ_1 from Eq. (1), and σ_2 and P_s from Eq. (4)) are obtained independently while in SKCF model for obtaining a unique k we estimate parameters of Eqs. (2) and (5) dependently and it is a factor to increase errors of the model. L_p is also estimated by the model while in SKCF
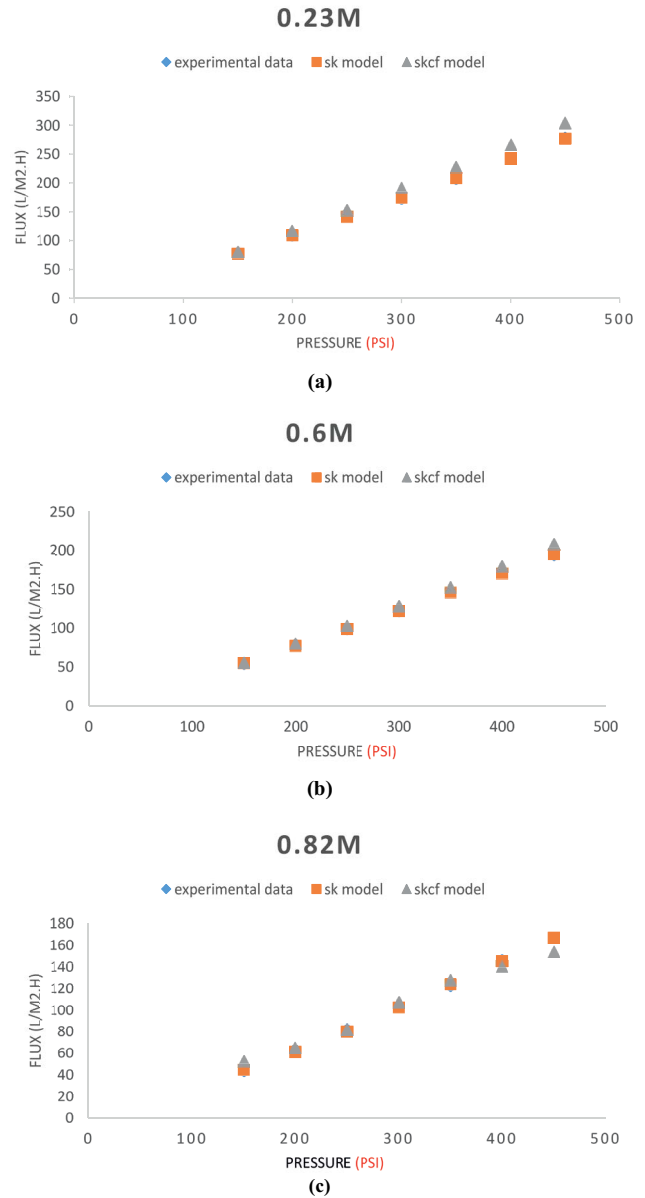

Fig. 1. Comparison between errors estimated by SK model and SKCF model using Ahmed's data [19] for NF270 (a) 0.23 M, (b) 0.6 M and (c) 0.82 M NaCl.

this parameter is obtained using laboratory methods so that it can be a factor to increase the model errors.

4. Conclusion

In this paper, SK model and its application have been introduced. According to that, the parameters of each equation of the model should be estimated independently. The application of SK model combined with the film theory (SKCF) model is problematic because in two equations of the model [Eqs. (2) and (5)] mass transfer coefficient is a common parameter, and we have different mass transfer coefficients. A new method has been introduced. This method is based on rewriting equations of SKCF

Table 1
Different estimated mass transfer coefficient using the equations of the model using Ahmed's data [19] for NF270 obtained from the same initial feed concentrations and various pressures

Concentration	k (L/m² h) Eq. (2)	L_p (L/m² h bar)	σ_1	k (L/m² h) Eq. (5)	P_s (L/m² h)	σ_2
0.23 M NaCl	1,180	0.7	0/6	501	51.1	0.6
0.6 M NaCl	22,613	0/506	0/50	614	74.1	0.42
0.82 M NaCl	41,376	0/465	0/66	731	57.1	0.3

Table 2
Estimated unique mass transfer coefficient using the new method using Ahmed's data [19] for NF270 obtained from the same initial feed concentrations and various pressures

Concentration	k (L/m² h)	P_s (L/m² h)	σ_2	L_p (L/m² h bar)
0.23 M NaCl	388	56.51	0.655	0.89
0.6 M NaCl	290.5	115	0.635	0.78
0.82 M NaCl	209.5	129	0.635	0.75

model and obtaining a correlation between two equations of the model and showing a way to estimate the model parameters so that mass transfer coefficient which is common in the model equations is obtained uniquely. Using this method, the errors of SKCF model are higher than those of SK model because by removing mass transfer coefficient which is common in the model equations, we can estimate the parameters of each equation independently and according to that better results are obtained. From a different point of view, combining the film theory with SK model is not recommended for reverse osmosis process because considering mass transfer coefficient gives insights into mass transfer phenomenon at the boundary layers, and it is a contrast to the concept of SK model which doesn't consider any insights into mass transfer phenomenon and assumes the membrane acts as a black box (the black box begins at the feed side and ends at the permeate side). In addition, discussion on the concentration gradient inside the membrane is also not recommended using this model. Wu [10] the author combined mechanistic dependent SDI model equations [20] with mechanistic independent SK model equations and concluded SK model has a contradictory method for FO processes, but the present modified SKCF model seems to be able to predict FO process (which has no applied pressure) because our model fully matches the main concept of SK model introduced in the paper.

Data availability statement

Acknowledgment

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
$J_{Sconvective}$	—	Total convective solute flux
$J_{Sconvective1}$	—	Convective solute flux in first part
$J_{Sconvective2}$	—	Convective solute flux in second part
J_v	—	Total permeate flux
J_{v1}	—	Permeate flux in first part
J_{v2}	—	Permeate flux in second part
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
$\Delta \pi$	—	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 firs part
σ_{22}	—	Solute and solution coefficient in second part
υ	—	Van't Hoff factor

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