



Comparison of the intrinsic parameters (A , B , and S) of a forward osmosis membrane using pressurized and non-pressurized methods

S.N.S.A. Aziz^a, A.F.H.A. Rahman^a, M.N. Abu Seman^{a,*}, N. Hilal^b

^aFaculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia, Tel. +60 95492904; Fax: +60 95492889; emails: mazrul@ump.edu.my (M.N. Abu Seman), nudraaziz@gmail.com (S.N.S.A. Aziz), fikrihadi@gmail.com (A.F.H.A. Rahman)

^bCentre for Water Advanced Technologies and Environmental Research (CWATER), College of Engineering, Swansea University, Fabian Way, Swansea, SA1 8EN, UK, Tel. +44 1792 606644; email: n.hilal@swansea.ac.uk

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ABSTRACT

Generally, forward osmosis (FO) membrane performance is defined based on its intrinsic parameters, namely the water permeability (A), solute permeability (B), and structural parameter (S). This study was conducted to examine the performance of the commercial membrane NF2 in an FO system and to validate and compare the intrinsic value of A , B , and S obtained by single stage-stage and two-stage methods. The NF2 membrane was unable to demonstrate a good configuration for an FO membrane due to its membrane structure. Comparing the two different orientations in the single-stage method, it appears that both orientations display distinct sets of intrinsic values for the same membrane type. A comparison on the two-stage methods between the pressure-retarded osmosis -FO and reverse osmosis (RO)-FO methods reveals a new standard for the two-stage methods where higher fluxes must be produced from the first stage in order to attain an accurate value of S at the second stage. Additionally, the RO-FO methods were found to be not relevant for testing the ability of a membrane for FO application due to the hydraulic pressure involved during the compaction procedure. The two-stage method with proposed new standards can be the ideal testing procedure for the membrane in FO applications. This is because all the intrinsic values can be separately determined considering all the possible concentration polarization that might occur with both orientations compared with the attempts of fitting all possible values in the generated equations, as in single-stage methods.

Keywords: Intrinsic parameters; Forward osmosis; Single-stage method; Two-stage method; Concentration polarization

1. Introduction

Forward osmosis (FO) is an osmotic membrane separation process that has applications in diverse fields such as desalination of seawater, wastewater treatment, and power generation [1]. FO has recently received great attention due to its advantages, particularly the low energy consumption as the driving force for FO membrane processes is the osmotic pressure difference between the feed solution (FS) and draw solution (DS) [1]. Many have reported on the methods of

FO membrane fabrication including phase inversion, interfacial polymerization, and the layer-by-layer method [2–6]. The development of the FO membrane based on these methods leads to numerous improved FO membranes which have resulted in the membranes with high-water fluxes and low-solute fluxes.

The membrane that allows low-solute flux, resistance to fouling, and has appropriate thickness is ideal for FO systems [7]. Quantitatively, the FO membrane performance is defined based on its water flux (J_w), solute flux (J_s), and mass transfer coefficient (k). Because these parameters depend on

* Corresponding author.

the experimental operating conditions, which vary, the comparison of the performance is of low relevance. Therefore, several approaches have been proposed and applied previously which consider the intrinsic parameters of a membrane [8,9]. The intrinsic parameters are the water permeability (A), solute permeability (B), and structural parameter (S) and because they are constant, they can be considered as the indicators for the characteristic of an FO membrane. Commonly, the standard protocol that is used to characterize the pressurized membrane is the reverse osmosis (RO) test. The bench-scale test equipment is comprised mainly of the membrane test cell and high-pressure pump in which pressure is applied to the membrane to allow the water to permeate through. The method is also applied together with FO test method in the characterization of the FO membrane, known as RO-FO test method. In RO-FO method, the value of A and B are first to be determined through RO method followed by the determination of S value through the FO method [10,11].

Most pressurized membranes, particularly NF/RO membrane, consist of a thin sheet of active layer, thicker porous layer, and a fabric support whereas the FO membrane is usually thinner so that the water can easily permeate, even at very low or no hydraulic pressure, and does not require a fabric back layer as a mechanical support. Therefore, it indeed sounds irrelevant for an FO membrane to be tested using the RO-FO-based test method. Although lower hydraulic pressure is applied after considering the structure of FO membrane, the tests results are likely to be inapplicable to the FO process. This is because the permeate fluxes in the FO process could deviate much compared with when hydraulic pressure is applied [12]. Besides, the applied pressure for the FO membrane needs to be reduced when testing on high permeability FO membranes, in which a limit of permeability is fixed when using RO-FO method on FO membrane [13].

Previously, several tests have been implemented using non-pressurized methods as they are more relevant to demonstrate the ability of the membrane for the FO process. The non-pressurized tests can be categorized as single-stage method (FO or pressure-retarded osmosis [PRO]) and two-stage method which comprises two different orientations of FO experimental setup namely PRO-FO. For instance, an inclusive discussion on the single-stage FO test protocols was presented by Tiraferri et al. [8]. The authors also provided very useful supplementary materials that can be used to obtain the characteristic values of a membrane. Besides, as they compare the FO test with the RO-FO test, they remarked that the advantage of using single-stage FO method over the RO-FO is that the fitted values obtained by the applied models. In fact, overall discussions in their works were focusing on how to control and conduct the test cautiously so that better-fitted values could be attained. Moreover, it is widely elaborated in the study that several assumptions need to be accounted when employing this test. Even though it is concluded that the RO-FO methods shows deviated values from the FO single-stage method, it is not proven that the tested membranes behaving similarly as if when it is tested using single-stage PRO method. It is crucial to know the characteristics of the membrane through a single stage at a different orientation. Usually, the performance parameters obtained by PRO is higher than the FO [13]; however, it is supposing not to affect the value of the intrinsic parameter of the membrane.

It is also important to note that the single-stage method is extensively been employed only after the Tiraferri's calculation model is released. Most studies employing the single-stage methods of both FO and PRO solely compare the flux performance between the two tests but not the intrinsic parameters [12,14,15]. This might be due to the fact that the models developed by Tiraferri's in the excel spreadsheets is the first established single-stage method and is specific for FO orientation only. Therefore, the unavailability of the ready-to-use solver for PRO modes limits the comparative studies on the characteristics of both modes. Although all these methods have been conducted by many researchers (refer Table 1), yet no comprehensive study on comparing between the single stage of two different orientations and two stages of two different configurations is discussed in a single study.

The first discovered two-stage PRO-FO method was proposed by Kim et al. [16], yet was not experimentally demonstrated. Their theory seems reliable as both transport parameters and structural parameters were separately determined based on its corresponding layer. This is similar to the findings presented by Liu et al. [17], where they concluded that the surface modification on the active layer of the membrane changes the values of A and B while S remains the same as before the modification was implemented. Because there is no recognized study that conducted the two-stage method earlier, we took the initiative to conduct the test and compare it with all available methods.

Table 1
Summary of the previous works on the determination of structural parameter, S

Method	Membrane	S (μm)	Reference
FO	Hand-cast TFC	374	[8]
	HTI-CTA	498	
	SW30 No PET	1,557	
	Oasys TFC	513	
RO-FO	Hand-Cast TFC	370	[8]
	HTI-CTA	326	
	SW30 No PET	1,850	
	Oasys TFC	434	
RO-PRO	HTI-CTA	388	[18]
RO-FO	HTI-CTA	467	[18]
RO-FO	HTI-CTA	481	[19]
RO-FO	PVDF-TFC	329	[6]
	PES/SPSf-TFC	238	
RO-FO	Oasys TFC	550	[20]
	HTI-CTA	700	
RO-PRO	Oasys TFC	220	
	HTI-CTA	450	
FO	PES-TFC	217	[14]
	CN/rGO 0.5-PES	163	
	CN/rGO 1.0-PES	463	
FO	TFC-O-II	31.9	[15]

TFC, Thin film composite; HTI-CTA, Hydration Technology Innovations (Manufacturer's name)-cellulose triacetate; PET, polyester; PVDF, polyvinylidene difluoride; PES, polyether sulfone; SPSf, sulfonated polysulfone.

Therefore, the objectives of this paper are to investigate the performance of a commercial asymmetric nanofiltration polyethersulfone membrane (NF2) in an FO system and validate the two-stage FO-based method proposed by Kim et al. [16] in obtaining the intrinsic value of A , B , and S and compare it with the single-stage FO-based method of both orientations. This study will also shed light on the reliability of RO-FO methods by comparing the intrinsic values obtained through this method and the non-pressurized method. The comparison is made by utilizing the NF2 membrane without removing the fabric support for all the test modes in order to minimize the effect of pressure, especially during RO protocol.

2. Materials and methods

2.1. Materials

All the tests were utilized on an asymmetric commercial NF2 membrane purchased from Amfor Inc. (China). The additional details of the membrane are provided in Table 2. The DS is prepared by using the ultrapure water provided by a Milli-Q ultrapure water system and sodium chloride of $\geq 99.5\%$ purity supplied by Sigma-Aldrich.

2.2. Methodology

Table 3 presents the operating conditions applied to FO system throughout this research and are independent of the membrane orientation.

2.2.1. Single-stage method

Although the single-stage FO has been proposed by many, there is still an insufficient number of researchers that are conducting the intrinsic characterization test using this method. This is mainly because the most established method is the RO-FO method and the lack of clarification on the non-pressurized method. A single-stage test can be

conducted in two ways: with the active layer facing the FS with support layer facing DS, known as active layer facing feed solution (ALFS) (FO mode); and active layer facing DS with support layer facing the FS known as active layer facing draw solution (ALDS) (PRO mode). Initially, the NF2 membrane was pre-wetted overnight. The test took place using a CF042P-FO cell, which poses a membrane active area of 42 cm^2 with 2.28 mm and 3.9 cm of depth and width, respectively. The system works in a co-current equipped with the peristaltic pump to circulate the DS and FS in the FO cell at a velocity of 3.75 cm s^{-1} . The experiment began by circulating the ultrapure water on both the DS and FS sides to ensure temperature equilibrium throughout the system. Once thermally stable, a certain amount of concentrated NaCl solution is combined with the DS to reach to an approximate concentration of 0.5 M while FS remained as ultrapure water. Alternatively, 1 L NaCl of 0.5 M can be prepared earlier and employed to initiate the test as the initial concentration. The mass change was automatically recorded every 5 min using WinCT© software, whereas the conductivity was measured by conductivity meter (Eutech Instruments PC2700). The J_w is then determined after the system reaches the steady state after approximately 60 min. Next, the DS is replaced with the second concentration at 0.75 M, and the same parameters were observed. The procedures were repeated for third and fourth concentrations of 1.0 M and 1.25 M accordingly. These protocols were similar for both modes (ALFS and ALDS) except for the orientation of the membrane and the modeling equations used to obtain the A , B , and S values, as shown in Fig. 1. Eqs. (1) and (2) are the derived equations for the J_w and J_s in ALFS system, respectively, while Eqs. (3) and (4) are the derived equations for the J_w and J_s in ALDS system, respectively [13]. Additional details on the following equations can be found elsewhere [8,18,20].

$$J_w = A \frac{\left[\pi_{D,b} \exp\left(-\frac{J_w S}{D}\right) - \pi_{F,b} \exp\left(\frac{J_w}{k}\right) \right]}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w}{k}\right) - \exp\left(-\frac{J_w S}{D}\right) \right]} \quad (1)$$

$$J_s = B \frac{\left[C_{D,b} \exp\left(-\frac{J_w S}{D}\right) - C_{F,b} \exp\left(\frac{J_w}{k}\right) \right]}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w}{k}\right) - \exp\left(-\frac{J_w S}{D}\right) \right]} \quad (2)$$

$$J_w = A \frac{\left[\pi_{D,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \exp\left(\frac{J_w S}{D}\right) \right]}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{k}\right) \right]} - \Delta P \quad (3)$$

$$J_s = B \frac{\left[C_{D,b} \exp\left(-\frac{J_w}{k}\right) - C_{F,b} \exp\left(\frac{J_w S}{D}\right) \right]}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{k}\right) \right]} \quad (4)$$

Table 2

The detailed data of the commercial NF2 membrane

Type	NF2
Test pressure (psi)	150
Solute concentration (mg/L)	2000
MgSO ₄ rejection (%)	95
Water flux @ 25°C @ 1.0 MPa (L m ⁻² h ⁻¹)	100

Table 3

Typical operating conditions for standards FO test experiments

Variable	Draw solution (DS)	Feed solution (FS)
Temperature (°C)	23 ± 1	23 ± 1
Gauge pressure (bar)	0	0
NaCl concentration (M)	0, 0.5, 0.75, 1.0, 1.20	0
Initial liquid volume (L)	1	1
Hydraulic flow rate (cm ³ s ⁻¹)	3.3333	3.3333

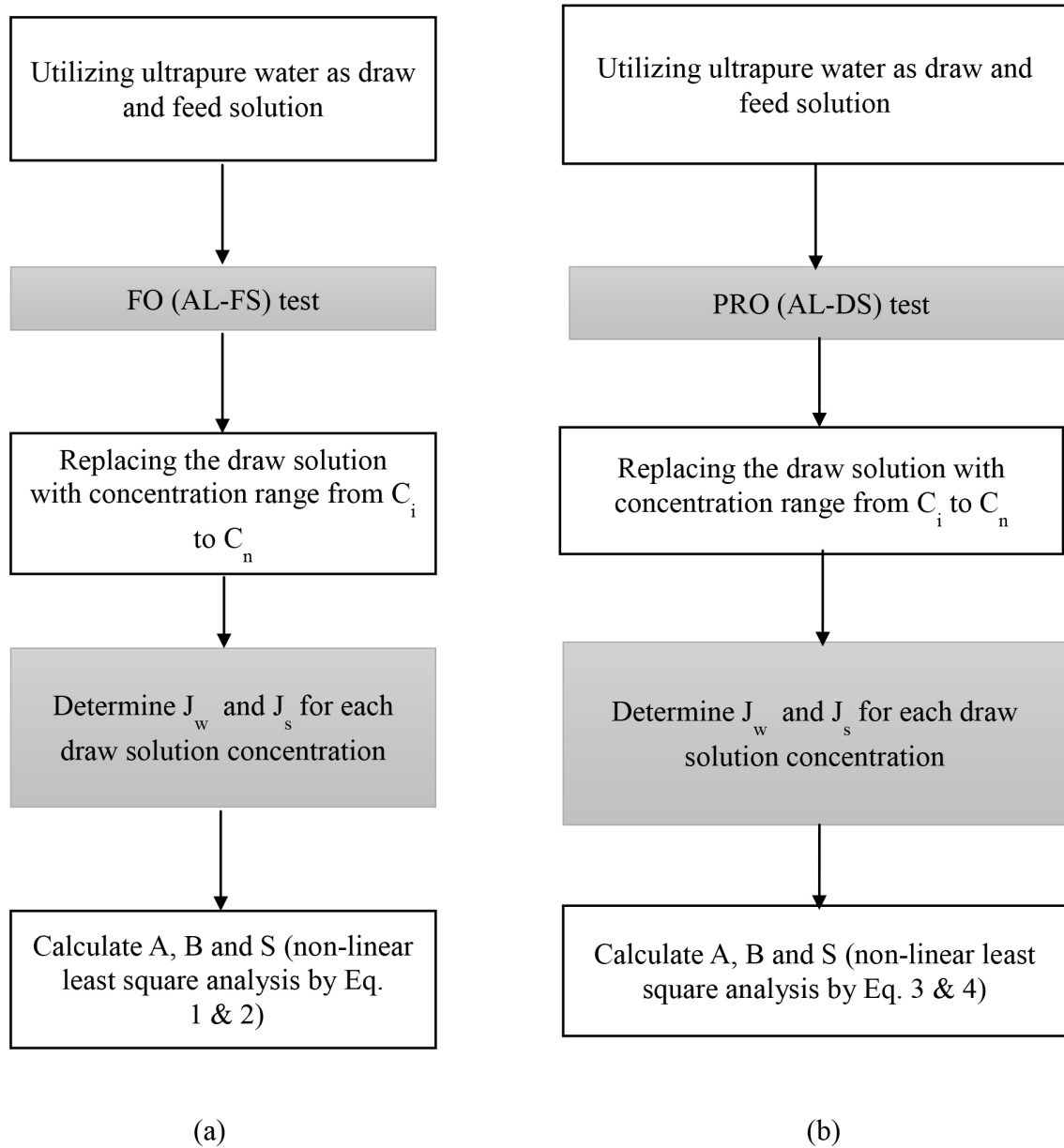


Fig. 1. Flow chart of the single-stage method for (a) FO mode [8] and (b) PRO mode [13].

where $\pi_{D,b}$ is the bulk osmotic pressure of the DS at the concentration $C_{D,b}$; $\pi_{F,b}$ is the bulk osmotic pressure of the FS at the concentration $C_{F,b}$; and P is the hydraulic pressure applied, which is considered zero in this case. Both terms $(J_w S/D)$ and (J_w/k) depict the internal concentration polarization (ICP) and external concentration polarization (ECP), respectively; D is the diffusion coefficient value and k is the mass transfer coefficient. The negative and positive of the exponents indicate the concentrative and dilutive at that particular time, respectively.

The ECP and ICP are the main issues occurring in FO membrane process even though the fouling is less severe in FO compared with the pressurized membrane. They both affect the osmotic pressure between the two substrates as either making the FS and DS more diluted or concentrated at the membrane surface compared with the bulk concentration. The details on this concentration polarization (CP)

are described elsewhere [21–23]. Eventually, there should be eight equations with three unknowns for each test. Numerically, the value of A , B , and S should be obtained easily using a non-linear least square analysis.

2.2.2. Two-stage method

2.2.2.1. First-stage test

PRO mode (ALDS)

The active layer of a membrane is evaluated based on the values of water and solute permeability (A and B), while S is related to the support layer of the membrane. Therefore, the two-stage test comprises both orientations of FO membrane. The membrane is first operated in the ALDS system with ultrapure water utilized as FS and DS until steady state

is achieved. Similar protocols of the single stage are repeated, except here the value of J_w obtained at each concentration is applied to the following equation [18]:

$$J_w = A\Delta\pi \quad (5)$$

where $\Delta\pi$ is the difference of osmotic pressure value between the FS and DS which, after correction for the effect of ECP, becomes as follows [18]:

$$J_w = A \left[\pi_{D,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \right] \quad (6)$$

The calculated value of A is reported as the average of four independent measurement at each concentration of DS or alternatively. A can be obtained as a slope from the graph of J_w plotted against the $\left[\pi_{D,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \right]$. Meanwhile the J_s is calculated based on the following expression [8]:

$$J_{s,i} = \frac{C_{F,i}(V_{F0,i} - J_{w,i}A_m t) - C_{F0,i}V_{F0,i}}{A_m t} \quad (7)$$

where $C_{F,i}$ and $C_{F0,i}$ are the final and initial NaCl concentrations in the FS, respectively; $V_{F0,i}$ is the initial volume of FS; A_m is the membrane effective area; and t is the length of time taken for the process. Corresponding value of J_s at different concentration was then taken to obtain the value of solute permeability, B , which can be yielded by the following [24]:

$$J_s = B\Delta C \quad (8)$$

where ΔC is the difference between the concentration of DS and FS. Considering the CP in PRO mode, both bulk concentration of DS ($C_{D,b}$) and the bulk concentration of FS ($C_{F,b}$) is corrected with the ECP modulus and ICP modulus, respectively. For an asymmetric membrane that is composed of active and porous support layers, the concentration of DS at the surface of the active layer is different compared with the bulk solution concentration and is much lower. Similarly, the concentration of FS within the porous layer near to the active layer is higher than that of FS bulk concentration. Thus rearranging Eq. (8) yields the following [16]:

$$B = \frac{J_s}{C_{D,b} \exp\left(-\frac{J_w}{k}\right) - C_{F,b} \exp\left(-\frac{J_w}{k}\right)} \quad (9)$$

The summary of the first-stage procedures method for PRO mode and RO mode is presented in Fig. 2.

RO mode

The water flux, J_w , is measured in a stirred-cell RO system (Sterlitech, HP4750, WA, USA) by using pure water at different hydraulic pressures within the range of 3–8 bar:

$$J_w = \frac{\Delta V}{A_m \times \Delta t} \quad (10)$$

where ΔV is the permeate volume and Δt is the time interval of the process. Thus, the water permeability, A , then can be obtained by determining the slope of the linear equation between J_w and hydraulic pressure difference ΔP [24]:

$$J_w = A\Delta P \quad (11)$$

By using NaCl with a concentration of 200 mg/L tested at 7 bar (at a constant stirring rate of 100 rpm), the rejection value, R , can be determined from the concentration difference between the feed and permeate as follows [25]:

$$R = 1 - \frac{C_p}{C_f} \quad (12)$$

where C_p and C_f are the permeate concentration and the feed concentration, respectively. Therefore, the solute permeability, B , can be easily obtained by the following expression [26]:

$$B = J_w \left(\frac{1-R}{R} \right) \exp\left(-\frac{J_w}{k}\right) \quad (13)$$

2.2.2.2. Second-stage test in FO mode (ALFS) After the value of A and B has been obtained from the first stage, the runs for this stage is employed in a way that the DS is facing porous support layer of the membrane to attain the value of S . Similar protocols were again repeated at this stage except for the orientation of the membrane. The J_w and J_s were calculated in the same manner as described earlier using the newly recorded data of ALFS system. Finally, the S value can be calculated using either of Eqs. (1) and (2) as described in Fig. 3. Specifically, this stage is also similar to the second stage in RO-FO method as described previously.

3. Results and discussion

3.1. Single-stage method

The single-stage FO methods were employed in the two different orientations known as ALFS (FO mode) and ALDS (PRO mode). In our study, for PRO mode, there is no hydraulic pressure was applied to the unit. As described earlier, both tests were conducted separately, and all the measured parameters were calculated based on four different DS concentration. The variation of DS concentration is introduced to improve the accuracy of the intrinsic value obtained from each mode. The coefficients A , B , and S were used as the regression parameters in a least-squares nonlinear fitting. The predicted water fluxes were calculated based on Eq. (1) using the fitted data of A , B , and S . The measured and the ideal value of water fluxes are plotted and presented in Fig. 4. Comparing the two results at different orientations, the measured water

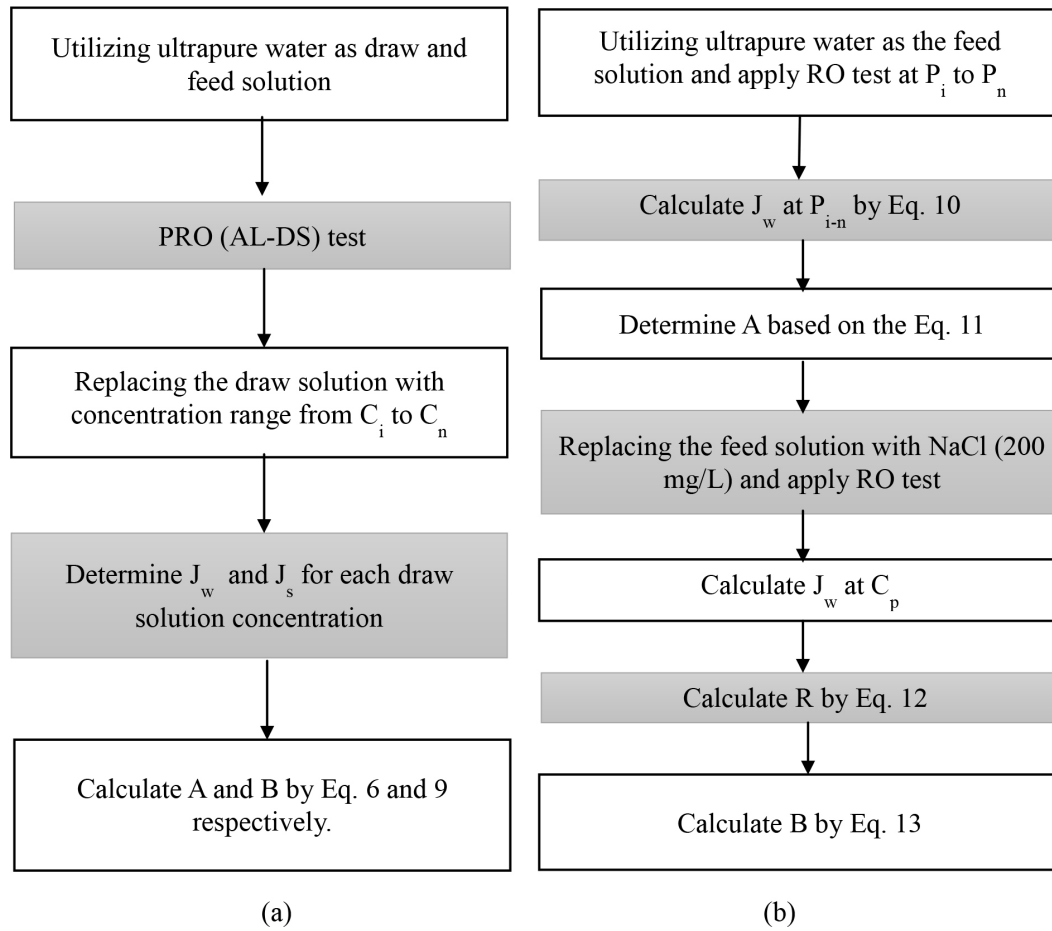


Fig. 2. Flow chart of the first stage in the two-stage method for (a) PRO-FO [16] mode and (b) RO-FO [13] mode.

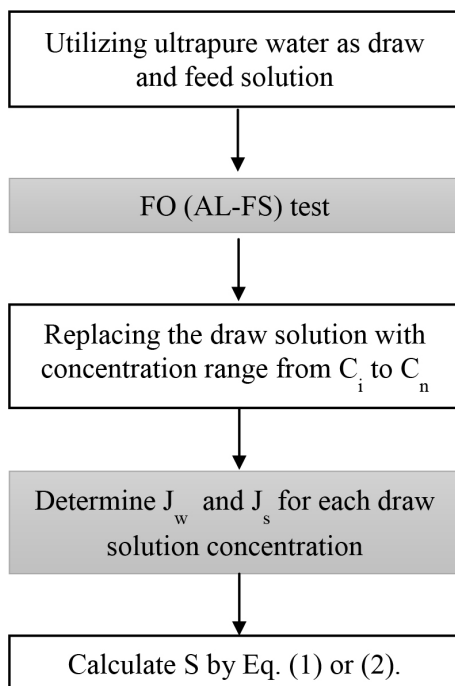


Fig. 3. Flow chart of the second stage in the two-stage method for both PRO-FO [16] and RO-FO [13] modes.

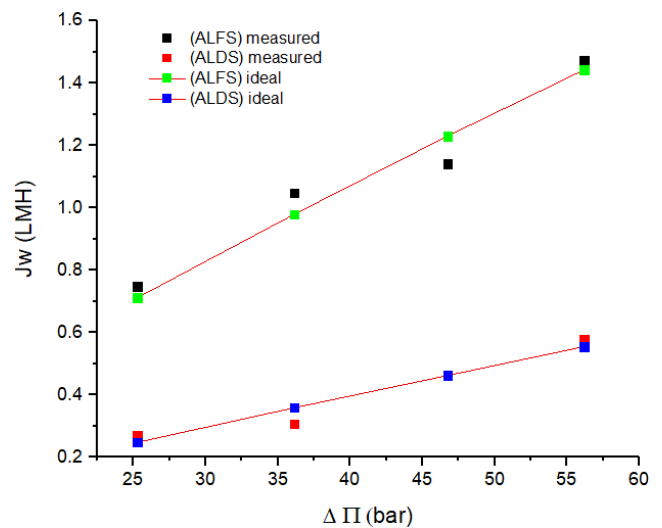


Fig. 4. Measured and predicted (ideal) water flux, J_w in both FO and PRO mode.

fluxes were absolutely tabulated between the ideal water flux values.

It is interesting to note that the water flux observed in ALDS is lower than ALFS in this study, which is contradict to what has been established earlier [27–29]. This inconsistency may

be due to the intrinsic values of the membrane or the hydrodynamic factor during the test. Accounting the proportional relation between osmotic pressure and DS concentration, both J_w and J_s increase with the increase of DS concentration as observed in Fig. 5. From these data, it is clear that the solute flux, J_s , is higher than the water flux, J_w , for both orientations. Based on Eq. (7), the determination of J_s is mainly dependent on the concentration of the FS which means that high J_s would be measured when the final FS concentration is high. In other words, this shows that more solutes have been allowed to diffuse across the NF2 membrane from the DS to FS.

Table 4 shows different values of J_w and J_s at different concentrations, and the corresponding values of A , B , and S for NF2 membrane. Although similar protocols and membrane were applied to both methods, the intrinsic values obtained are significantly different between the two modes. For example, the structural parameter of the membrane in the orientation of ALFS is 831 μm is higher than that obtained through the orientation of ALDS which is at 208 μm . These values could be explained by the transport permeability coefficient calculated correspondingly. Generally, the A and B are proportional to S , therefore a large value of S would lead to a higher permeability coefficient [8,30].

The solute permeability coefficient, B , for this membrane (NF2) is higher than the water permeability coefficient, A , in both modes, which express a bad configuration for an FO membrane where A supposedly higher than B . This is because NF2 is a commercial NF asymmetric membrane that is commonly used in pressurized systems and has a greater thickness than a common FO membrane. The thicker the membrane, the harder for the permeate to pass through. This occurrence further supports the findings of a previous study where a very low flux was recorded when the TFC NF membrane is applied to the FO system [31].

Considering that the surface of the active layer has low hydrophilicity and that the crossflow velocity of the system is very low (3.75 cm s^{-1}); therefore, the values of solute and water permeation are relatively low. These results match those observed in earlier studies where they conclude that the low crossflow velocity plays a role in increasing the ECP effect and thus reducing the water fluxes [20,32]. For instance, Bui et al. [20] stated that an increment of 40% of water flux is obtained in both FO and PRO modes when they increase the velocity from 10.3 to 20.7 cm s^{-1} . Nevertheless, this is consistent with the discussion provided by Xu et al. [33] where they claimed that the effect of the crossflow rate on a membrane

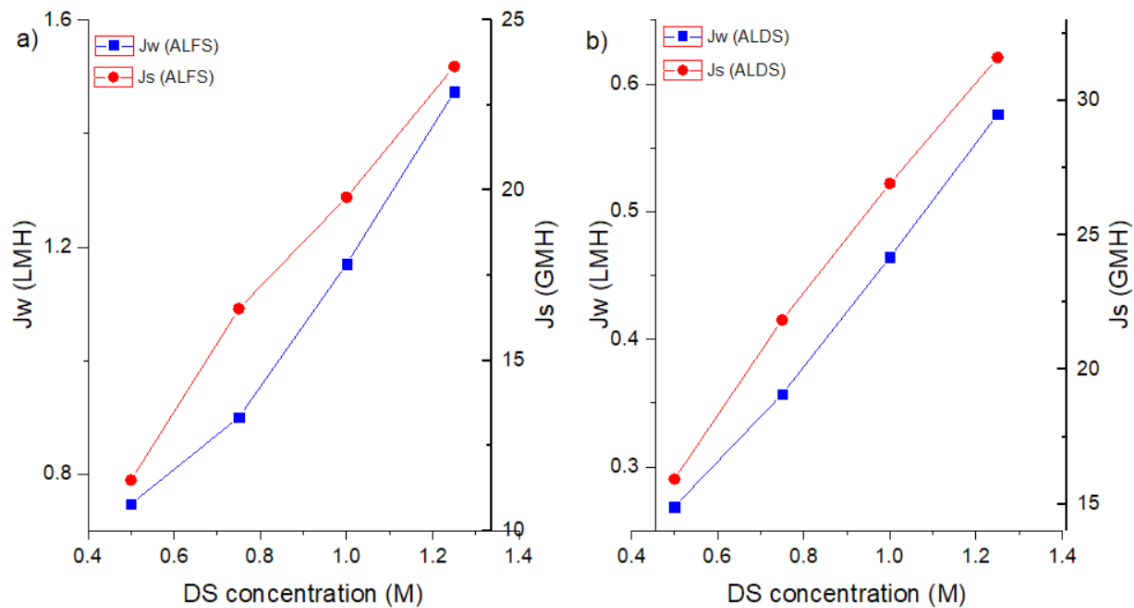


Fig. 5. Overall water and solute flux behavior over the range of DS concentration for (a) ALFS and (b) ALDS.

Table 4
Summary of the primary findings of two different single-stage method

Mode	Concentration phase (M)	J_w ($\text{L m}^{-2} \text{ h}^{-1}$)	J_s ($\text{g m}^{-2} \text{ h}^{-1}$)	A ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	B ($\text{L m}^{-2} \text{ h}^{-1}$)	S (μm)
ALFS (FO mode)	0.5	0.7476	11.49	0.03	0.375	831
	0.75	1.0476	17.52			
	1.0	1.1405	19.25			
	1.20	1.4738	23.64			
ALDS (PRO mode)	0.5	0.2690	15.93	0.01	0.512	208
	0.75	0.3071	21.85			
	1.0	0.4643	26.92			
	1.20	0.5762	31.61			

became more prominent at the active layer prior to ECP, compared with the porous support layer whereas is prone to ICP. Commonly, at an average crossflow velocity ($10\text{--}20\text{ cm s}^{-1}$), the ECP is negligible due to the significant presence of ICP within the porous layer and the velocity is adequate to reduce the possibility of additional concentration profile at the surface of the active layer [33]. Because the FS in this study is ultrapure water, the ECP effect in the ALFS mode and the ICP effect in ALDS mode can be neglected. Prior to the ECP effect that is more significant in the case of low crossflow velocity as in this case, the ALDS recorded rather lower fluxes compared with ALFS mode. While these findings did not confirm that it is because of the low performances of the NF2 membrane that the intrinsic values are dissimilar for the different orientations, yet it did partially prove that the application of the single-stage method for determining the intrinsic values is not consistent as it diverges when different orientation is applied.

3.2. Two-stages method

The two-stage methods were observed in two ways, namely PRO-FO and RO-FO methods. It is truly crucial to compare between the parameters obtained through this research and that obtained by conventional two-stage RO-FO method. The findings as presented in Table 5 confirm the discussion on the earlier methods (see above) as the solute permeability for NF2 membrane is higher than the water permeability thus not suitable to be directly applied in FO system.

During the PRO-FO method, the A and B parameters, which were obtained from PRO phase, were used as the permeability coefficients in Eq. (1) to measure S using the data logged for FO phase. A strong relationship between A , B , and S has been reported earlier, where larger structural parameters lead to lower fluxes consequently showing low-transport permeability coefficient [16,34]. Surprisingly, see Fig. 6, the S in this condition falls within the range of negative values which is an illogical amount for S . It seems possible that this result is due to the low-transport permeability coefficients calculated from the first stage. Yet again the lower transports permeability coefficients in ALDS compare with ALFS are due to the crossflow velocity that enhances the ECP effect in ALDS mode [35]; hence, low fluxes and permeability coefficients are obtained. For an average crossflow velocity of two stages PRO-FO method, the PRO phase usually yields higher water fluxes [36,37], thus the S parameter can be easily determined. However, in RO-FO method, the value of A and B attained in the RO mode is higher (mainly due to high fluxes) than that obtained through PRO method leading to a very high value of S which is $15,127\text{ }\mu\text{m}$. The higher value of S also obtained for RO commercial membranes (BW30, $S\approx 37,500\text{ }\mu\text{m}$ and SW30-XLE, $S\approx 80,000\text{ }\mu\text{m}$) by other studies [38,39] using the same RO-FO mode method. This indicates that for a successful test using two-stage methods, the first stage must have attained higher water flux than the second stage or otherwise an accurate value of S cannot be achieved. For example, taking into consideration the value of A and B from the single-stage FO mode, which was $0.03\text{ Lm}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$ and $0.375\text{ Lm}^{-2}\text{ h}^{-1}$ as the permeability coefficient of the first stage and applied for the calculation of S for the second stage, the value would fall within the logical range of S as marked in Fig. 6. Another possible conclusion to this is that the RO-FO

Table 5
Summary of the primary findings of two different two-stage methods

Method	Mode phase	A ($\text{L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$)	B ($\text{L m}^{-2}\text{ h}^{-1}$)	S (μm)
PRO-FO	PRO (ALDS)	0.01	0.512	–
	FO (ALFS)	–	–	*
RO-FO	RO	9	15.37	–
	FO (ALFS)	–	–	15,127

*The value obtained is in the negative range.

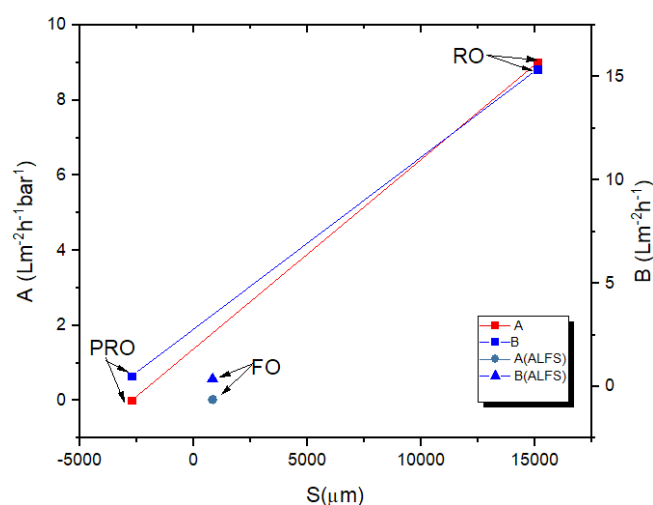


Fig. 6. The summary of A and B in the large range of S values.

method is rather unreliable for determining the intrinsic value for an FO configuration due to high hydraulic pressure applied during the stage of RO. This was previously investigated by several researchers and is explained elsewhere [9,16,40]. In fact, the RO stage is more laborious compared with FO method as clearly shown in Fig. 2(b) earlier.

4. Conclusions

In the FO process, the mass transfer boundary layers occur on both sides of the selective interface of the membranes known as ICP when it occurs within the porous layer and ECP when it occurs right on the surface of the active layer. In most cases of FO process, the ECP is neglected due to the significant presence of ICP. As ICP occurs within the porous layer, it becomes complicated to flush away as it is with ECP where ECP is usually swept easily by increasing the flow velocity. Although ICP could be reduced by increasing the crossflow velocity, this is not effective at higher velocity rates because the major influence on the ICP is the concentration of the DS [33]. Nevertheless, in this study, at a very low crossflow velocity, the potential ECP has increased significantly beyond the ICP itself as it proved through the water and solute flux obtained in all the test modes except RO. It can be easily stated that NF2 membrane has a very low-intrinsic value for the FO system. Further works including enhancing the hydrophilicity of the membrane and/or increasing the crossflow velocity of the operation are required to establish this membrane relevantly.

The comparison of ALFS and ALDS single-stage method in this study is quite uncertain due to low crossflow velocity used during the operation. However, regardless of the cross-flow velocity, both measured parameters for ALDS and ALFS are inconsistent, with ALDS showing very low fluxes, low transport permeability coefficient, and low structural parameter. Although low structural parameter is good for an FO membrane, in this case, it is believed that the low value of S was associated with the low A and B values.

The most interesting findings in this study were that the first stage in the two-stage method must have higher permeate fluxes than the second stage in order to obtain the value of S using the governing equations mentioned in the first section. However, we suggest that if the low fluxes obtained in the first stage are to be used to calculate the value of S , then Eqs. (1)–(4) should be modified to reflect the conditions. In addition, the discoveries through RO-FO methods confirm the hypotheses that the irrelevancy of RO stages in RO-FO method is undeniably correct as the values obtained in RO stages are considerably higher than those obtained from the PRO method.

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References

- [1] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: opportunities and challenges. *J. Membr. Sci.*, 396 (2012) 1–21.
- [2] N. Joseph, P. Ahmadian, R. Hoogenboom, I. Vankelecom, Layer-by-layer preparation of polyelectrolyte multilayer membranes for separation. *Polym. Chem.*, 5 (2014) 1817–1831.
- [3] A.F. Ismail, W.J. Lau, A.F. Ismail, Synthesis of thin film nanocomposite forward osmosis membrane with enhancement in water flux without sacrificing salt rejection. *Desalination*, 330 (2013) 90–99.
- [4] X. Liu, H.Y. Ng, Fabrication of layered silica–polysulfone mixed matrix substrate membrane for enhancing performance of thin-film composite forward osmosis membrane. *J. Membr. Sci.*, 481 (2015) 148–163.
- [5] M.A.M. Yusof, M.N. Abu Seman, N. Hilal, Development of polyamide forward osmosis membrane for humic acid removal. *Desal. Wat. Treat.*, 57 (2016) 29113–29117.
- [6] K.Y. Wang, T.S. Chung, G. Amy, Developing thin-film-composite forward osmosis membranes on the PES/SPSf substrate through interfacial polymerization. *AIChE J.*, 58 (2012) 770–781.
- [7] R. Revanur, I. Roh, J.E. Klare, A. Noy, O. Bakajin, Thin Film Composite Membranes for Forward Osmosis, and Their Preparation Methods, 2014, Google Patents.
- [8] A. Tiraferri, N.Y. Yip, A.P. Straub, S.R.-V. Castrillon, M. Elimelech, A method for the simultaneous determination of transport and structural parameters of forward osmosis membranes. *J. Membr. Sci.*, 444 (2013) 523–538.
- [9] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia–carbon dioxide forward osmosis: influence of draw and feed solution concentrations on process performance. *J. Membr. Sci.*, 278 (2006) 114–123.
- [10] X. Liu, H.Y. Ng, Double-blade casting technique for optimizing substrate membrane in thin-film composite forward osmosis membrane fabrication. *J. Membr. Sci.*, 469 (2014) 112–126.
- [11] D. Emadzadeh, W.J. Lau, T. Matsuura, A.F. Ismail, M. Rahbari-Sisakht, Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization. *J. Membr. Sci.*, 449 (2014) 74–85.
- [12] D. Stillman, L. Krupp, Y.-H. La, Mesh-reinforced thin film composite membranes for forward osmosis applications: the structure–performance relationship. *J. Membr. Sci.*, 468 (2014) 308–316.
- [13] T.Y. Cath, M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio, A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, J. Lampi, L.D. Nghiem, M. Xie, N.Y. Yip, Standard methodology for evaluating membrane performance in osmotically driven membrane processes. *Desalination*, 312 (2013) 31–38.
- [14] Y. Wang, R. Ou, H. Wang, T. Xu, Graphene oxide modified graphitic carbon nitride as a modifier for thin film composite forward osmosis membrane. *J. Membr. Sci.*, 475 (2015) 281–289.
- [15] R.C. Ong, T.-S. Chung, J.S. de Wit, B.J. Helmer, Novel cellulose ester substrates for high performance flat-sheet thin-film composite (TFC) forward osmosis (FO) membranes. *J. Membr. Sci.*, 473 (2015) 63–71.
- [16] B. Kim, G. Gwak, S. Hong, Review on methodology for determining forward osmosis (FO) membrane characteristics: water permeability (A), solute permeability (B), and structural parameter (S). *Desalination*, 422 (2017) 5–16.
- [17] C. Liu, J. Lee, C. Small, J. Ma, M. Elimelech, Comparison of organic fouling resistance of thin-film composite membranes modified by hydrophilic silica nanoparticles and zwitterionic polymer brushes. *J. Membr. Sci.*, 544 (2017) 135–142.
- [18] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. *J. Membr. Sci.*, 284 (2006) 237–247.
- [19] W.A. Phillip, J.S. Yong, M. Elimelech, Reverse draw solute permeation in forward osmosis: modeling and experiments. *Environ. Sci. Technol.*, 44 (2010) 5170–5176.
- [20] N.-N. Bui, J.T. Arena, J.R. McCutcheon, Proper accounting of mass transfer resistances in forward osmosis: improving the accuracy of model predictions of structural parameter. *J. Membr. Sci.*, 492 (2015) 289–302.
- [21] M. Gruber, C.J. Johnson, C.Y. Tang, M.H. Jensen, L. Yde, C.H. -Nielsen, Computational fluid dynamics simulations of flow and concentration polarization in forward osmosis membrane systems. *J. Membr. Sci.*, 379 (2011) 488–495.
- [22] J. Heikkinen, H. Kyllönen, E. Järvelä, A. Grönroos, C.Y. Tang, Ultrasound-assisted forward osmosis for mitigating internal concentration polarization. *J. Membr. Sci.*, 528 (2017) 147–154.
- [23] S. Subramani, R.C. Panda, B. Panda, Studies on performances of membrane, draw solute and modeling of forward osmosis process in desalination – a review. *Desal. Wat. Treat.*, 70 (2017) 46–63.
- [24] K. Lee, R. Baker, H. Lonsdale, Membranes for power generation by pressure-retarded osmosis. *J. Membr. Sci.*, 8 (1981) 141–171.
- [25] P. Hajighahremanzadeh, M. Abbaszadeh, S.A. Mousavi, M. Soltanieh, H. Bakhshi, Polyamide/polyacrylonitrile thin film composites as forward osmosis membranes. *J. Appl. Polym. Sci.*, 133 (2016) 44130.
- [26] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: principles, applications, and recent developments. *J. Membr. Sci.*, 281 (2006) 70–87.
- [27] S.J. Zaidi, F. Fadhillah, Application of Multilayer Thin Film Technology in Desalination Membrane, in *Desalination*, InTech, London, UK, 2017.
- [28] A. Zirehpour, A. Rahimpour, S. Khoshhal, M.D. Firouzjaei, A.A. Ghoreyshi, The impact of MOF feasibility to improve the desalination performance and antifouling properties of FO membranes. *RSC Adv.*, 6 (2016) 70174–70185.
- [29] S.Y. Yeo, Y. Wang, T. Chilcott, A. Antony, H. Coster, G. Leslie, Characterising nanostructure functionality of a cellulose triacetate forward osmosis membrane using electrical impedance spectroscopy. *J. Membr. Sci.*, 467 (2014) 292–302.
- [30] Y.C. Kim, M. Elimelech, Adverse impact of feed channel spacers on the performance of pressure retarded osmosis. *Environ. Sci. Technol.*, 46 (2012) 4673–4681.

- [31] S.O. Alaswad, S. Al-aibi, E. Alpay, A. Sharif, Efficiency of organic draw solutions in a forward osmosis process using nano-filtration flat sheet membrane, *J. Chem. Eng. Process Technol.*, 9 (2018) 1–10.
- [32] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, *Environ. Sci. Technol.*, 43 (2009) 6769–6775.
- [33] Y. Xu, X. Peng, C.Y. Tang, Q.S. Fu, S. Nie, Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis performance in a spiral wound module, *J. Membr. Sci.*, 348 (2010) 298–309.
- [34] S.S. Manickam, J.R. McCutcheon, Understanding mass transfer through asymmetric membranes during forward osmosis: a historical perspective and critical review on measuring structural parameter with semi-empirical models and characterization approaches, *Desalination*, 421 (2017) 110–126.
- [35] K.M. Julie, Arias-Paic, Final Report 2015-01-7911 in Forward Osmosis Evaluation and Applications for Reclamation, U.S., Denver, CO, USA, 2015.
- [36] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, *J. Membr. Sci.*, 354 (2010) 123–133.
- [37] G. Blandin, A.R.D. Verliefde, C.Y. Tang, A.E. Childress, P. L-Clech, Validation of assisted forward osmosis (AFO) process: impact of hydraulic pressure, *J. Membr. Sci.*, 447 (2013) 1–11.
- [38] J. Wei, C. Qiu, C.Y. Tang, R. Wang, A.G. Fane, Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes, *J. Membr. Sci.*, 372 (2011) 292–302.
- [39] J.T. Arena, S.S. Manickam, K.K. Reimund, B.D. Freeman, J.R. McCutcheon, Solute and water transport in forward osmosis using polydopamine modified thin film composite membranes, *Desalination*, 343 (2014) 8–16.
- [40] B. Kim, S. Lee, S. Hong, A novel analysis of reverse draw and feed solute fluxes in forward osmosis membrane process, *Desalination*, 352 (2014) 128–135.