A state-of-the-art protocol to minimize the internal concentration polarization in forward osmosis membranes

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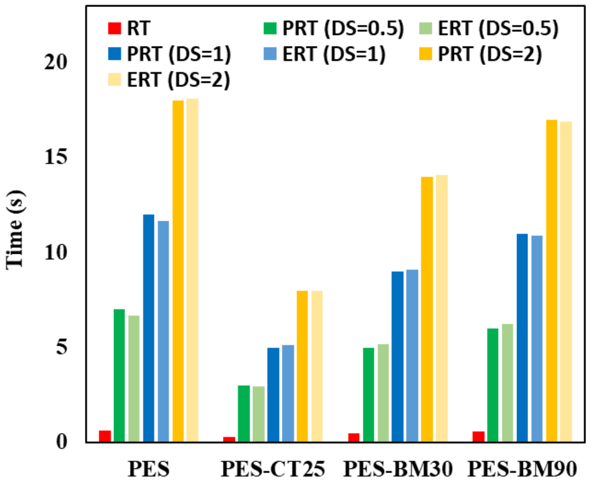
Graphical Abstract



Abstract

The main reason for the lower than expected water flux in the forward osmosis (FO) process is the concentration polarization (CP) phenomenon. In the FO process, dilutive internal concentration polarization (DICP) is the most important reason that drops water flux when the draw solution faces the support layer. Usually, the structural parameter (S) has been used as an indicator of the intensity of DICP. Small S value is desirable for the FO membrane due to the reduced DICP. However, due to design and construction problems, structural parameter reduction has some drawbacks. In this work, DICP reduction in FO membranes will be investigated using an approach other than structural parameter reduction. This approach tries to minimize the driving force drop by applying the change in the run of the FO process in the form of the proposed protocol. Accordingly, during the FO process, the feed solution (FS) valve is opened and closed at a constant period of time (feed valve timing (FVT)). Four types of porous matrix membrane (PMM)-based TFC FO membranes with different S parameters were used. The effects of proposed protocol on the water flux (J_w), reverse salt flux (J_s), specific reverse solute flux (J_s/J_w) and effective driving force were investigated. The effects of S parameter and draw solution (DS) concentration were investigated separately. The results show that at all DS concentrations, the proposed protocol will significantly increase the J_w. Also, the values of J_s/J_w decreased with increasing the FVT values and reaches the lowest level in the practical recovery time (PRT). Results of the estimated method show that the PRT estimation by the retention time (RT) values can greatly reduce the volume of experimental processes. Also, the proposed method almost independent of structural parameter.

Keyword**:** Forward osmosis, ICP, TFC, structural parameter, retention time.

1. Introduction

As an emerging technology, forward osmosis (FO) has been recently developed in fields of water and wastewater treatment, and energy harvesting, owing to its potentially low energy consumption, low fouling tendency, and high separation efficiency [1-6]. FO process is a spontaneous membrane process that employs the osmotic pressure difference to extract fresh water from the lower osmotic pressure solution (feed solution-FS) to the higher osmotic pressure solution (draw solution-DS) across a semipermeable membrane [7]. The typical FO membrane is the thin film composite (TFC) membrane, containing a thin defect-free polyamide (PA) active layer (AL), and a porous support layer (SL) [8,9]. In the FO process, the TFC membrane can either be used with AL facing the DS (PRO mode) or with AL facing the FS (FO mode) [10]. Because of the less prone of the FO mode to fouling, this mode is commonly used [10].

However, previous studies revealed that real water flux (J_w) is much lower than theoretical water flux, which is attributed to the phenomenon of concentration polarization (CP) [11-13]. Generally, CP is divided into four types, named concentrative internal concentration polarization (CICP), dilutive internal concentration polarization (DICP), concentrative external concentration polarization (CECP), and dilutive external concentration polarization (DECP) [11-17]. Among the four types of CP, DICP is the most severe CP and it is responsible for a sharp drop in water flux in the FO process [17-18]. In this phenomenon, the drop in water flux is attributed to reduction in the effective driving force due to the dilution of the DS [17-18]. The structural parameter, S, has been used as an indicator of the intensity of DICP [19-21]. In TFC FO membranes, S parameter is related to the SL. Small S value is desirable for FO membranes due to the reduced DICP. Accordingly, the SL should be manufactured with small thickness (t), high porosity (ε), and low tortuosity (τ) ($S = \tau \times t/\varepsilon$) [19-25]. Thus, it seems that the optimization of the SL is the main step in controlling the intensity of DICP.

In recent years, different strategies were applied to the optimization of the SL, such as template-assisted technique [18, 25-29], chemical-etching [30,31], in-situ mineralization [32], blending technique [21,33], and surface modification [17,34]. In all of these strategies, the primary objective is to reduce the DICP by reducing the structural parameter. Although lowering the structural parameter reduces the DICP, but increasing the water flux several times requires a significant reduction in the structural parameter. Unfortunately, due to design and construction problems, structural parameter reduction has some limitations. Therefore, studies on strategies to decrease the DICP of specific FO membranes (with constant structural parameters) should be put on the agenda.

In this study, DICP reduction in TFC FO membranes will be investigated using a method other than structural parameter reduction. As stated earlier, in DICP phenomenon, after water diffusion in the SL pores the effective driving force will be decreased and reduces the theoretical water flux. The main purpose of this study is to minimize the drop in the driving force by applying a change in the run process of the FO membranes in a form of a proposed protocol. The FO process was operated in the FO mode because it is less prone to fouling. In order to provide a more comprehensive analysis and to more accurate results, studies have been carried out on several TFC FO membranes. The only major difference between these membranes should be the structural parameter. Accordingly, four types of porous matrix membrane (PMM)-based TFC FO membranes with different structural parameters, denoted as TFC-PES, TFC-(PES-CT25), TFC-(PES-BM30), and TFC-(PES-BM90) were used in this study [29]. The effects of proposed protocol on the effective driving force, water flux (J_w), reverse salt flux (J_s), and specific reverse solute flux (J_s/J_w) were investigated. Also, the effects of DS concentration and the effects of the structural parameter were examined separately. Finally, a theoretical approach for simulating the experimental behavior of the proposed protocol is presented by providing a fingerprint estimation. To the best of our knowledge, at least with this strategy, no investigation has ever been done so far to minimize the DICP by applying a change in the run process of the FO membranes.

2. Experimental

2.1. Membranes and Chemicals

Four TFC FO membranes, denoted as TFC-PES, TFC-(PES-CT25), TFC-(PES-BM30), and TFC-(PES-BM90), were employed in the present study. The SL in these membranes is made of metal-organic framework (MOF)-based PMM strategy and differs only in the structural parameters. The TFC membranes were received as flat sheet and were stored dry at 5$^{\circ C}$. Table 1 and Table 2 shows the key physicochemical parameters of these PMM and TFC membranes, respectively [29]. Sodium chloride (NaCl, 99% purity) and deionized (DI) water were also purchased from Merck-Millipore, Germany.

Table 1
Physicochemical parameters of PMMs.

Membrane Type	t (μm)	ε (%)	PWP* (L/m^2.h.bar)
PES	50 ± 1	63 ± 1	91.29
PMM-(PES-CT25)	55 ± 3	78 ± 1	282.38
PMM-(PES-BM30)	55 ± 1	79 ± 3	161.79
PMM-(PES-BM90)	52 ± 2	82 ± 2	132.40

*Pure Water Permeance

Table 2
Physicochemical parameters of TFCs.

Membrane Type	A (L/m^2.h.bar)	B (L/m^2.h)	R (%)	S (μm)	J_w (L/m^2.h)			J_s (g/m^2.h)		
					DS=0.5	DS=1	DS=2	DS=0.5	DS=1	DS=2
TFC-PES	2.43	0.35	97.20	614.59	10.94	16.76	25.55	1.8700	2.97	4.3790
TFC-(PES-CT25)	2.37	0.32	97.37	438.95	13.08	21.32	32.24	2.1000	3.28	5.1800
TFC-(PES-BM30)	2.40	0.34	97.24	529.89	11.69	18.56	29.27	1.9700	3.08	4.9350
TFC-(PES-BM90)	2.42	0.34	97.27	552.19	11.43	18.29	28.58	1.9100	3.03	4.7780

3.2. Membrane Test Unit

The performance of selected TFC FO membranes was studied using across-flow laboratory-scale FO system (Fig. 1). Osmotic flux tests were carried out in the FO mode. The membrane surface area, A_m, was 30 cm^2. During experiments, a thin spacer was used to provide favorable mixing to reduce ECP. The initial volumes of DS (0.5, 1, and 2 M NaCl) and FS (DI water) were 2.5 and 2 L, respectively. To pump the both FS and DS, two diaphragm pumps were used (Headon, 2.2 LPM). In both FS and DS channels the velocity was adjusted at 21 cm/s by two velocity flow meters. The temperature of the both FS and DS were controlled and fixed using a water bath system.

The J_w was directly measured by connecting DS tank to a digital balance (Mettler Toledo). During experiment, the conductivity of the both DS and FS were controlled and recorded. According to the absolute volume change of the FS, ΔV_{feed}, over a predestine time, Δt, the J_w was determined by following equation:

$$J_w = \frac{\Delta V_{feed}}{A_m \times \Delta t} \quad (1)$$

were A is pure water permeability, and $\Delta\pi_{eff}$ is effective osmotic pressure (effective driving force). Also based on conductivity increment in the FS, the J_s is calculated by by following equation:

$$J_s = \frac{V_t \times C_t - V_0 \times C_0}{A_m \times \Delta t} = B \times \Delta C_{eff} \quad (2)$$

where B is salt flux, ΔC_{eff} is the effective solute concentration difference, and V_0 and V_t are the initial and final volumes of FS, respectively. Also, C_0 and C_t are the initial and final salt concentrations of FS, respectively.

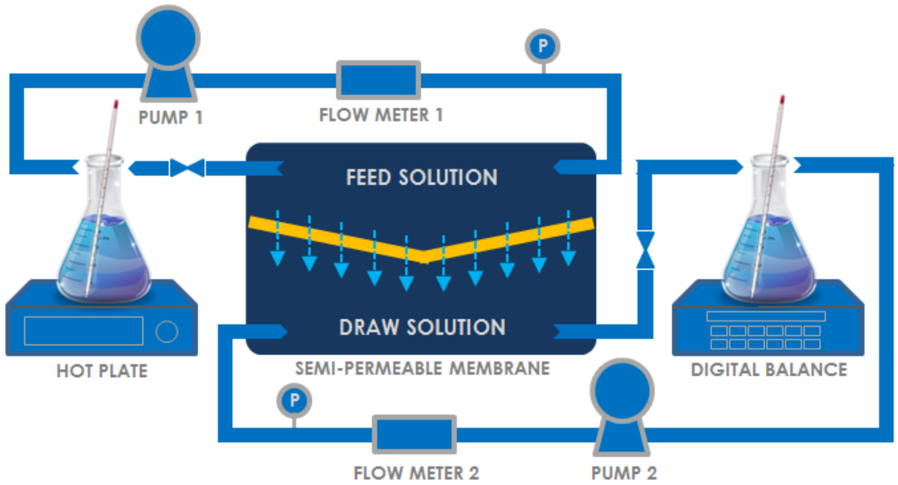


Fig. 1 Schematic of the laboratory-scale FO experiment used in this study.

2.3. Experimental Procedure

water and salt permeability coefficients (A & B, respectively) were calculated for each FO membrane used in the test. Table 2 shows the values of A and B, membrane rejection rate, structure parameter, and concentration of draw solution for different membranes. ~~According to the relationships expressed in the *Membrane Test Unit* section, the J_w and J_s values will be calculated as two main parameters. As a traditional process, this experiment was conducted by our research team and the results are presented in Table 2. These results have been obtained in one-hour period.~~

In this study, these procedures are repeated in the same way, but with a change in the run process. Accordingly, as a new approach, during the FO experiment and for each membrane, the FS valve is opened and closed at a constant period of time (feed valve timing, FVT). This is while the DS valve will always stay open. For example, FVT=1s means that during the one-hour period of the experiment the FS valve will be closed for one second after being open for one second and this trend will continue steadily for one hour.

3. Results and discussion

3.1. Effects of the proposed protocol on the performance of FO membranes

According to the proposed protocol, the FO water flux, J_w, were measured for all TFC membranes as the functions of feed valve timing (FVT), and the results shown in Fig. 2. The results show that at all three DS concentrations, the proposed protocol will increase J_w. Based on the obtained results, it can be concluded that low FVT values had less impact on J_w. As the FVT increases, the J_w increases and reaches a maximum value before it drop again by increasing the value of FVT. This is due to reverse salt diffusion from the draw solution side and filling the SL cavities. It is likely that closing the FS valve in two ways will improve the performance of the FO process: (1) DS salt will have the opportunity to penetrate into the SL cavities, and (2) stopping the water flux will stop the process of DS dilution in the SL cavities. The combination of these two phenomena caused to increase the concentration of DS in the SL cavities and thus can increase the effective driving force (see Fig. 3). In this study, the value of FVT at which the J_w (and also effective driving force) reaches a maximum value is considered as the practical recovery time (PRT). Naturally, as the FVT values further increase, the amount of J_w should be constant. The justification for this behavior is that if the experiment duration were infinite, it can be expected that as the FVT further increase, the amount of J_w will remain constant at its highest level. This is while, the experiment time for all membranes is limited to one hours. This means that a FVT values greater than PRT reduces the useful life of the experiment and reduces the J_w. Obviously, by further increasing the values of FVT, the slope of the J_w decrease will increase.

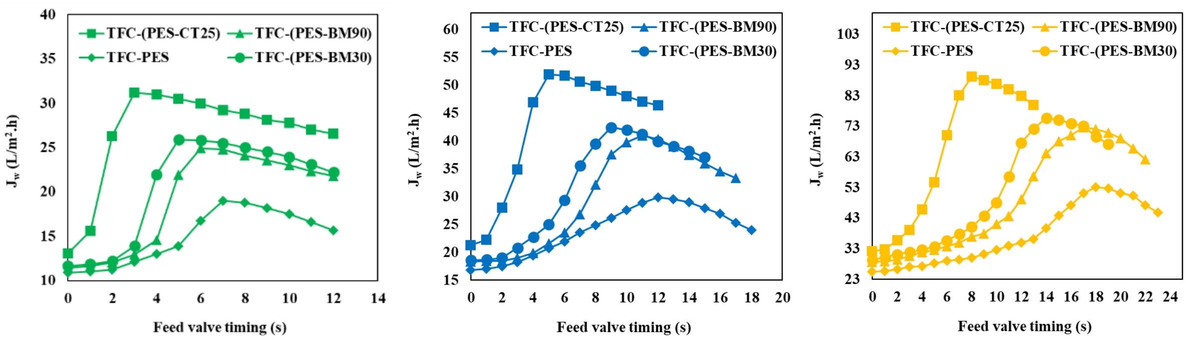


Fig. 2 Effect of the proposed protocol on the FO water flux; (a) DS=0.5 M, (b) DS=1 M, and (c) DS=2 M

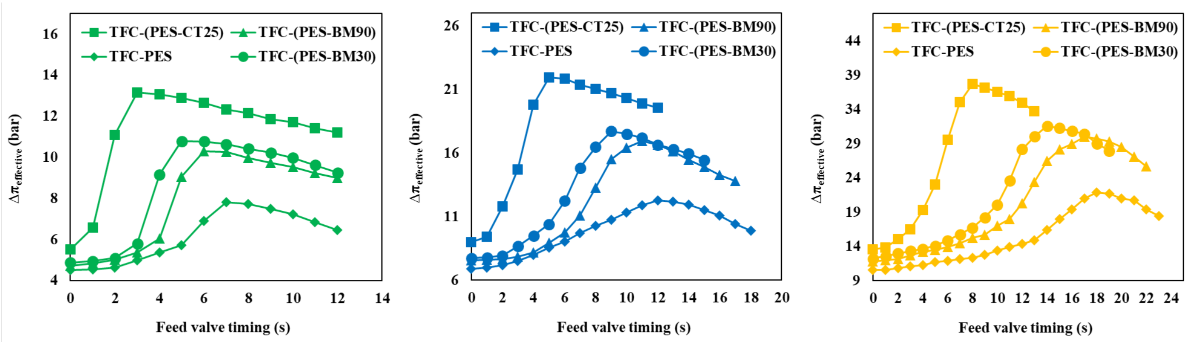


Fig. 3 Effect of the proposed protocol on effective driving force; (a) DS=0.5 M, (b) DS=1 M, and (c) DS=2 M.

Although, the increasing J_w can be very beneficial, these results will only be attractive if the FO reverse salt flux, J_s, is low. The J_s is an important parameter to estimate the amount of salt lost during the FO process. Similar to J_w, the J_s were measured for all membranes as the functions of FVT, and the results presented in Fig. 4. According to obtained results, for each membranes and at all three DS concentrations, the proposed protocol will increase the J_s. Therefore, it can be concluded that the openness of DS valve and the closure of FS valve will increase reverse salt diffusion from the DS into the FS.

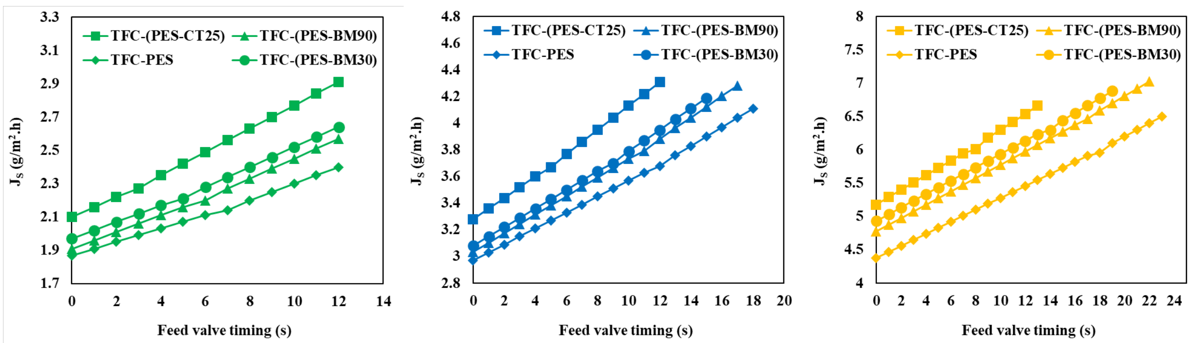


Fig. 4 Effect of the proposed protocol on the FO reverse salt flux; (a) DS=0.5 M, (b) DS=1 M, and (c) DS=2 M.

The study on performance of the proposed protocol will be complemented by analyzing on J_s/J_w factor (Fig. 5). The results show that the values of J_s/J_w decreased with increasing the FVT values and reaches the lowest level in the PRT. Then, by increasing the FVT values the J_s/J_w will be decreased, as a result of decreasing the J_w.

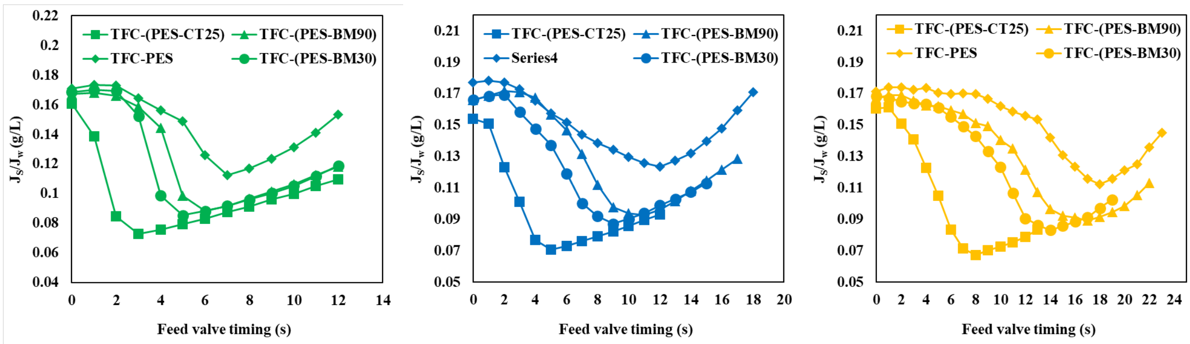


Fig. 5 Effect of the proposed protocol on the specific reverse solute flux; (a) DS=0.5 M, (b) DS=1 M, and (c) DS=2 M.

3.2. Effects of DS concentration

The results presented in Fig. 2 show that the value of PRT for each membrane at different concentrations of DS. Fig. 6 shows the amount and trends of these changes for each membranes. Due to the use of MOF-based PMM strategy in the fabrication of SL, the major difference between the TFC membranes is only the structural parameter. The results showed that PRT increases with increasing the concentration of DS. In other words, for a TFC membrane with a constant structural parameter, the higher the DS concentration the longer it takes for the DS solute to fill the SL cavities. The effect that DS solutes have on each other at higher concentrations may be the main cause of this phenomenon. Also, in order to better understand the intensity of the changes, the PRT changes were linearized by varying the DS concentration for each membrane. According to the results, it can be concluded that by decreasing the structural parameter, the sensitivity of the PRT to the variation in the concentration of DS decreases. This suggests that decreasing the structural parameter will facilitate the pathway of penetration of DS solutes into the SL cavities.

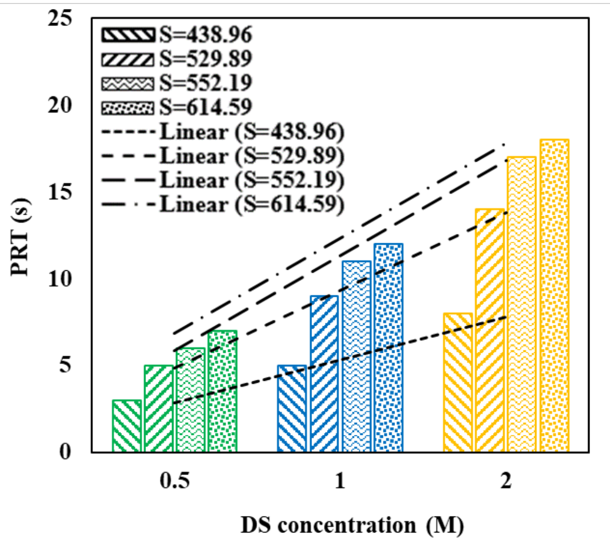


Fig. 6: The trends of PRT variation by changing the DS concentration.

3.3. Effects of structural parameter

The obtained results in Figs. 2 and 6 show the impact of varying the DS concentrations on the PRT for different membrane structural parameters. Fig. 7 shows the trends of these changes for three DS concentration used. Similarly to Fig. 6, in order to better understand the intensity of these changes, the PRT changes were linearized by varying the structural parameters for each DS concentration. The results show that the PRT value increasing with increasing the structure parameter for all DS concentrations. It is clear from Figure 7 that the sensitivity of PRT to variation in the structure parameter increases by increasing the concentration of DS.

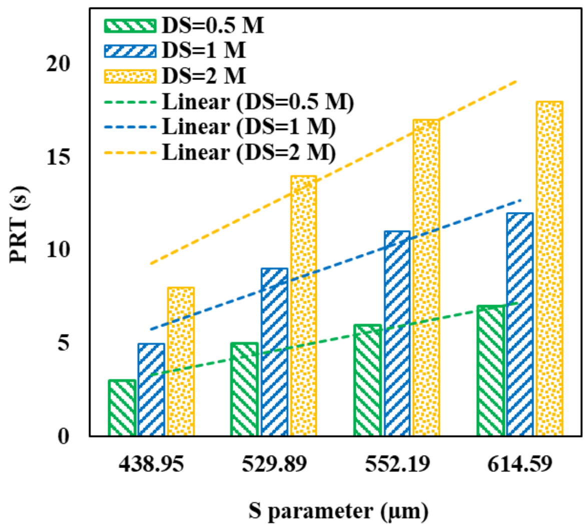


Fig. 7 The trends of PRT changes by changing the structural parameter.

3.4. Fingerprint Estimation of PRT

As stated in the previous sections, the use of the proposed protocol can significantly increase the efficiency of TFC FO membranes. However, the experimental steps to obtain the PRT, as the optimal feed valve timing, is time consuming. Therefore, it is important to provide a solution to estimate PRT. As stated in the previous sections, the use of the proposed protocol can significantly increase the efficiency of TFC FO membranes. However, the experimental steps to obtain the PRT, as the optimal feed valve timing, is time consuming. Therefore, it is important to provide a solution to estimate PRT. As stated earlier, PRT represents the time required to fill all the SL cavities with DS molecules. This definition is somewhat similar to the retention time (RT). RT is a measure of the time taken for solute to pass through a specific space. It is calculated as the time from injection to detection. If this specific space is the same as the SL cavity space, then the RT can be calculated using the following equation:

$$\mathrm{RT} = \frac{\varepsilon * \mathrm{t}}{\mathrm{PWP} * \mathrm{P}} \quad (3)$$

where ε is porosity of SL, t is thickness of SL, P is hydraulic pressure, and PWP is pure water permeation (listed in Table 1). The calculated RT for each of the TFC membranes are shown in Fig. 8. Results for RT are much lower than those for PRT. There are three main reasons to justify this difference: (1) The type of flow in the RT calculations is dead-end but the PRT calculations are performed in a cross flow mode, (2) the feed solution in the RT calculations is DI water, but the feed used in calculation the PRT is DS with different concentration of NaCl, and (3) the driving force in the RT is the hydraulic pressure but the driving force in the PRT calculations is the osmotic pressure difference. In order to further investigate the difference between RT and PRT for each TFC membrane at different DS concentrations, the PRT obtained at each DS concentration was divided by the calculated RT to obtain a correction coefficient. This correction factor is denoted by K and we call it recovery time constant. Then the arithmetic average of the K parameter obtained at each DS concentration will be calculated and denoted by $\overline{K}$. RT values were multiplied by the $\overline{K}$ parameter to estimate the recovery time (ERT). The ERT results are presented along with the PRT results in Fig. 8. The results show that the PRT and ERT values for each TFC membrane are very close. These results show that the PRT estimation by the RT values almost independent of structural parameter.

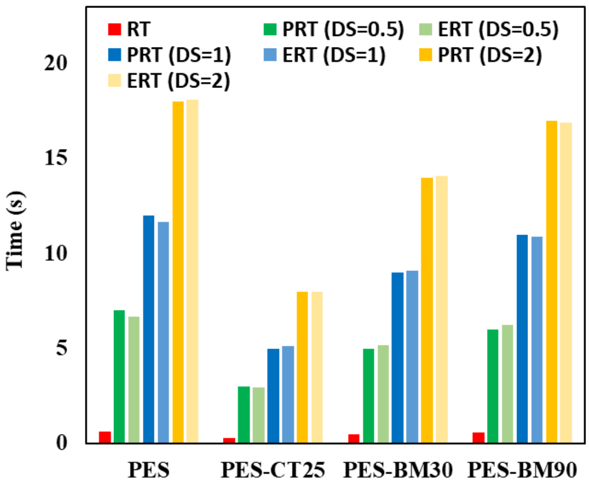


Fig. 8 RT, PRT, and ERT for each of the TFC membranes in various DS concentration.

Furthermore, the trend of changing $\overline{K}$ parameter by changing the DS concentration was investigated and the results are [Fig. 9]. As shown in Fig. 9, the $\overline{K}$ parameter increases with increasing DS concentration. Regarding the linearization of the results, it can be said that the trend of $\overline{K}$ parameter changes relative to DS concentration changes with high accuracy ($R^2 \approx 0.99$) is linear and follows the $\overline{K} = 11.988 \times M + 5.5681$ relation. It seems that this relation can be used with a great accuracy if the DS is NaCl and its concentration is in the range of 0.5 to 2 M. Although this method may not be quite accurate, it can be used as a reliable fingerprint estimator and can greatly reduce the volume of experimental processes.

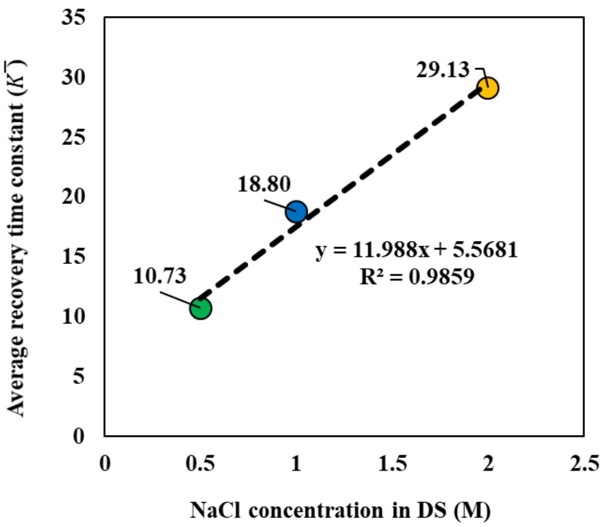


Fig. 9 The trends of $\overline{\mathrm{K}}$ parameter changes by changing the DS concentration.

4. Conclusions

The current study proposed a novel protocol to minimize the DICP in TFC FO membranes by applying the change in the run process. The following key points were concluded from this work: (1) at all DS concentrations, the proposed protocol will increase the J_w, (2) low FVT values will have less impact on J_w, (3) by increasing the FVT, the J_w increases and reaches a maximum point named PRT, (4) a FVT values greater than PRT reduces the useful life of the experiment and reduces the J_w, (5) for each membranes and at all three DS concentrations, the proposed protocol will increase the J_s, (6) the J_s/J_w decreased with increasing the FVT values and reaches the lowest level in the PRT, (7) for each membrane, increasing the DS concentration increases the value of PRT, (8) by decreasing the S parameter, the PRT sensitivity to DS concentration changes will decrease, (9) for each DS concentration, by increasing the S parameter the value of PRT will be increased, (10) by increasing the DS concentration, the PRT sensitivity to S parameter changes will increase, (11) the PRT estimation by the RT values almost independent of structural parameter, (12) the PRT estimation by the retention time (RT) values can greatly reduce the volume of experimental processes, and (13) estimated method almost independent of S parameter.

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