

© <2020>. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
<http://creativecommons.org/licenses/by-nc-nd/4.0/>
The definitive publisher version is available online at <https://doi.org/10.1016/j.jwpe.2020.101492>

Caspian seawater desalination and whey concentration through
forward osmosis (FO)-reverse osmosis (RO) and FO-FO-RO hybrid
systems: Experimental and theoretical study

Mehrzaad Arjmandi^a, Mahdi Pourafshari Chenar^{a*}, Ali Altaee^b, Abolfazl Arjmandi^c, Majid Peyravi^c,
Mohsen Jahanshahi^c, Ehsan Binaeian^d

^aDepartment of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

^bCentre for Technologies for Water and Wastewater, School of Civil and Environmental Engineering,
University of Technology Sydney, Australia

^cMembrane Research Group, Nanotechnology Research Institute, Babol Noshirvani University of Technology,
Babol, Iran

^dState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese
Academy of Sciences, Fuzhou, Fujian, China

*Corresponding author: Mahdi Pourafshari Chenar (pourafshari@um.ac.ir)

Abstract	24
The current experimental and theoretical study proposes forward osmosis (FO)-reverse	25
osmosis (RO) (FR*) and FO-FO-RO (FFR) hybrid systems to combine concentration of cheese	26
whey and Caspian seawater desalination. The powerful TF-PMM was used as a FO membrane.	27
The impact of sales of concentrated cheese whey on reducing Caspian seawater desalination	28
costs was studied. The results showed that the TF-PMM has good potential for concentration	29
of cheese whey with a water flux of about 12.62 L/m ² h. In terms of permeate concentration	30
(C _p) and at low recovery rates (RR), the choice of FR* and FFR hybrid systems with 0.3 M	31
NaCl as the draw solution (DS) should be the priority. At high RR, although the sensitivity of	32
the type of system is reduced, the FR* system should not be used. The total power consumption	33
(E _{st}) for the FR*-30% and FR*-50% systems are lower than that of a single RO unit. In FR*	34
hybrid system by increasing the RR ^{FO1} , the power consumption of the FO unit and also the E _{st}	35
decreased. Also, in the FFR system, by increasing the concentration of the DS, while increasing	36
the E _{st} , the power consumption portion of the FO unit decreased. The existence of a valuable	37
by-product in the proposed hybrid systems increases the allowable limit of the cost of required	38
equipment and other operating costs to achieve profitability and reach the break-even point. In	39
the meantime, the FR*-50% system generates the most revenue, and also the quality of	40
produced freshwater from the FFR-50%-0.3M system is the highest.	41
Keywords: Forward osmosis, reverse osmosis, hybrid, Caspian seawater, cheese whey.	42

43

44

45

46

1. Introduction

47

The exploitation of seawater for freshwater supply is an affirmative method to combat water scarcity worldwide [1]. Different techniques have been proposed for seawater desalination such as thermal and membrane technologies [2-4]. Although the energy requirement of thermal desalination processes is very high, the membrane technologies have successfully reduced the energy requirements of desalination. The most popular membrane process for seawater desalination is reverse osmosis (RO) because of its reliability, high salt rejection and water recovery, and its capability to treat a wide range of seawater concentrations [5]. Although the RO process has several advantages, high power consumption is the main disadvantage of this process [6]. Reducing power consumption in the RO process is the main goal of many research studies [7-9]. Also, RO membranes are prone to fouling by organic and inorganic matters which present in seawater and cause reduction of water flux. Thus, besides the reduction in power consumption, the reduction of the fouling phenomenon in the RO process is another important concern of researchers [10]. The use of hybrid systems as an effective solution is of interest to researchers. Recently, the number of reports on the hybrid systems in which RO and other processes are combined has increased. RO-evaporator systems [11], Microfiltration (MF)-RO systems [12,13], Ultrafiltration (UF)-RO systems [14], Nanofiltration (NF)-RO systems [15-17], Pervaporation (PV)-RO systems [18], Pressure-Retarded Osmosis (PRO)-RO systems [19], and Forward Osmosis (FO)-RO systems [20] are examples of these hybrid processes. Due to the low power consumption and high rejection rate of the FO process, the FO-RO (FR) hybrid systems have attracted more attention [21-24].

In FO process, water flows from the solution of lower concentration (as feed solution (FS)) to the solution of higher salt concentration (as draw solution (DS)), across a semipermeable membrane due to the natural osmosis pressure, when the osmotic pressure difference is higher than the transmembrane pressure difference [25]. Low energy requirement, low membrane

fouling tendency, and high water recovery are the major advantages of the FO process [26]. In recent years, FO has been given special attention as a pretreatment stage in water and wastewater treatment systems. Feed concentration (dewatering) has also been reported as the other potential application of the FO process. In fact, unlike the water and wastewater treatment, in the feed concentration applications, the FO process operates as a stand-alone process [27-30]. However, due to the lack of high-performance membranes in the feed concentration process, this part of the application of FO membranes has not yet made significant progress. In our previous work, we prepared a new membrane, named thin-film porous matrix membrane (TF-PMM) that was able to handle Orange juice concentration with good performance [31].

In wastewater or seawater treatment applications, the FR hybrid systems (named FR1) are better than the RO stand-alone system [32-34]. In this case, when the FO unit coupled with the RO unit, FO pretreatment will reduce the fouling of the RO membrane, minimizes the downtime of the RO system, minimizes chemical consumption, and increases RO recovery rate. As a new approach, the FR hybrid systems can be used simultaneously to wastewater and seawater treatment (named FR2) [35,36]. In these cases, the purpose of the FO stage is the dilution of seawater. The dilution of seawater reduces the high-pressure requirement of the RO system. Accordingly, seawater and wastewater can be provided into the FO as the DS and FS, respectively, to dilute the seawater. The diluted seawater from FO unit is then subjected to the RO unit to produce freshwater. The simultaneous hybrid systems are still in the early stages. Fig. 1 shows a schematic diagram of the RO process for seawater desalination and the basic design of the FR hybrid systems for wastewater or seawater treatment (FR1) and simultaneously wastewater and seawater treatment (FR2). One disadvantage of FR hybrid systems is rather the low FO membrane flux. To overcome this drawback, Altaee and Hilal proposed the NF-FO-BWRO hybrid system [37]. The simulation of the proposed systems showed that 90% of product water recovery is possible, 75% of which comes from NF.

SW: Seawater
 WW: Wastewater
 DS: Draw solution
 DDS: Dilutive draw solution
 CDS: Concentrative draw solution
 CSW: Concentrative seawater
 DSW: Dilutive seawater
 CWW: Concentrative wastewater
 P: Product
 C: Concentrate
 o: Output indicator
 i: Input indicator

System	A	B	C	D	E	F
RO	Q_i, C_i	Q_o, C_o	Q_p, C_p	---	---	---
FR1	Q_{SW}, C_{SW}	Q_{CDS}, C_{CDS}	Q_{CSW}, C_{CSW}	Q_{DDS}, C_{DDS}	Q_C, C_C	Q_P, C_P
FR2	Q_{WW}, C_{WW}	Q_{SW}, C_{SW}	Q_{CWW}, C_{CWW}	Q_{DSW}, C_{DSW}	Q_C, C_C	Q_P, C_P

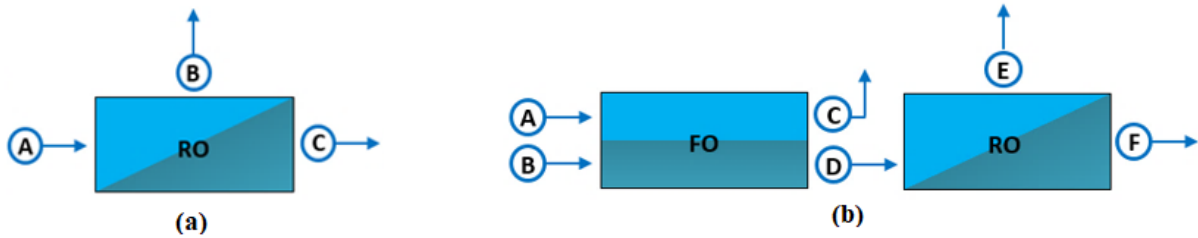


Fig. 1. Schematic diagram of (a) RO and (b) FR(1,2) process systems.

What is common to all hybrid systems is that using the FO pretreatment unit increases the power consumption of the desalination plant [6]. Since the FO membranes are still under development and their prices are largely varied, the capital expenditures (CapEx) analysis will be meaningless until the FO membrane is fully commercialized. However, recent studies have been conducted in this area that could be a broader path for economic studies [38, 39]. As shown in Fig. 1 (b), the combined FR system has three output streams that in both FR1 and FR2 hybrid systems, the streams C and E have no revenue value. This means that the only valuable product in the single RO system and the FR hybrid systems are freshwater (stream F). This suggests that the increase in lateral revenue in FR hybrid systems should be considered as a necessity. Dilution of inlet seawater through the concentration (dewatering) of a valuable feed (i.e. fruit juice, cheese whey, etc.) in an initial FO unit can be considered as an economic approach to increase lateral revenue by selling concentrated feed. In this study, the first report of two novel hybrid systems for Caspian seawater desalination based on producing a valuable by-product was proposed.

2. Proposed system configurations and model development

The schematic diagram of the proposed hybrid systems is shown in Fig. S1. In the proposed systems, Caspian seawater (as DS) is fed to an initial FO membrane (named FO1) to be diluted by concentrating a valuable feed. Diluted Caspian seawater in the FO1 membrane (stream C) can directly enter the RO membrane (named FR* hybrid system) or enter the RO membrane after crossing the FO2 membrane (named FFR hybrid system). In fact, in the proposed FFR system, the diluted Caspian seawater from the FO1 stage is sent to the FO2 stage as the feed solution for concentrating. In the FO2 membrane, freshwater transports from the diluted Caspian seawater to the DS because of the osmotic pressure difference across the membrane. Because seawater has been diluted in the FO1 membrane, so in the FFR system, the desired results can be achieved using only low concentrations of DS. Finally, the diluted DS (in the FFR system) or the diluted Caspian seawater (in the FR* system) is regenerated in the RO membrane for freshwater production. Optimal results achievement in proposed systems depends on high-performance membrane selection and also valuable feed solution in the FO1 system. Using an inappropriate membrane in the FO1 system can reduce the recovery rate as well as the return of compounds in seawater to the feed solution. Therefore, contamination of feed should be considered as a major concern. Also, as the osmotic pressure of the Caspian seawater is lower than the common DS (10 times less than the 2 M NaCl solution), therefore, selection of a feed with low osmotic pressure should be a priority. If valuable products with high osmotic pressure are used in the FO1 unit, and the DS is the same as the Caspian seawater, the water flux (J_w) will be drastically reduced, and this will increase the CapEx and operating expenses (OpEx). It is clear that if the Caspian seawater is changed by other seawater with higher osmotic pressures, then more valuable products with higher osmotic pressures can be used in the FO1 unit. Accordingly, in these two proposed systems, the cheese whey will be used as a valuable feed in the FO1 unit for concentrating (dewatering). The first step in the production of cheese whey powder typically involves increasing the percentage of dry matter. Then cheese whey can either be transported to another site for further processing (e.g.

evaporation and drying) or dried directly on site. Therefore, the concentration of stream D by the first FO unit in the proposed hybrid systems (Fig. S1) is the first stage in the production of cheese whey powder. The price of cheese whey is determined by the factories according to the percentage of its solid matters. The higher the percentage of solid matters, the more valuable the cheese whey. So the stream D is more valuable than the stream A. Hence the concentrated cheese whey in the FO1 unit is collected and sold as a valuable by-product to reduce the operating cost of Caspian seawater desalination. The powerful TF-PMM [31] as the FO1 membrane in the cheese whey concentration process was studied experimentally and theoretically. A comparison between the RO, FR1, FR2, FR*, and FFR systems was carried out using developed RO and FO software models [40,41]. Reverse Osmosis System Analysis (ROSA) was used to model the RO process. The effect of seawater dilution in the FO1 unit on the reduction of power consumption in the FR* system as well as the effect of this dilution on reducing the required DS concentration in the FFR system has been investigated. The impact of DS concentration on the system performance was also investigated. The impact of selling concentrated cheese whey in the FO1 unit on the desalination cost of Caspian seawater has been studied and compared with the RO, FR1, and FR2 systems. The study also investigated the power requirements of RO, FO, FO1, and FO2 and the total specific power consumption for the entire systems. To analyze the costs, we note once again that FO membranes have not yet been fully commercialized. Also, since an in-house made membrane has been used in this study, cost analyzes are not related to CapEx. On the other hand, considering that not all operating costs will be considered in this study, the cost analysis does not reflect the total OpEx. Thus, the cost analysis in this study related to the cost of required equipment (i.e. FO and RO membranes, pumps, pipes, valves, etc.) and other operating costs (i.e. physical and chemical cleaning) for achieving the economic feasibility of the hybrid systems (M_{st}). M_{st} is the break-even point and reflects the allowable cost increase.

A computational procedure was developed in this study to estimate the performance of proposed hybrid systems. A combination of experimental results, simulations, and mathematical modeling can determine the impact of the hybrid systems over a single RO system [6]. Recovery rate (RR), quality (concentration) of the permeate (C_p), and power consumption (E_s) are the most important factors that must be considered. Due to design limitations, the recovery rate of single RO membranes in seawater desalination should not be more than 50% [6]. However, under the same conditions, only by changing the feed solution from seawater to diluted NaCl (in FFR proposed system) or diluted seawater (in FR* proposed system) the recovery rate will be increased significantly. Thermodynamically, all hybrid systems are balanced because the recovery rate in the different units of a hybrid system is equal. For a single RO system, the water flux for seawater desalination, J_W^{RO} , is obtained from the following equation:

$$J_W^{RO} = A_w \times \Delta P \quad (1)$$

where, A_w is the water permeability coefficient, and ΔP is the hydraulic pressure difference across the RO membrane. The permeate concentration, C_p^{RO} , is also calculated by the following equation [6]:

$$C_p^{RO} = B \times CP \times R^{RO} \times C_{Fc}^{RO} \times \frac{A_m}{Q_p^{RO}} \quad (2)$$

where, B is the salt flux, CP is the concentration polarization factor, R^{RO} is the membrane rejection rate, Q_p^{RO} is the permeate flow rate, A_m is the membrane area, and C_{Fc}^{RO} is the average concentration of seawater on the feed side, that is calculated from the following equation:

$$C_{Fc}^{RO} = C_F^{RO} \times \frac{\ln(1/(1 - RR^{RO}))}{RR^{RO}} \quad (3)$$

where C_F^{RO} is the salt concentration in seawater. The RR^{RO} also represents the recovery rate in the RO process obtained from the following equation:

$$RR^{RO}(\%) = \left(\frac{Q_P^{RO}}{Q_{swi}} \right) \times 100 \quad (4)$$

where Q_{swi} is the seawater flow rate to the single RO membrane. The CP value is also calculated from the following equation:

$$CP = \exp(0.7 \times RR^{RO}) \quad (5)$$

Finally, the amount of power consumption for a single RO system, E_S^{RO} , is calculated from the following equation [42]:

$$E_S^{RO} = \frac{P_f \times Q_{swi}}{36 \times \eta \times Q_P^{RO}} \quad (6)$$

where P_f is the feed pressure, and η is the pump efficiency assumed to be equal to 0.8.

Also, for a single FO system, the water flux for seawater desalination, J_W^{FO} , is obtained from the following equation:

$$J_W^{FO} = A_w \times \Delta\pi \quad (7)$$

where $\Delta\pi$ is the osmotic pressure difference between the FS and DS. Also, the permeate concentration and the recovery rate, C_P^{FO} and RR^{FO} respectively, in a single FO membrane are calculated from the following equations [42]:

$$C_P^{FO} = \frac{B \times C_{swi}}{J_W^{FO} + B} \quad (8)$$

$$RR^{FO}(\%) = \left(\frac{Q_P^{FO}}{Q_{swi}} \right) \times 100 \quad (9)$$

where Q_P^{FO} is the permeate flow rate, and C_{swi} is the concentration of seawater to the FO membrane. 206
207

Finally, the amount of power consumption for a single FO system, E_S^{FO} , is calculated from the following equation [42]: 208
209

$$E_S^{FO} = \frac{(P_F \times Q_{swi}) + (P_{DS} \times Q_{DSi})}{36 \times \eta \times Q_P^{FO}} \quad (10) \quad 210$$

where, P_F is the feed pressure, P_{DS} is the draw solution pressure, Q_{swi} is the feed flow rate to the FO membrane, and Q_{DSi} is the draw solution flow rate to the FO membrane. 211
212

In hybrid systems consisting of FO and RO unit, the output product quality, the total power consumption, and the recovery rate depend on the performance of the FO process. In the FR hybrid systems (Fig. 1(b)), the RR factor in RO and FO should be equal to maintain a steady-state process ($RR^{RO}=RR^{FO}=RR$). That means the flow rate of the DS in the FO process should be equal to the RO concentrate ($Q_P^{FO} = Q_P^{RO}=Q_P$). Therefore, according to Fig. 1(b), the mass balance for the FR hybrid systems is as follows: 213
214
215
216
217
218

$$Q_{DSO} = Q_P^{FO} + Q_{DSi} = Q_{swi} \times RR^{FO} + Q_{DSi} \quad (11) \quad 219$$

Finally, in the FR1 hybrid system (and also FR2 system by changing the indexes) the total specific power consumption, E_{st} , is the sum of E_S^{RO} and E_S^{FO} : 220
221

$$E_{st} = E_S^{RO} + E_S^{FO} = \frac{P_F \times Q_{DSO}}{36 \times \eta \times Q_P^{RO}} + \frac{(P_F \times Q_{swi}) + (P_{DS} \times Q_{DSi})}{36 \times \eta \times Q_P^{FO}} \quad (12) \quad 222$$

Although it has been proven that the use of FR hybrid systems increases the recovery rate and product quality, the FR hybrid system will not be superior to the single RO system in terms of power consumption [6]. However, more than 95% of power consumption in FR hybrid systems is related to the RO unit. Since power consumption is directly related to the cost, therefore, 223
224
225
226

even in an optimized design, as long as the only product of FR hybrid systems is freshwater, one cannot expect these systems to be optimized in terms of power consumption. Therefore, the design of a hybrid system that, in addition to freshwater production, includes a valuable by-product for sale, could make the hybrid systems more preferable than a single RO system (Fig. S1). According to Fig. S1, the concentrated feed from the FO1 membrane should be considered as a by-product. So, unlike the FO2 membrane, the main task of the FO1 membrane is to concentrate a valuable feed. In FO1 membrane seawater will act as DS. Diluted seawater (stream C) after leaving the FO1 membrane can be used in two ways. In the first proposed system, the stream C directly enters the RO membrane, and the final product is obtained with the stream J. This is called the FR* hybrid system and is similar to the FR2 system, except that in the FR* system the input feed to the FO membrane is valuable. In the second proposed system, stream C enters the FO2 membrane as a feed and returns to Caspian seawater after concentration with a DS (stream F). This is called the FFR hybrid system. All equations expressed for FR hybrid systems can be applied to the proposed FR* system (by changing the indexes). The FFR hybrid system modeling and simulation process is also a combination of the modeling and simulation process of the single FO membrane and the FR hybrid system. At first, based on the abovementioned equations, the FO1 stage will be evaluated separately. Unlike the recovery rates in FO2 and RO membranes, which must be equal in order to maintain the process in a steady-state, the recovery rate in the FO1 stage can be selected different from that of FO2 and RO units ($RR^{FO1} \neq RR^{FO2} = RR^{RO}$). Initially, according to different values of RR^{FO1} , the amount of changes in concentration and flow rate of seawater, C_{swi} and Q_{swi} respectively, will be calculated using the following equations:

$$Q_{swi}^{FO2} = Q_{swi} + Q_P^{FO1} = Q_{swi} + Q_{whi} \times RR^{FO1} \quad (13)$$

$$C_{swi}^{FO2} = \frac{(Q_{swi} \times C_{swi}) + (Q_P^{FO1} \times C_P^{FO1})}{Q_{swi}^{FO2}} \quad (14)$$

Therefore, considering the changes in inlet seawater, the modeling and simulation relationships of the FR hybrid systems can be similarly applied to the modeling and simulation of the proposed FR* and FFR systems. Also, given the dilution of seawater in the FO1 membrane, the range of recovery rate in the FR* and FFR hybrid systems are expected to be higher than the FR hybrid systems. The amount of power consumed for the FR* hybrid system, E_s^{FR*} , is similar to the provided by the equations for the FR hybrid systems (by changing the indexes). Finally, the total power consumption for the FFR hybrid system, E_{st}^{FFR} , is calculated from the following equation:

$$E_{st}^{FFR} = \frac{P \times Q_{DSO}}{36 \times \eta \times Q_P} + \frac{(P \times Q_{whi}) + (P_{DS} \times Q_{swi})}{36 \times \eta \times Q_P^{FO1}} + \frac{(P \times Q_{swi}^{FO2}) + (P_{DS} \times Q_{DSi})}{36 \times \eta \times Q_P^{FO2}} \quad (15)$$

In 2019, the average price per kWh of electrical power in Iran was approximately \$0.1. Thus, the cost of energy consumed for producing one cubic meter of freshwater by proposed hybrid systems, M_{st}^E , will be estimated using the following equation:

$$M_{st}^E = Q_P^{RO} \times E_{st}^{FFR} \times 0.1 \quad (16)$$

On the other hand, according to the value of primary and concentrated cheese whey (M_0 and M_c , respectively), the amount of income from whey concentration process, M_{st}^i , will be calculated using the following equation:

$$M_{st}^i = Q_P^{FO1} \times (M_c - M_0) \quad (17)$$

Finally, the allowable cost increase, M_{st} , will be estimated using the following equation:

$$M_{st} = M_{st}^E - M_{st}^i = (Q_P^{RO} \times E_{st}^{FFR} \times 0.1) - (Q_P^{FO1} \times (M_c - M_0)) \quad (18)$$

3. Materials and experiments

As mentioned earlier, Caspian seawater was used in this study as DS (in FO1 unit) and FS (in FO2 unit). The composition of water in the Caspian Sea is shown in Table S1. Also, fresh cheese whey was purchased from the Kalleh dairy company and used as FS in the FO1 unit (Table 1). Fig. 2 shows the relationship between the price and percentage of dry matter of cheese whey presented from Kalleh dairy company. NaCl was used as a DS in the FO2 unit because of wide availability, high rejection by RO membranes, high osmotic pressure, and high solubility in water. Reverse Osmosis System Analysis (ROSA) software was applied to predict the performance of the RO membrane. For all systems, the Q_{swi} was assumed 25 m³/h. The SW30HRLE-400i RO membrane was used in the single RO unit and the regeneration of diluted DS in the hybrid systems because of its high rejection value and appropriate water flux. The high-performance TF-PMM was used for the FO unit in this work [31]. The specifications of the membranes used are given in Table 2. The performance of the TF-PMM FO membrane was studied using a cross-flow laboratory-scale FO filtration system, as described in our previous studies [31,43].

Table 1: Analysis of cheese whey.

Properties	Unit	Average
Total protein	%	0.89
Mineral substances	%	0.55
Lactose	%	4.41
Fat	%	0.06
Dry matter	%	5.91
Osmotic pressure	bar	$\cong 4.5$

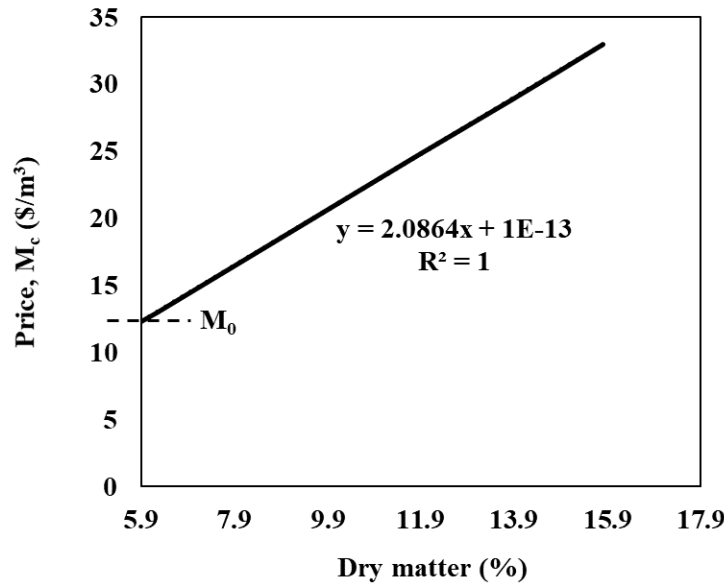


Fig. 2. Relationship between the price and percentage of dry matter of Kalleh cheese whey.

Table 2: Technical specifications of the RO and FO membranes used in the proposed hybrid systems [6,31].

Parameters	SW30HRLE-400i	TF-PMM
Salt rejection (%)	99.80	98.02
Maximum operating pressure (bar)	83	---
Active Area (m ²)	37	---
Water permeability, A (L/m ² .h.bar)	1.06	6.21
Salt flux, B (L/m ² .h)	0.08	0.55
FO water flux (J _w) (l/m ² .h)	---	140.91
FO salt flux (J _s) (mol/m ² .h)	---	0.32

4. Results and discussion

As stated, the first process in the proposed hybrid systems is the FO1 unit and the TF-PMM was used as the FO1 membrane. Accordingly, the potential of the TF-PMM FO membrane for cheese whey concentration was investigated, while FS was faced with the active layer (AL) of the membrane (AL-FS mode). In this process, the Caspian seawater was used as DS. Fig. 3a shows the results for the FO water flux. As shown in Fig 3a, TF-PMM represented a water flux of about 12.62 L/m².h for cheese whey concentration, while the FO water flux for DI water as FS was approximately 20.51 L/m².h (DS= Caspian seawater). These results show that a decrease in water flux (approximately 38%) was observed when DI water was replaced by cheese whey. The decrease in water flux is related to the membrane fouling or drop in the

driving force. However, the rate of water flux reduction was not high, which indicates a favorable TF-PMM performance in cheese whey concentration.

Also, TF-PMM was used continuously in the cheese whey concentration process, and the results of the water flux are presented in Fig. 3b. As shown in Fig. 3b, during the first 30 hours, the TF-PMM demonstrated over 20% decrease in water flux. The decrease in water flux is related to the FS concentration and/or DS dilution, and membrane fouling. Membrane cleaning is an important way to recover the water flux in the FO process, which also increases the life of the membrane. Universally, in FO membranes, the foulants are weakly attached to the surface of the membrane and can be cleaned with flushing. Accordingly, the effect of the cleaning process was investigated after 30 h cheese whey concentration. During 90 h of separation operation, the cleaning process was carried out every 30 h. According to the obtained results, the cleaning process caused about 16% water flux recovery (Fig. 3b). In general, the results showed that the TF-PMM has good potential for reuse after a continuous cleaning procedure which can significantly reduce the operating costs of the FO process.

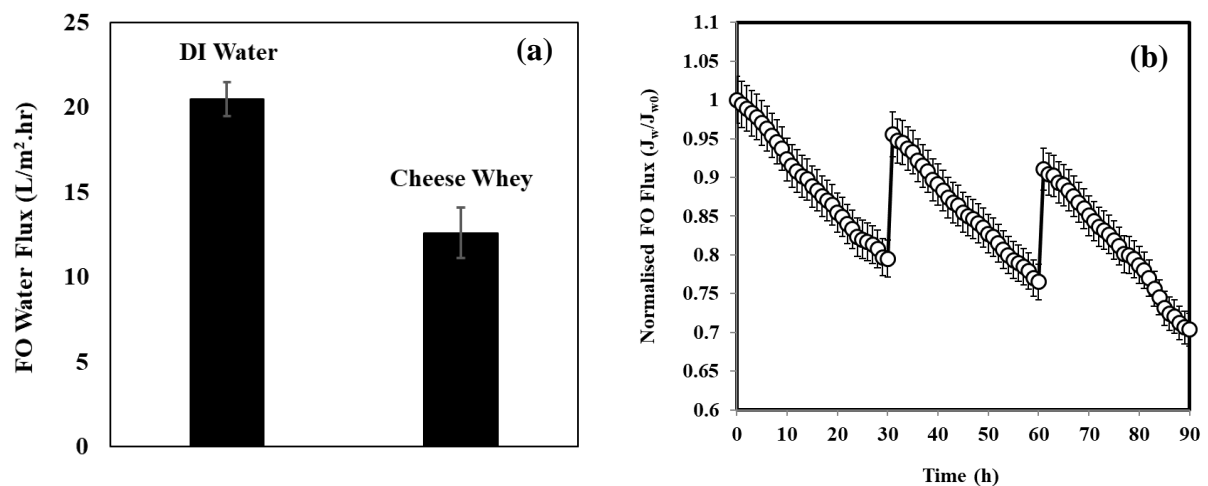


Fig. 3. (a) A comparison between TF-PMM FO water flux for DI water (left), and cheese whey (right) as FS, (b) normalized TF-PMM FO water flux (J_w/J_{w0}) decline and the process of recovering flux in 3 steps over a long time, (Orientation = AL-FS mode, FS= cheese whey, DS = Caspian seawater).

RO is the last stage in all FR1, FR2, FR*, and FFR hybrid systems and it is designed for DS regeneration and freshwater production. Fig. 4a shows the permeate concentration (C_p) and

water flux (J_w) at different recovery rates for a single RO unit. The permeate concentration decreased with increasing the recovery rate of the RO process due to the higher dilution factor. The actual J_w value also increased by increasing the recovery rate. Also, the effects of increasing the recovery rate on the average concentration of the feed as well as the amount of power consumed (E_s) are shown in Fig. 4b. According to the results, with increasing the recovery rate, the average concentration of the Caspian seawater (as FS) increased from 14000 mg/l up to 19000 mg/L in RR=48%. Also, assuming constant hydraulic pressure, the amount of power consumed to produce each cubic meter of freshwater decreases with increasing the recovery rate. The obtained results for a single RO system are similar to the trend of changes reported in other studies [6,37,40-42].

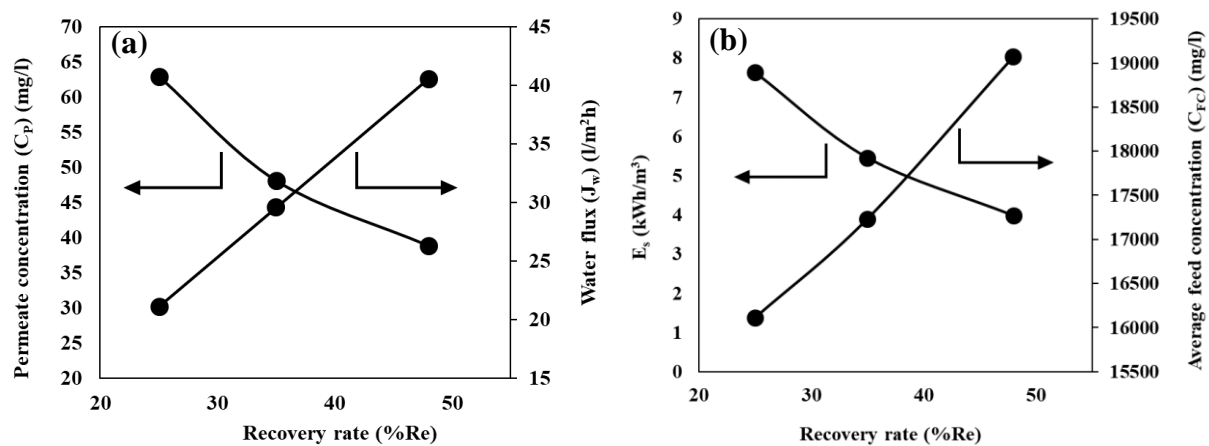


Fig. 4. (a) C_p and J_w , and (b) E_s and average feed concentration in single RO system at different recovery rates.

To investigate the impact of using the TF-PMM FO membrane before the RO membrane, the traditional FR1 hybrid system was investigated (see Fig. 1). NaCl solution with different concentrations of 0.5 and 0.8 M was used as DS. Analysis of the impact of using the FR1 hybrid system instead of the single RO system has been performed by Altaee et al. [6]. The simulation results in this study are shown in Fig. 5. The results presented in this section were compared with those obtained for the proposed hybrid systems (presented in the next section). Fig. 5a shows the effect of the recovery rate on the output DS concentration from the TF-PMM FO membrane. According to the results, it can be concluded that increasing the recovery rate

decreases the output DS concentration. Also, as shown in Fig. 5b, by increasing the recovery
rate, the FO water flux (J_w) increased. The permeate concentration (C_p) is another important
factor that is shown versus the recovery rate in Fig. 5c. The results show that permeate
concentration decreased with increasing the recovery rate. According to obtained results, it can
be said that although the recovery rate in RO cannot exceed 50% (see Fig. 4), this is not an
issue in TF-PMM FO, because of the high purity of the DS. Thus, the recovery rate of the RO
in the FR1 process was increased up to 65%. This indicates the strength of the TF-PMM
membrane in enhancing the performance of the RO membrane. It can also be concluded that
the DS concentration will have a great impact on the overall performance of the FR hybrid
system, especially at low recovery rates. In fact, as the recovery rate increases, the sensitivity
of the FR hybrid system to DS concentration decreases.

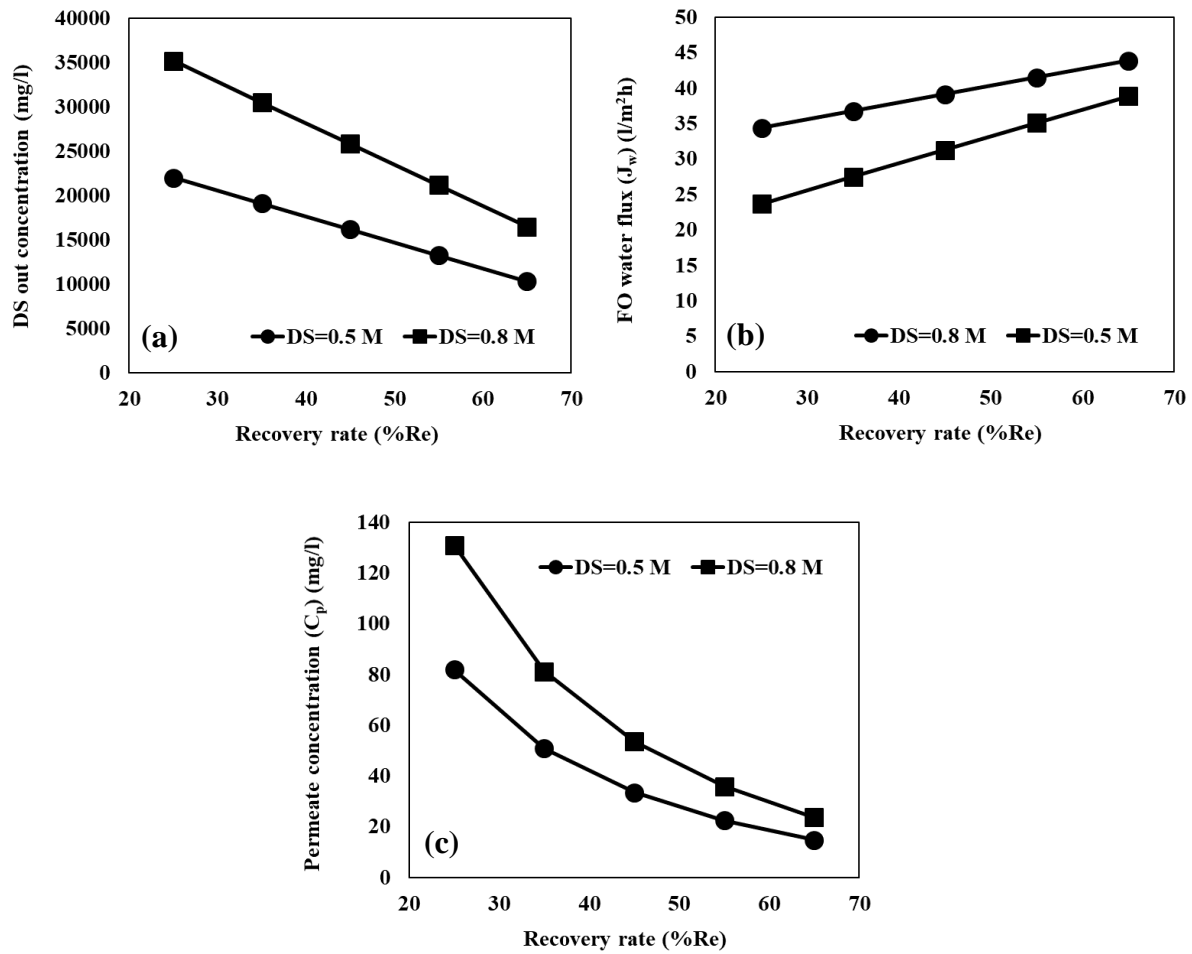


Fig. 5. (a) DS concentration output from the TF-PMM FO membrane, (b) FO water flux, and (c) final permeate concentration in the FR1 hybrid system at different recovery rates.

In the proposed FR* and FFR hybrid systems, the FO1 unit is common to both systems. In the FO1 unit, the Caspian seawater enters as DS and is diluted after the concentration of cheese whey. Given the different percentages of RR^{FO1} , the amount of changes in concentration (C_{sw0}) and flow rate (Q_{sw0}) of Caspian seawater were determined as the feed of the FO2 unit (in FFR) or RO unit (in FR*), as shown in Fig. 6. The results showed that by increasing the percentage of RR^{FO1} , the C_{sw0} and Q_{sw0} values decreased and increased, respectively. The impact of the proposed systems on the final permeate concentration (C_p) and the allowable cost increase will be discussed in the following sections.

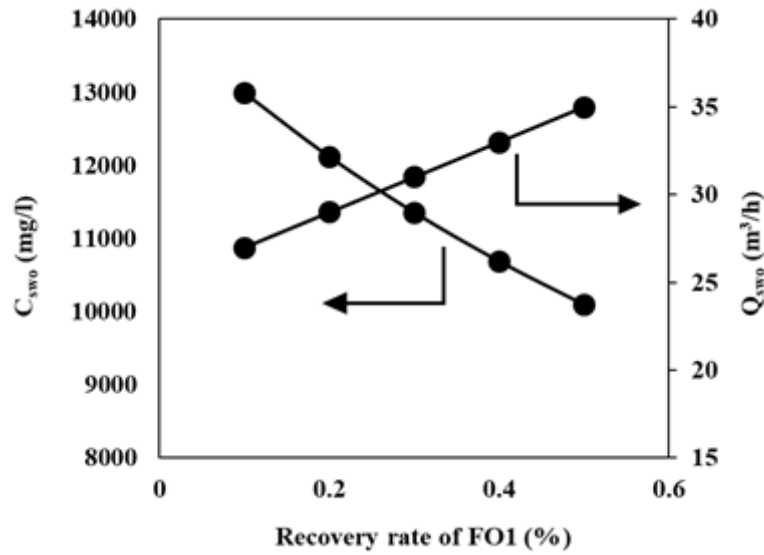


Fig. 6. C_{swo} and Q_{swo} in the FO1 membrane at different recovery rates.

The change in water flux in the FO2 unit by changing the concentration of Caspian seawater (as FS) at different DS concentrations in AL-FS mode was obtained experimentally, and the results are shown in Fig. 7. For different concentrations of DS, the FO2 water flux increased by decreasing the inlet seawater concentration (increasing RR^{FO1}), as a result of the osmotic pressure difference increment. Also, at higher DS concentrations, the dilution of seawater has a greater effect on increasing the FO2 water flux. As the DS concentration decreased, the sensitivity of FO2 water flux to dilution of DS decreased.

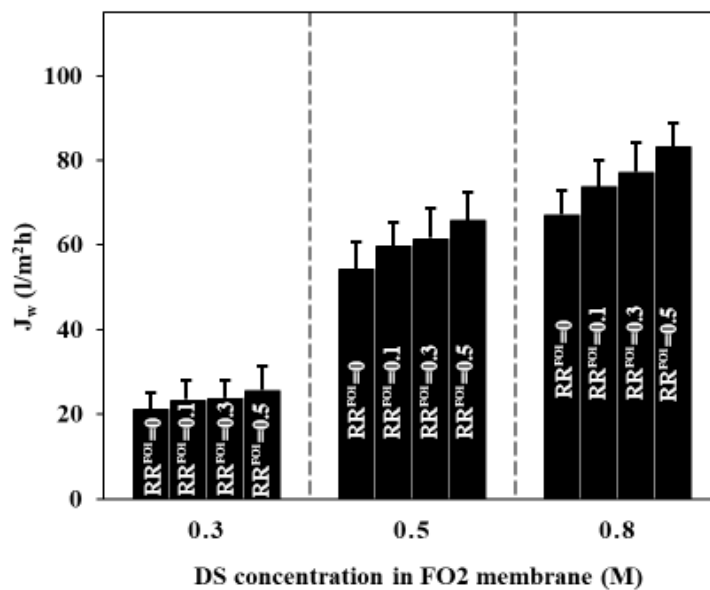


Fig. 7. FO2 water flux at different DS concentration and different recovery rates.

Fig. 8 shows the changes of final permeate concentration, C_p , with recovery rate, at different values of RR^{FO1} for FR* and FFR hybrid systems. The results of the FR1 hybrid system, as well as the single RO system, were also compared, as presented in Fig. 8. It is clear that with increasing RR^{FO1} , C_p decreased in both FR* and FFR hybrid systems. By decreasing the RR^{FO1} , the change trends of C_p in FR* and FFR systems were similar to those in single RO and FR1 systems, respectively. At low recovery rates, increasing the RR^{FO1} has the most positive effect on the FR* system performance, so that in $RR^{FO1}=0.5$, the FR* at $RR=0.25$ presents the lowest C_p value (Fig. 8c). At the $RR=0.25$, by decreasing the RR^{FO1} , the lowest C_p value is obtained for FFR system using 0.3 M of DS (Fig. 8a). At the constant values of RR^{FO1} , the difference between the results of C_p for each system at low recovery rates is quite clear. Also, in this condition, the effect of increasing recovery rate on C_p reduction in FR and FFR systems is much greater than the single RO system as well as the FR* system. At low RR^{FO1} and at all recovery rates, only FR* and FFR hybrid systems with a concentration of DS=0.3 M (Fig. 8a) are capable of producing higher quality products than a single RO system. By increasing the RR^{FO1} up to 50%, it is also possible to obtain such a product at all recovery rates by FFR hybrid system using 0.5 M of DS (Fig. 8c). Achieving a product with better quality than that achieved by a single RO membrane is not limited to these systems. In fact, for all RR^{FO1} , by increasing the recovery rate, it is possible to obtain a high-quality product by all hybrid systems. Finally, it can be said that in all RR^{FO1} , at low recovery rates, the choice of FR* and FFR hybrid systems with the concentration of DS=0.3 M should be the priority. Also, at high recovery rates, although the sensitivity of the type of system is reduced (only in terms of C_p), what is important is that the choice of the FR* system should not be included.

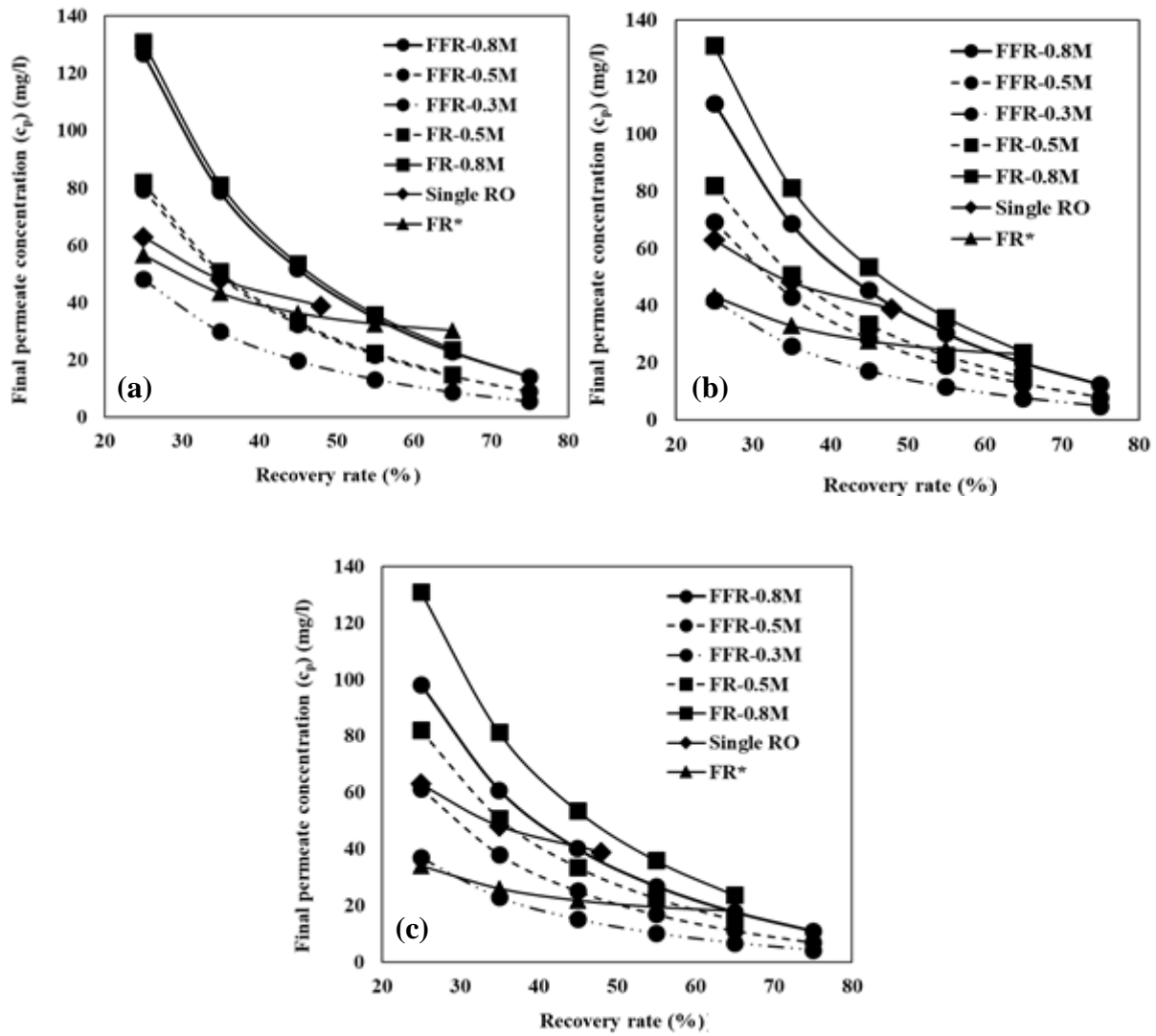


Fig. 8. Trend of changes in final permeate concentration at different recovery rates for (a) $RR^{FO1} = 0.1$, (b) $RR^{FO1} = 0.3$ and (c) $RR^{FO1} = 0.5$.

The single RO unit and the FR1, FR* and FFR hybrid systems were also compared in terms of power consumption, E_{st} , and the results are shown in Fig. 9. In all presented results, a constant value of RR was considered, i.e. $RR = 0.35$. The results show that except for FR* system with $RR^{FO1} = 0.3$ and 0.5 , in all other cases the amount of power consumed is higher than that of a single RO unit. It is also clear that the major portion of power consumption in all systems is related to the RO unit and each of the FO units has a small share of the total power consumed. In the FR1 system, by increasing the DS concentration, while increasing the total power consumption, the power consumption portion of the FO unit decreased. A similar trend was

observed in the FFR system. The results of the FFR system show that at low RR^{FO1} values, the power consumption share of the FO1 unit is several times higher than the power consumption of FO2 unit, and by increasing the RR^{FO1} values, the power consumption shares of FO1 and FO2 units were equivalent. The results of the FR* system also show that by increasing the RR^{FO1} , the amount of power consumed by the FO unit and also the total power consumption decreased. Finally, it was found that the FFR hybrid system with a concentration of $DS=0.3$ M at the $RR^{FO1}=0.1$ has the lowest power consumption share for the RO unit.

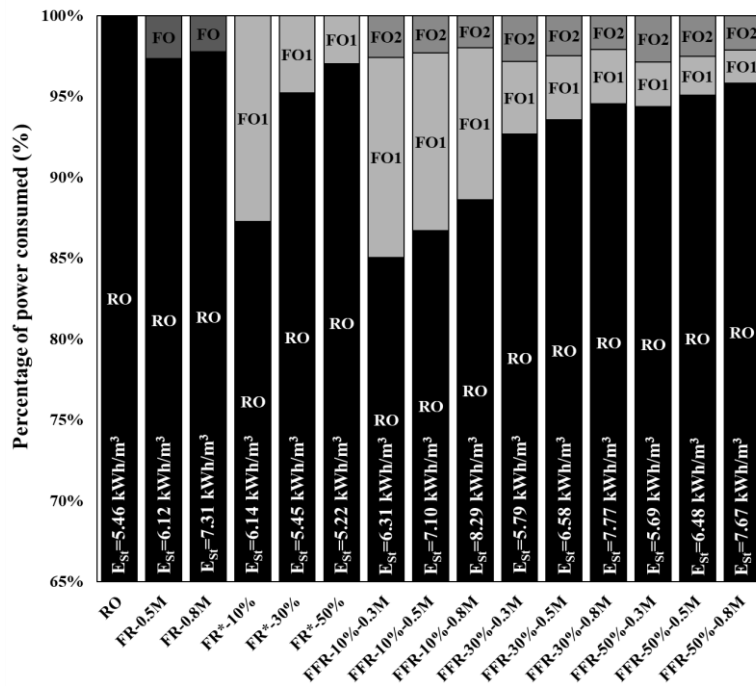


Fig. 9. The amount of power consumption, E_{st} , in the desalination process of the Caspian seawater by various systems at $RR=35\%$.

Although for all systems the Q_{swi} was assumed $25 \text{ m}^3/\text{h}$, since the Q_i^{RO} in the FR* and FFR systems is greater than Q_i^{RO} in the RO and FR systems (see Fig. 6), so the Q_p^{FR*} and Q_p^{FFR} are higher than Q_p^{RO} and Q_p^{FR} . Accordingly, based on the assumed price for energy ($\approx \$0.1/\text{kWh}$), the allowable cost increase (M_{st}) for each of the systems is calculated separately and is shown in Fig. 10. Negative values indicate the allowable limit of the cost of required equipment and other operation costs to achieve profitability and reach the break-even point. Also, due to the absence of valuable by-products in the RO and FR systems, the results showed that these

systems are not profitable and the cost of energy for the production of freshwater in the FR system exceeded the single RO system. As shown in Fig. 10, reach the break-even point for each system is strongly dependent on the amount of RR^{FO1} . Although at a constant amount of RR^{FO1} the revenue of all systems is close to each other, the FR*-50% system has the highest chance of profitability. However, the quality of produced freshwater, C_p , from each system must also be taken into account.

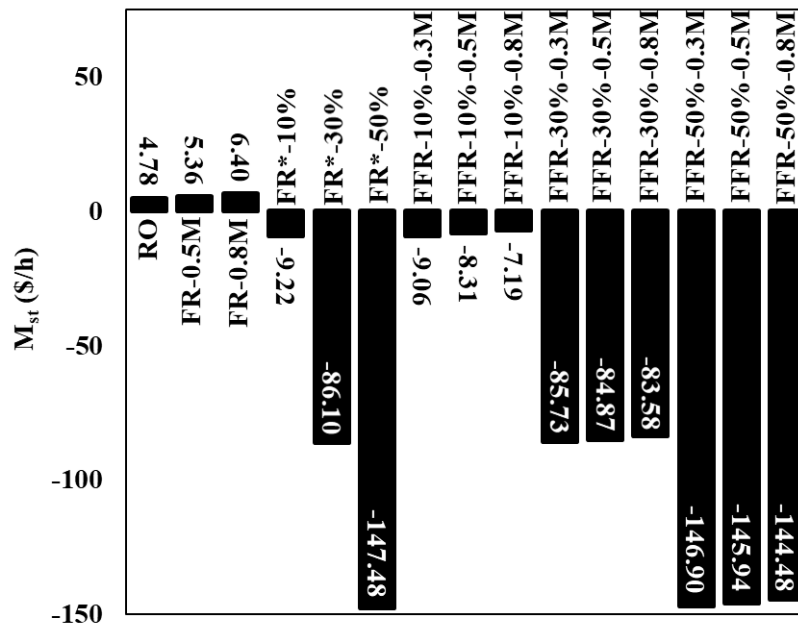


Fig. 10. allowable cost increase for reaching the break-even point (M_{st}).

Fig. 11 shows the quality of produced freshwater in each system, along with the M_{st} values of each system. According to Fig. 11, it can be said that the quality of produced freshwater, in FR* and FFR systems are more sensitive to the RR^{FO1} and concentration of DS, respectively. It can also be said that although the FR*-50% system has the highest chance of profitability, the quality of produced freshwater from the FFR-50%-0.3M system is highest. Given that the difference between M_{st} values of these two systems is not high, if the cost of each FO unit is reasonable, the choice of the FFR-50%-0.3M system should be the top priority.

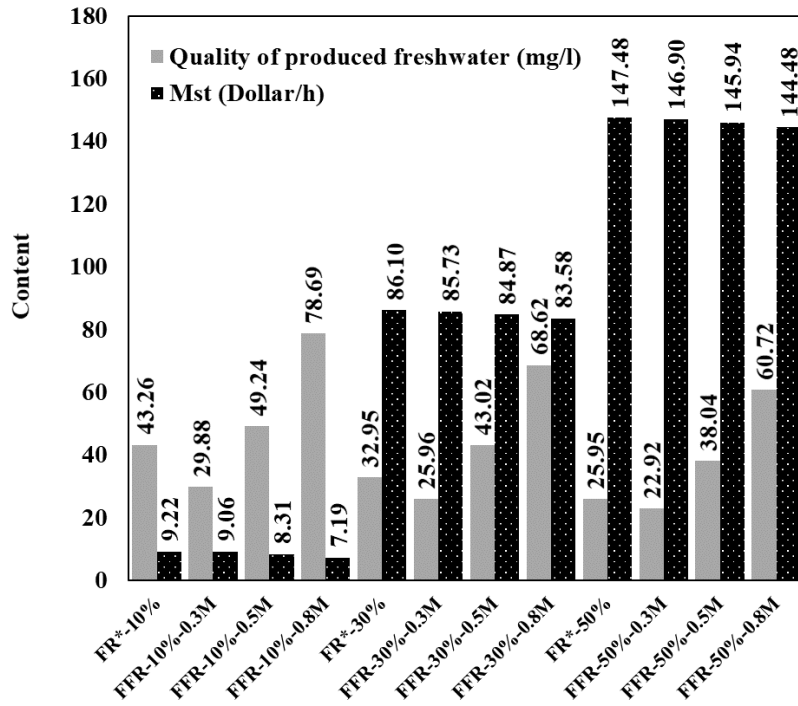


Fig. 11. Quality of produced freshwater in each system, along with the M_{st} value of each system.

5. Conclusion

The current experimental and theoretical studies evaluated the feasibility of FR* and FFR hybrid systems for combining concentration of cheese whey and Caspian seawater desalination. The TF-PMM was used as FO membrane and showed the good potential for concentration of cheese whey. According to obtained results, due to the absence of valuable by-products in the RO and FR systems, it is certain that these systems are not profitable and the cost of energy consumption for the production of freshwater in the FR system exceeded the single RO system. However, the existence of a valuable by-product in the proposed hybrid systems may help to achieve profitability and reach the break-even point. In terms of C_p , in both FR* and FFR hybrid systems and all RR^{FO1} values, at low RR, the choice of FR* and FFR hybrid systems with the concentration of DS=0.3 M should be a priority. Also, at high RR, although the sensitivity of the type of system is reduced, what is important is that the choice of the FR* system should not be included. In terms of E_{st} , except for FR* system with $RR^{FO1}=0.3$ and 0.5, in all other cases, the amount of E_{st} is higher than a single RO unit. In the FFR system,

by increasing the DS concentration, while increasing the E_{st} , the power consumption portion of the FO unit decreased. In the FR* system by increasing the RR^{FO1} , the amount of E_s by the FO unit and also the E_{st} decreased. The FFR hybrid system with concentration of DS=0.3 M at the $RR^{FO1}=0.1$ has the lowest power consumption share for the RO unit. Also, the net income of each system strongly depends on the amount of RR^{FO1} . Although the FR*-50% system has the highest chance of profitability, the quality of produced freshwater from the FFR-50%-0.3M system is the highest. Since the difference in allowable cost increase for reaching the break-even point between these two systems is not high, if the cost of each FO unit is reasonable, the choice of the FFR-50%-0.3M system should be the top priority.

Acknowledgement

The authors acknowledge financial support from Iran Nanotechnology Initiative Council.

References

- [1] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science* 333 (2011) 712-717.
- [2] O.A. Hamed, Overview of hybrid desalination systems-current status and future prospects, *Desalination* 186 (2005) 207-14.
- [3] M.A-K. Al-Sofi, Seawater desalination-SWCC experience and vision, *Desalination* 135 (2001) 121-39.
- [4] K. Jamal, M.A. Khan, M. Kamil, Mathematical modeling of reverse osmosis systems. *Desalination* 160 (2004) 29-42.
- [5] L. Malaeb, G. M. Ayoub, Reverse osmosis technology for water treatment: state of the art review, *Desalination* 267 (2011) 1-8.

[6] A. Altaee, G. Zaragoza, H. Rost van Tonningen, Comparison between Forward Osmosis-Reverse Osmosis and Reverse Osmosis processes for seawater desalination, <i>Desalination</i> 336 (2014) 50-57.	503 504 505
[7] A. Altaee, A.O. Sharif, Alternative design to dual stage NF seawater desalination using high rejection brackish water membranes, <i>Desalination</i> 273 (2011) 391-397.	506 507
[8] C.M. Galanakis, G. Fountoulis, V. Gekas, Nanofiltration of brackish groundwater by using a polypiperazine membrane, <i>Desalination</i> 286 (2012) 277-284.	508 509
[9] C. Liu, K. Rainwater, L. Song, Energy analysis and efficiency assessment of reverse osmosis desalination process, <i>Desalination</i> 276 (2011) 352-358.	510 511
[10] H. Maddah, A. Chogle, Biofouling in reverse osmosis: phenomena, monitoring, controlling and remediation, <i>Applied Water Science</i> 7 (2017) 2637-2651.	512 513
[11] J.K. Gienger, R.J. Ray, Membrane-based hybrid processes, <i>AIChE</i> 84 (1988) 168-177.	514
[12] S.B. Sadr Ghayeni, S.S. Madaeni, A.G. Fane, R.P. Schneider, Aspects of microfiltration and reverse osmosis in municipal wastewater reuse, <i>Desalination</i> 106 (1996) 25-29.	515 516
[13] S.B. Sadr Ghayeni, P.J. Beatson, R.P. Schneider, A.G. Fane, Water reclamation from municipal wastewater using combined microfiltration-reverse osmosis (ME-RO): Preliminary performance data and microbiological aspects of system operation, <i>Desalination</i> 116 (1998) 65-80.	517 518 519 520
[14] P.H. Wolf, S. Siversns, S. Monti, UF membranes for RO desalination pretreatment, <i>Desalination</i> 182 (2005) 293-300.	521 522
[15] H. Kim, J. Choi, S. Takizawa, Comparison of initial filtration resistance by pretreatment processes in the nanofiltration for drinking water treatment, <i>Separation and Purification Technology</i> 56 (2007) 354-362.	523 524 525

[16] B. Van Der Bruggen, C. Vandecasteele, Distillation vs. membrane filtration: overview of process evolutions in seawater desalination, <i>Desalination</i> 143 (2002) 207-218.	526 527
[17] A.M. Hassan, A.T.M. Jamaluddin, A.M. Farooque, A. Rowaili, A.G.I. Dalvi, N. M. Kither, G.M. Mustafa, I.A.R. Altisan, A new approach to membrane and thermal seawater desalination processes using nanofiltration membranes (part 1), <i>Desalination</i> 118 (1998) 35-51.	528 529 530 531
[18] R. Ray, D. Friesen, R. Wytcherley, R.P. Schofield, Pervaporation-based hybrid systems, in: <i>Proceedings of 4th International Conference of Pervaporation Process in Chemical Industry</i> , Bakish Materials Corp, New Jersey, (1989) 200-214.	532 533 534
[19] J. Kim, K. Jeong, M.J. Park, H.K. Shon, J.H. Kim, Recent advances in osmotic energy generation via pressure-retarded osmosis (PRO): A review, <i>Energies</i> 8 (2015) 11821-11845.	535 536
[20] L. Chekli, S. Phuntsho, J.E. Kim, J. Kim, J.Y. Choi, J.-S. Choi, S. Kim, J.H. Kim, S. Hong, J. Sohn, H.K. Shon, A comprehensive review of hybrid forward osmosis systems: Performance, applications and future prospects, <i>Journal of Membrane Science</i> 497 (2016) 430-449.	537 538 539
[21] B.D. Coday, B.G.M. Yaffe, P. Xu, T.Y. Cath, Rejection of trace organic compounds by forward osmosis membranes: A literature review, <i>Environmental Science & Technology</i> 48 (2014) 3612-3624.	540 541 542
[22] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis, <i>Water Research</i> 46 (2012) 2683-2692.	543 544 545
[23] C. Kim, S. Lee, H.K. Shon, M. Elimelech, S. Hong, Boron transport in forward osmosis: Measurements, mechanisms, and comparison with reverse osmosis, <i>Journal of Membrane Science</i> 419 (2012) 42-48.	546 547 548

[24] D.L. Shaffer, N.Y. Yip, J. Gilron, M. Elimelech, Seawater desalination for agriculture by integrated forward and reverse osmosis: Improved product water quality for potentially less energy, <i>Journal of Membrane Science</i> 415 (2010) 1-8.	549 550 551
[25] M. Arjmandi, M. Peyravi, A. Altaee, A. Arjmandi, M. Pourafshari Chenar, M. Jahanshahi, E. Binaeian, A state-of-the-art protocol to minimize the internal concentration polarization in forward osmosis membranes, <i>Desalination</i> 480 (2020) 114355.	552 553 554
[26] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, <i>Journal of Membrane Science</i> 396 (2012) 1-21.	555 556
[27] B.S. Chanukya, N.K. Rastogi, Ultrasound assisted forward osmosis concentration of fruit juice and natural colorant, <i>Ultrasonics Sonochemistry</i> 34 (2017) 426-435.	557 558
[28] B. Jiao, A. Cassano, E. Drioli, Recent advances on membrane processes for the concentration of fruit juices: a review, <i>Journal of Food Engineering</i> 63 (2004) 303-324.	559 560
[29] N.K. Rastogi, Opportunities and Challenges in Application of Forward Osmosis in Food Processing, <i>Critical Reviews in Food Science and Nutrition</i> 56 (2016) 266-91.	561 562
[30] V. Sant'Anna, L.D.F. Marczak, I.C. Tessaro, Membrane concentration of liquid foods by forward osmosis: Process and quality view, <i>Journal of Food Engineering</i> 111 (2012) 483-489.	563 564
[31] M. Arjmandi, M. Peyravi M. Pourafshari Chenar, M. Jahanshahi, A new concept of MOF-based PMM by modification of conventional dense film casting method: Significant impact on the performance of FO process, <i>Journal of Membrane Science</i> 579 (2019) 253-265.	565 566 567
[32] V. Yangali-Quintanilla, Z. Li, R. Valladares, Q. Li, G. Amy, Indirect desalination of red seawater with forward osmosis and low pressure reverse osmosis for water reuse, <i>Desalination</i> 280 (2011) 160-166.	568 569 570

[33] N.T. Hancock, P. Xu, D.M. Heil, C. Bellona, T.Y. Cath, Comprehensive bench-and pilot-scale investigation of trace organic compounds rejection by forward osmosis, <i>Environmental Science & Technology</i> 45 (2011) 8483-8490.	571 572 573
[34] G. Blandin, A.R.D. Verliefde, C.Y. Tang, P. Le-Clech, Opportunities to reach economic sustainability in forward osmosis–reverse osmosis hybrids for seawater desalination, <i>Desalination</i> 363 (2015) 26-36.	574 575 576
[35] A. Achilli, T.Y. Cath, E.A. Marchand, A.E. Childress, The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes, <i>Desalination</i> 239 (2009) 10-21.	577 578
[36] K.S. Bowden, A. Achilli, A.E. Childress, Organic ionic salt draw solutions for osmotic membrane bioreactors, <i>Bioresource Technology</i> 122 (2012) 207-216.	579 580
[37] A. Altaee, N. Hilal, High recovery rate NF-FO-RO hybrid system for inland brackish water treatment, <i>Desalination</i> 363 (2015) 19-25.	581 582
[38] R.V. Linares, Z. Li, V. Yangali-Quintanilla, N. Ghaffour, G. Amy, T. Leiknes, J. Vrouwenvelder, Life cycle cost of a hybrid forward osmosis–low pressure reverse osmosis system for seawater desalination and wastewater recovery, <i>Water Research</i> 88 (2016), 225-234.	583 584 585 586
[39] K. Park, D.Y. Kim, Y.H. Jang, M. Kim, D.R. Yang, S. Hong, Comprehensive analysis of a hybrid FO/crystallization/RO process for improving its economic feasibility to seawater desalination, <i>Water Research</i> 171 (2020), 115426.	587 588 589
[40] A. Altaee, A. Mabrouk, K. Bourouni, A novel Forward osmosis membrane pretreatment of seawater for thermal desalination processes, <i>Desalination</i> 326 (2013) 19-29.	590 591
[41] A. Altaee, Computational model for estimating reverse osmosis system design and performance: part-one binary feed solution, <i>Desalination</i> 291 (2012) 101-105.	592 593

- [42] A. Altaee, G. Zaragoza, A conceptual design of lowfouling and high recovery FO-MSF desalination plant, *Desalination* 343 (2014) 2-7. 594 595
- [43] M. Arjmandi, M. Peyravi, M. Pourafshari Chenar, M. Jahanshahi, Channelization of water pathway and encapsulation of DS in the SL of TFC FO membrane as a novel approach for controlling dilutive internal concentration polarization, *Environmental Science: Water Research & Technology* 5 (2019) 1436-1452. 596 597 598 599