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Research Paper

Seawater Desalination by Using Nanofiltration (NF) and Brackish Water Reverse Osmosis (BWRO) Membranes in Sequential Mode of Operation

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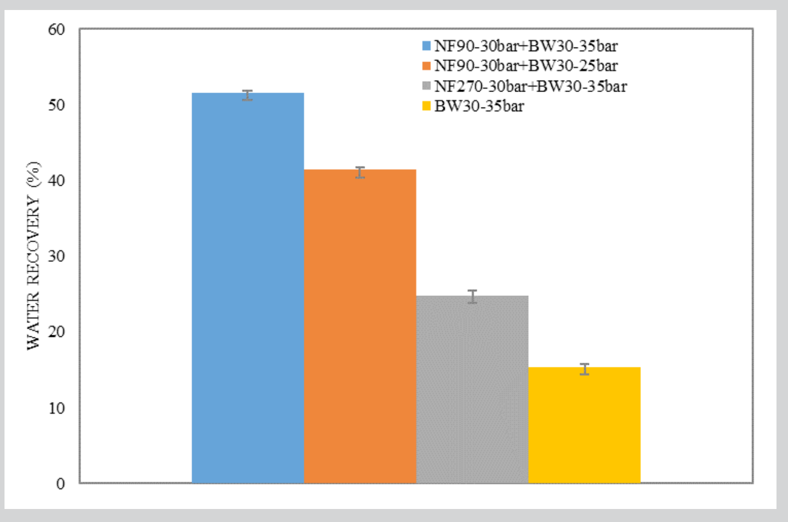
Highlights

- NF is an ideal pre-treatment step for BWRO desalination
- The highest water recovery with NF90-30 bar + BW30-35 bar system
- NF+BW30 combination is suitable for irrigation except boron problem

Graphical abstract



Abstract

In this study, the applicability of nanofiltration (NF) membranes as a pretreatment prior to reverse osmosis (RO) in seawater desalination was investigated. The membranes used were NF270 and NF90 as the NF membranes, while the brackish water (BW) RO membrane BW30 was used as the RO membrane. In desalination tests, permeates of the NF membranes were collected and used as the feed to the BW30 membrane. The calculated permeate fluxes were 6.7 L/h.m^2, 11.3 L/h.m^2, 24.3 L/h.m^2, and 36.6 L/h.m^2 for single BW30-35 bar, NF270-30 bar + BW30-35 bar, NF90-30 bar + BW30-25 bar and NF90-30 BW30-35 bar, respectively. The calculated water recovery and rejected salt values were 51.6%, 41.4%, 24.8%, 15.4% and 98.2%, 98.2%, 96.0%, 91.0% for NF90-30 bar + BW30-35 bar, NF90-30 bar + BW30-25 bar, NF270-30 bar + BW30-35 bar and single BW30-35 bar, respectively. The qualities of the product waters of integrated systems (NF+BWRO) and the single BWRO system were also investigated. Boron rejection was fairly well with average boron rejections of 59.3% and 60.2% by NF90-30 bar + BW30-25 bar and NF90-30 bar + BW30-35 bar combinations, respectively while single BW30-35 bar gave an average rejection of 49.6%. The results obtained showed that the quality of product water obtained using single BWRO did not comply with the irrigation standards, while the integrated systems provided total compliance to irrigation standards with the exception of boron.

1. Introduction

One of the most abundant compounds in the universe is water covering about 70.9% of the earth surface. Despite the large abundance of water on earth, water scarcity continues to be a threat to our life. Because 97% of this water is seawater which contains almost all elements, while 2.5% is fresh water which can be found in rivers, lakes, underground water and polar ice caps, the accessible fresh water cannot meet the human demand [1]. Due to some health issues, the available seawater cannot be used directly [2]. According to the World Health Organization the permissible salt

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concentration in drinking water should be less than 500 mg/L while in seawater it ranges from 35,000 up to 45,000 mg/L [3]. According to United Nations World Water Assessment Program (WWAP), only 60% of the world water demand can be supplied by 2030 [4]. Fresh water withdrawal will increase by 55% by the year 2050 and this will cause about 40% of the world population to live under a water-stressed region [5].

Therefore, it is necessary to look for alternative source of fresh water and seawater desalination will play a vital role in the provision of fresh water. The technologies used in the desalination of seawater generally are based on thermal and membrane processes [6]. The thermal desalination technologies include solar distillation, multi-effect evaporation, multi-stage flash distillation, thermal vapor compression and mechanical vapor compression, while the membrane technologies include electrodialysis (ED), electrodialysis reversal (EDR), nanofiltration (NF) and reverse osmosis (RO) [7]. About 44% of the world installed desalination plants are membrane based and 66% are thermal based. About 87% of the thermal-based processes are used in the Middle East countries [8]. However, due to fuel depletion and environmental concerns with the use of fossil fuel, inefficiency in the energy usage, high capital and operating cost make thermal based desalination decline gradually [9].

The RO process is the most widely used technology in the desalination of seawater due to the improvements in the membrane modules, decrease in membrane cost, increase in membrane lifetime, enabling energy recovery systems etc [10]. However, concentration issue and low recovery ratio (RR) are the main drawbacks of this process. Most of the RO desalination plants are designed for 0.35-0.5 RR making the concentrate account for about 50% of the treated seawater [11]. Therefore, increasing the RR will drastically decrease both the capital and operating costs of this process. Also, valorization of the brine produced as concentrate such as in NaCl, acid and base production will address some economic challenges of the system as well as decreasing the negative effect on the environment [12].

There are many ways to address these issues like increasing the applied pressure or coupling the RO process with other installations (ED, EDR, bipolar membrane ED or hybrid membrane systems). Increasing the pressure will not solve the problem since every membrane has its maximum operating pressure also it will create another problem like membrane fouling, scaling, concentration polarization and so on [13]. For this purpose, selection of proper pretreatment method will help to reduce the effect of scaling and fouling on productivity [14]. Microfiltration (MF) and ultrafiltration (UF) processes are widely used in the pretreatment of RO process [15] due to their ability to reject suspended particles, colloids, macromolecules, algae bacteria and virus [16], but this type of pretreatment only solves the problem of fouling and membrane clogging. Several efforts were made in order to increase the water recovery of RO systems without decreasing the life span of the membranes. The performance of NF processes cannot meet the standard of irrigation and drinking water due to its inability to reduce the salinity in seawater to the permissible level [17-19]. However, NF method can be used prior to RO process as a pretreatment since divalent ions like calcium, magnesium and sulfate ions exist in seawater are highly rejected, which are major sources of scaling in the RO process [20-22]. The NF membranes can be applied in order to increase the water recovery of the RO processes.

There are a lot of published papers showing the potential use of NF membranes prior to RO process in desalination systems. Tay et al. [23] used the combination of NF-MBR+RO processes for higher water recovery. It was mentioned in their study that NF membranes showed pretreatment ability since it has a good rejection with respect to divalent ions which are responsible for causing scaling on the surface of RO membranes. Dissolved organic matter (DOM) is inevitable in seawater and it consists of polysaccharides, proteins, amino acids, carbohydrates and humic substances [24]. If RO membranes are used directly in this type of water, the membranes will be fouled in a short period of time. For that reason, Yin et al. [24] investigated the potential use of NF membranes prior to RO membrane. It was reported in the study that about 80-90% of the foulants were removed by the NF membranes. Coupling UF-NF-RO in a sequential manner has improved the overall recovery in seawater desalination, the system worked with 90, 40-50 and 50% of water recoveries for UF, NF and RO processes, respectively. In this case NF membrane was used as a softener in the treatment of wastewater from gold mining industry [25]. Song et al. [26] also investigated the fouling behavior for integrated NF-SWRO process in seawater desalination and the results showed good impact of the use of NF membranes prior to RO systems with respect to membrane fouling in seawater desalination. Parlar et al. [27] also used NF membranes as a pretreatment prior to RO membranes in the treatment of MBR effluent, they also investigated the reusability of the permeate water for irrigation purpose. Integrating NF to RO membrane systems will increase the complexity of the system [28]. However, it was shown that, NF membranes will eliminate scalants as well as reduce osmotic pressure to some extent thereby reducing the load on the RO membranes [29]. Increasing additional unit to RO membranes will definitely increase both operation and capital costs. AlTaee and Sharif [30] carried out the cost analysis on a dual NF-NF, NF-RO and single RO systems. Their results showed that NF-NF combination was the cheapest followed by RO then NF-RO systems. Depending on the required quality of the product water, proper selection must be done. In our previous study [29], the applicability of NF membranes prior to SWRO system was also investigated. We reported that SWRO flux increased from 30.1 LMH to 55.1 LMH when NF was used as a pretreatment prior to seawater SWRO unit (flux of single SW30-RO membrane was 30.1 LMH at 55 bar, while the average flux of the integrated NF90 (30 bar) + SW30-RO (40 bar) system flux was 55.1 LMH). The results showed a good rejection with respect to all ions, therefore if such water is to be considered as irrigation water some nutrients must be added to the product water. As can be seen, most of the research conducted on seawater desalination were on NF+SWRO integration [24-26].

On the other hand, information about NF+BWRO integration on seawater desalination is very rare in the literature. From economic perspective, Ghaffour et. al. [31] conducted a review for large scale desalination plants. It was clearly shown that the total cost of BW30 membrane desalination is lower than that of SW30 membrane operation (0.5-1.2 $\$/m^3$ and 0.2-0.4 $\$/m^3$ for SWRO-30 and BWRO-30, respectively) while Bhojwani et. al. [32] found the cost as follows: 0.5-1.2 $\$/m^3$ and 0.2-0.4 $\$/m^3$ for SWRO-30 and NF90 membranes, respectively. Therefore, it is obvious if NF90 membrane is used as pretreatment for BW30 and SW30 membranes, the integration with BW30 membrane will be cheaper.

In this study, the applicability NF membranes (NF90 and NF270) was investigated as a pretreatment stage of seawater desalination process by BWRO-30 membranes using a mini pilot-scale desalination system installed in Urla Bay, Izmir, Turkey. In the desalination tests, two different NF membranes (NF90 and NF270) and BWRO (BWRO-30) membrane were used. At the beginning, individual membrane test was conducted in a closed-loop operation. Then, permeate of the NF membranes was collected in a tank and it was used as feed of BWRO membrane (BWRO system was operated in a closed-loop). Performances of single NF membranes (NF270 and NF90) and BWRO membrane, NF+BWRO sequential system were compared with respect to the permeate quality and quantity for the use of the produced water for irrigation purpose.

2. Experimental

Seawater desalination tests were carried out using a mini pilot-scale desalination system installed in Urla Bay-Izmir, Turkey. The characteristics of the seawater used during desalination tests can be found from our previous work [29].

In this work, pH of the seawater ranges from 8.1 to 8.2 throughout the experiments. Therefore, we did not adjust the pH additionally. The NaOCl solution was used for disinfection of seawater. The Nalco PC100 antiscalant was employed in order to prevent the effect of inorganic scalants on the surface of the membranes and $Na_2S_2O_5$ was used for the removal of free chlorine from the feed.

The NF membranes used in this study were NF90-2540 and NF270-2540 (spiral wound FilmTec™ membranes of Dow Chem. Company). The used NF270 membrane consists of thin semi-aromatic with piperazine-based poly(amide) film which constitutes its active layer while the NF90 used in this study is composed of fully aromatic poly(amide) layer [33]. The BW30-RO-2540 (spiral wound FilmTec™ membrane of Dow Chem. Co.) was used as RO membrane. The properties of the membranes used in this study can be found in Table 1.

Table 1
Membranes properties [34]

	NF90-2540	NF270-2540	BW30-2540
Membrane	PA-TF Composite	PA-TF Composite	PA-TF Composite
Maximum Operating Temperature (^{o}C)	45	45	45
Maximum Operating Pressure (Bar)	41	41	41
Active Membrane Area (m^2)	2.6	2.6	2.6
MWCO (Da)	200 [29]	200-300 [33]	dense

2.1. Mini pilot-scale desalination system

The installed desalination system (mini pilot scale) was located in Urla Bay-Izmir, Turkey. The pilot desalination system consists of a 5-micron cartridge filter, sand filters, low and high-pressure pump, and two membrane modules which are about 1 m in length with a 2.5″-diameter membrane element inside the modules. The schematic diagram of the seawater desalination pilot system can be found in Figure 1.

The feed seawater was pumped to a storage tank followed by chlorination. The chlorinated seawater was pumped to the feed tank pumped to the low-pressure pump then to a sand filter and a cartridge filter for the removal of the suspended solids. Seawater was fed to BWRO membrane by high-pressure pump after physical and chemical treatment.

The seawater desalination tests were conducted in two phases. In phase I, the performance of single membrane was studied (NF90-2540 and NF270-2540 as NF membranes, while BW30-RO-2540 as RO membrane) in a closed-loop as seen in Figure 1. In the study with the single NF membranes, the operation pressure was kept constant at 30 bar while in the single study with RO membrane the operational pressure was 35 bar. In phase II, the produced product water (permeate) from NF membranes was collected, stored in a tank in a continuous study (operating pressure was 30 bar). The collected product water from NF membranes (NF permeate) was fed to BWRO membrane as a feed. BWRO was operated in a closed-loop as can be seen in Figure 2. For the sequential desalination test (phase II), the operating pressure of the NF membranes was 30 bar while BWRO membrane was operated at 25 and 35 bar of pressures.

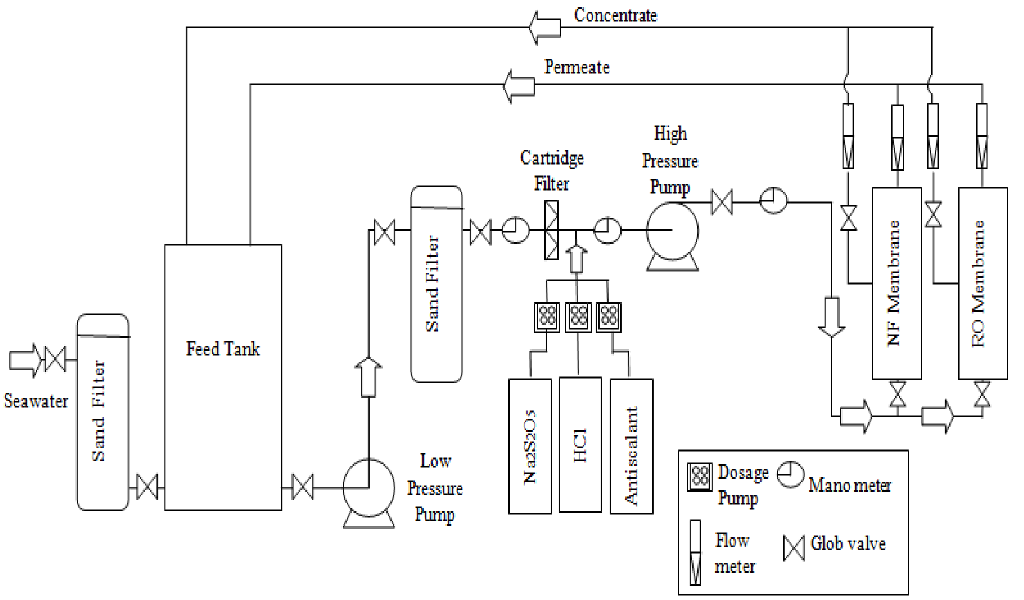

Fig. 1. Schematic flow diagram of the single membrane desalination setup (closed-loop configuration) [29]. (Copyright 2015. Reproduced with permission from Elsevier Science Ltd.)

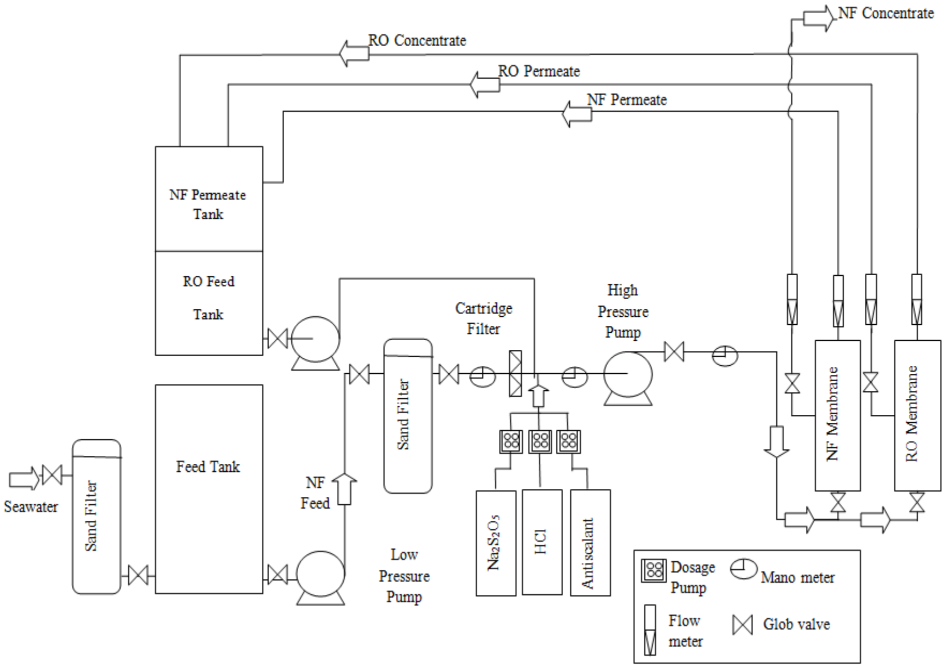

Fig. 2. Schematic flow diagram of the NF+BWRO integrated desalination setup [29]. (Copyright 2015. Reproduced with permission from Elsevier Science Ltd.).

2.2. Analytical methods

The product water produced from the pilot desalination system was checked with respect to its quality and quantity. The product water quantity was monitored by its flux. During the quality analysis of the feed and the product water (permeate), TDS, conductivity, salinity and temperature of the product water were measured with the help of portable Mettler Toledo conductivity meter. A pH meter (WTW pH 315i/SET) was used in the measurement of the pH in both feed and the filtrate (permeate). In the determination of bicarbonate concentration, acid-base titration method was used. An atomic absorption spectrophotometer (Varian 10 Plus Model) was used for the determination of concentrations of K^+, Na^+, Mg^{2+} and Ca^{2+} ions in the samples collected. The measurement of concentrations of SO_4^{2-} and Cl^- ions was carried out by A Shimadzu IC 10 Ai type ion chromatography equipment. The Azomethine-H method was used for boron analysis by Jasco V-530 model spectrophotometer.

2.3. Calculations

Rejection (R), product water flux (J_v) and product water recovery of the membranes tested were calculated as follows:

$$\text{Rejection (\%)} = \left(\frac{C_0 - C_p}{C_0}\right) \times 100 \tag{1}$$

$$J_v\ (\text{L/hm}^2) = V_p/A_m{\cdot}t \tag{2}$$

$$\text{Product water recovery (\%)} = [\text{product water flux / feed flux}] \times 100 \tag{3}$$

$$\text{Feed flux} = (\text{product water flux + concentrate flux}) \tag{4}$$

C_p, C_o, V_p, A_m, and t are permeate concentration, feed concentration, permeate volume, active area of the membrane and time of operation, respectively.

3. Results and discussion

The main driving force in a membrane based seawater desalination process is pressure and desalination cost is then directly proportional to the applied pressure [32]. The quantity of water produced from NF membranes is high but unfortunately the quality does not meet the standard for neither domestic nor agricultural purposes [29]. When RO membranes are used directly after pretreatment with MF and UF, scaling from Ca^{2+} and Mg^{2+} becomes a serious threat to RO membranes thereby decreasing the productivity. In literature, it was clearly mentioned that the cost of NF+SWRO process is high even though the quality of the product water is the best compared with other combinations [32]. Quality of water produced from seawater desalination is number one priority, however, some sectors does not need very high quality water if all the ions in the water are below the permissible limits. For example, some ions are needed for plant growth, for that reason, it is of prominent importance to explore the use of low pressure RO membranes in seawater desalination. This study was carried out in two phases: in phase I (single-membrane test) BW30-RO membrane was tested, while in phase II the integration of NF membranes with BWRO membrane (BW30) in sequential mode was investigated.

3.1. Phase I (single membrane tests)

NF membranes are capable of producing high water flux by applying low pressures [35]. In our previous study [29], the performances of NF90 and NF270 membranes were investigated with respect to flux and water recovery of the product water (permeate) from seawater. The operational pressures for two membranes were adjusted as 30 bar and the measured fluxes were 65.8 L/hm² and 19.0 L/hm² for NF270 and NF90, respectively. Permeate flux of single BW30-35 bar system was only 6.7 L/hm² at 35 bar. When we checked the properties of the membranes (Table 1), it can be clearly seen that NF270 is more loose membrane compared to NF90 and BW30 membranes. It can be clearly seen that the MWCO of NF270 is greater than that of NF90. It was also reported by Lui et al. [36] that the average pore radiuses of NF90 and NF270 membranes are 0.36 and 0.44 nm, respectively. This was the reason for higher flux obtained by NF270 membrane. The average water recovery values of NF270 and NF90 membranes were 64.6 and 33.9%, respectively. The lowest water recovery in a single study was found with BW30 membrane at 35 bar with an average value of 15.4%. As given in Table 1, the maximum applied pressure for BW30-RO membrane is 41 bar. This was the reason why we did the tests at 35 bar.

3.2. Salt rejection of RO membranes

Salt rejection of BW30 membrane at 35 bar is depicted in Figure 3. BWRO membranes revealed a high salt rejection. The BW30 membrane at 35 bar rejected salinity with an average salt rejection of 90.8%. The difference in the applied pressure has contributed to the higher salt rejection by SWRO membrane than by BWRO membrane [36]. The SWRO membrane structure is denser than BW30 membranes and it is produced for seawater desalination while BW30 membrane for desalination of brackish water.

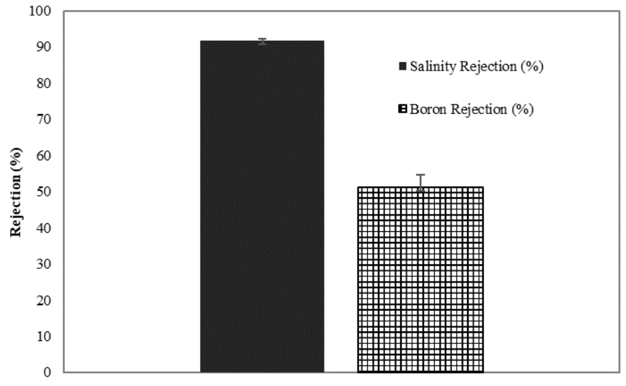

Fig. 3. Salinity and boron rejection for single BW30 membrane test.

Table 2
Integrated system working conditions.

System	Applied Pressure (bar)	
	NF	RO
NF90+BW30	30	25
NF90+BW30	30	35
NF270+BW30	30	35

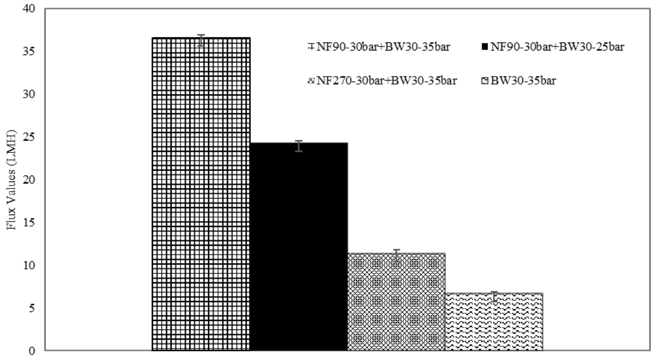

Fig. 4. Average permeate flux values for single BW30 and NF+BW30 integrated systems.

3.3. Divalent ion rejection

For Mg^{2+} ion rejection, BW30 exhibited similar performance with NF membranes and the average rejections were 99.0%, 97.0% and 98.9% for BW30, NF90 and NF270 membranes, respectively. One of the unique properties of NF membranes is their ability to reject multivalent ions effectively without changing the salinity of the seawater much as shown in our previous study [29]. An average Ca^{2+} rejection of 99.6% was obtained with BW30 membrane and this rejection is slightly lower than the Ca^{2+}

rejection obtained with NF membranes. The rejection of SO_4^{2-} ions was high with BW30 membrane giving an average rejection of 99.6%. According to the literature [6], the mechanism for separation of divalent ions is based on sieving because of the size difference between the pores of membranes and the ions. In addition, the charge of ions affects their rejections also.

3.4. Monovalent ion rejection

From our previous study [29], it was clearly shown that monovalent ions were weakly rejected by NF membranes. The NF90 membrane rejected Na^+ ions with an average rejection of 50.0%, while NF270 membrane achieved an average rejection of 15.4% for Na^+ ions. In the case of Na^+ ions, BW30 membrane gave a rejection of 89.3% which is quite high compared with rejections with NF membranes as shown by Kaya et al. [29]. The average rejection observed for K^+ ions was 89.9% by BW30 membrane while NF90 and NF270 membranes gave average rejections of 48.9% and 22.1%, respectively for K^+ ions. The BWRO membrane rejected Cl^- ions with an average rejection of 90.0% at 35 bar. This rejection is higher than the rejections obtained with NF membranes as can be seen in our previous study [29]. The rejection of Cl^- ions was 56.3% with NF90 membrane while 21.9% with NF270 membrane [29]. The reason for the lower rejection for monovalent ions was attributed to their small hydrated radius compared to divalent ions that make them easily pass through NF membranes [6].

3.5. Boron rejection

Single BW30 system at 35 bar rejected boron with an average rejection of 50.4% (as depicted in Figure 3) which is better than the single NF membranes as discussed in by Kaya et al. [29]. The NF90 membrane was able to reject only 17.0% of boron from seawater while NF270 gave an average boron rejection of 13.9% [29]. The boron found in seawater is generally in the form of boric acid (H_3BO_3). The pH of seawater during this study ranged from 8.1-8.2, therefore, the boric acid in the seawater during this study was considered to be mostly in molecular boric acid form [37]. This resulted in small rejection of boron by BW30 membrane.

3.6. Phase II (Sequential NF+RO tests)

For the sequential tests, three membranes (NF90-2540 and NF270-2540 membranes as NF membranes and FilmTec BW30-2540 membrane as RO membrane) were employed. During these studies, permeates of NF membranes were collected first in a 500 L tank under an operating pressure of 30 bar. Permeates produced by NF membranes were fed to RO (BW30) membranes in closed-loop tests. The tests with BW30 membrane were carried out under the operating pressures of 25 and 35 bar. The process conditions of integrated NF+BW30 system were given in Table 2.

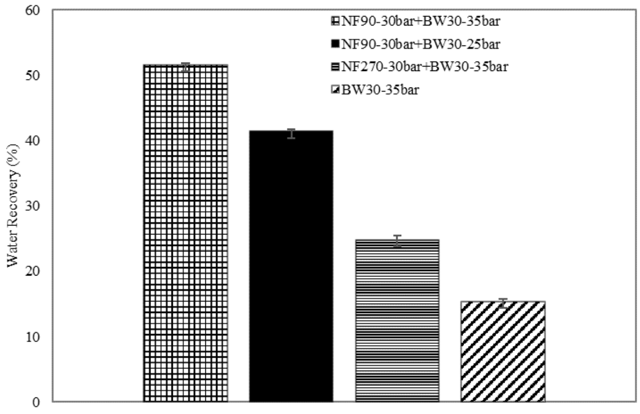

Fig. 5. Average water recovery values for single BW30 and NF+BW30 integrated systems.

3.7. Permeate flux and water recovery of sequential NF+BW30 systems

The performances of sequential NF90+BW30 and NF270+BW30 systems in terms of permeate flux were depicted in Figure 4. It was seen that permeate flux increased markedly when NF membrane was used for pretreatment step. Integrated NF90-30 bar + BW30-25 bar combination gave a permeate flux of 24.3 L/hm^2. Furthermore, as the applied pressure for BW30 membrane increased from 25 bar to 35 bar, the flux of NF90+BW30 sequential system increased to an average value of 36.6 L/hm^2. The permeate flux of integrated NF270-30 bar + BW30-35 bar system produced a better result (with respect to permeate flux) compared to single BW30 membrane, although NF270 membrane has low rejection performance for conductivity, TDS, salinity, etc. as discussed in phase I. In the sequential system of NF270-30 bar + BW30-35 bar, an average flux of 11.3 L/hm^2 was obtained.

Water recoveries in the sequential systems also showed a similar trend in terms of permeate flux (Figure 5). Highest water recovery was obtained with sequential NF90-30 bar + BW30-35 bar system with an average water recovery of 51.6%. In other combinations, sequential NF90-30 bar + BW30-25 bar and NF270-30 bar + BW30-35 bar systems exhibited average water recovery values of 41.4% and 24.8%, respectively. As can be seen, the difference in the water recovery was due to the lower salt rejection in NF270 than NF90 as explained in our previous study [29]. Permeate produced by NF270 has a higher osmotic pressure compared to permeate from NF90 membranes. In order to have higher water recovery, we should increase the operating pressure when NF270 is used prior to BWRO membrane. Related literature showed that pretreatment of seawater by NF membranes prior to RO desalination have reduced energy usage and increased water recovery in RO systems by reducing the osmotic pressure of feed [38, 39].

3.8. Conductivity, salt and TDS rejections of sequential NF+BW30 systems

Conductivity rejection increased significantly when the NF membrane was used as a pretreatment step. Conductivity rejection was effective with an average rejection of 97.4% and 97.5% for sequential NF90-30 bar + BW30-25 bar and NF90-30 bar + BW30-25 bar systems, respectively. Despite the pressure increase in BW30 step, rejection in terms of conductivity was not high for NF90+BW30 combination run at two different pressures of BWRO steps. The sequential NF270-30 bar + BW30-35 bar combination also showed a high performance in terms of conductivity removal with 95.0% of rejection.

NF90 membrane provided an average 55.1% of salt rejection while 20.8% of salt rejection by NF270 membrane was observed [29]. Salt was rejected with an average level of 96.0% for sequential NF270-30 bar + BW30-35 bar system. The respective value was around 98.2% for sequential NF90-30 bar +BW30-25 bar and NF90-30 bar + BW30-35 bar combinations. On the other hand, single BW30 membrane rejected salinity with an average salt rejection of 91.0%.

All sequential system combinations showed similar rejection towards TDS and conductivity as well. TDS was rejected with an average rejection of 95.0, 97.4 and 97.5% with sequential NF270-30 bar + BW30-35 bar, NF90-30 bar + BW30-25 bar and NF90-30 bar + BW30-35 bar combinations, respectively.

3.9. Divalent ion rejections

In all the integrated systems, Mg^{2+}, Ca^{2+} and SO_4^{2-} ions were highly rejected even though there was a little difference in some cases. For Mg^{2+} ion rejection, all three integrated combinations together with single BW30 membrane performed similarly and the average rejection was 99.9%. The rejection of Ca^{2+} ion also showed a similar trend with an average rejection of 99.7% with sequential NF90-30 bar + BW30-25 bar and NF90-30 bar + BW30-35 bar combinations. An average rejection of 96.6% was obtained for the sequential NF270-30 bar + BW30-35 bar system. In terms of SO_4^{2-} ion rejection, the trend was similar to Ca^{2+} ion rejection in which 99.9% of average rejection was observed in all the three combinations (NF270-30 bar + BW30-35, NF90-30 bar + BW30-25 bar and NF90-30 bar + BW30-35 bar). This was possible because almost all divalent ions were highly rejected by NF membranes. Also even with a single BW30 membrane, the divalent ions were highly rejected. Nevertheless, we should bear in mind that the use of single BW30 membrane yielded a low water recovery.

3.10. Monovalent ion rejections

Na^+ ions were highly rejected by sequential NF90-30 bar + BW30-25 bar combination with an average rejection of 97.7% at 25 bar, while with sequential NF90-30 bar + BW30-25 bar combination, the average rejection of Na^+ ions was 98.6%. Also, sequential NF270-30 bar + BW30-35 bar combination provided a good rejection with respect to Na^+ ions with a rejection value of 94.7%. It was shown that performances of all the integrated systems gave a better rejection for Na^+ ions compared with the single BW30 membrane tested at 35 bar.

All integrated systems tested exhibited similar performance in the rejection of K^+ ions as well. Sequential NF90-30 bar + BW30-25 bar combination revealed a high rejection for K^+ ions with an average of 96.7%, while sequential NF90-30 bar + BW30-35 bar combination gave a rejection of 97.1% for K^+ ions. Sequential NF270-30 bar + BW30-35 bar combination performed an average K^+ ion rejection of 92.2%. The rejection of Na^+ and K^+ ions were in accordance with the arrangement proposed by Baker [40] which states that for all RO membranes, the rejection of Na^+ ion is greater than that of K^+ ion. Average rejections of 97.9% and 98.0% were achieved for Cl^- ions with sequential NF90-30 bar + BW30-25 bar and NF90-30 bar + BW30-35 bar combinations, respectively.

3.11. Boron rejection

Boron rejection was fairly well with average rejections of 59.3% and 60.2% by sequential NF90-30 bar + BW30-25 bar and NF90-30 bar + BW30-35 bar combinations, respectively. A sequential NF270-30 bar + BW30-35 bar combination showed almost the same performances with an average boron rejection of 53.1%. According to Busch et al. [37], the boron found in seawater is mostly at its molecular form of boric acid and its size is quite small. That is the reason for the lower boron rejections even with the RO membranes. Moreover, when the pH is elevated to 10.2, boron rejection was observed to increase up to 98% since almost all the boric acid is transformed to borate ion which has higher hydrated radius than boric acid [41, 42].

3.12. Quality analysis of product water

There are several guidelines for irrigation water standards, however, these guidelines differ with countries, types of crops and irrigation system. Salinity, pathogenicity, nutrients and amount of heavy metals are the general water quality parameters considered for irrigation water [43]. In this study, the water quality of the treated seawater with single BW30, NF90+BW30 and NF270+BW30 integrated systems was compared with irrigation water standards. The quality analyses result by all integrated system combinations comply with FAO irrigation standards with the exception of boron and potassium as can be seen in Table 3. On the other hand, with single BW30 membrane, the quality of the treated seawater did not comply with the standards with the exception of HCO_3^- and divalent ions. In the integrated systems, boron can be reduced to the standards by a slight increase in the feed seawater pH since the difference with the standards is small as explained in phase II. Although potassium concentration exceeded that of the standard given by FAO, there is no standard for potassium in the Turkish irrigation water standards as reported by Solak [44]. It is good to mention that we did not cross any study in the literature showing a negative effect for K^+ ion at that concentration. For example, in the period of 1981 to 1987, there was a study in Tunisia by the Ministry of Agriculture and Public Health with assistance from the United Nations Development Program (UNDP) about the effect of treated wastewater and well water on crops yield. The result shows an increase in the productivity with treated wastewater compare to well water which attributed to the higher concentration of nitrogen, potassium and phosphorus. The potassium content in their treated wastewater was 36.5 mg/L while in the well water was 3.0 mg/L [45].

It was found that the quality of the permeate produced using NF90+BW30 system was better compared with results obtained with NF270+BW30 combination in integrated systems.

4. Conclusions

Seawater desalination tests were conducted with the installed desalination system (mini pilot-scale) which is located in Urla Bay-Izmir, Turkey. Seawater desalination performance of BW30 membrane was examined both separately and in the integrated systems for the applicability of NF as a pretreatment stage for BWRO for seawater desalination.

NF90 membrane tested exhibited a better rejection compared to NF270 membrane. However, in terms of permeate flux, NF270 gave a higher flux because NF270 membranes have higher pore size compared with NF90 membrane. In integrated system tests, it was concluded that NF process can be used for the pretreatment step prior to BWRO desalination processes in order to increase the water recovery and permeate flux by the elimination of divalent ions that can result in scaling problem, reducing osmotic pressure, and hence reducing the cost of the desalination process. Highest water recovery was found with NF90-30 bar + BW30-35 bar with an average recovery of 51.6% followed by sequential NF90-30 bar + BW30-25 bar (41.4%) then NF270-30 bar + BW30-35 bar (24.8%) systems.

The performance of NF+BW30 integrated system combination was better than that of single BW30 system. It was observed that all integrated system combinations of NF+BW30 comply with irrigation standards for all parameters analyzed with the exception of boron and potassium. However, it was seen that single BW30 permeate quality did not agree well with the irrigation water standards with the exception of divalent ions and HCO_3^- ions. Therefore, this study showed us that with integrating NF and BWRO membranes have great potential to drastically reduce water stress confronting the city of Izmir, Turkey. Considering the results obtained in this study, the amount of water withdrawn from underground especially for agricultural purposes can be reduced by producing irrigation water from seawater.

Table 3
Comparison of feed/permeate characteristics by single BW30 and NF+BW30 integrated system compared to irrigation water standards.

Parameters	**Unit**	**BW30-35 bar**		**NF90-30 bar + BW30-25bar**		**NF90-30 bar + BW30-35bar**		**NF270-30 bar + BW30-35bar**		**Irrigation water Standards** [46]
		Feed (Seawater)	Product water (Permeate)	Feed (Seawater)	Product water (Permeate)	Feed (Seawater)	Product water (Permeate)	Feed (Seawater)	Product water (Permeate)	
pH	-	8.2	7.8	8.2	7.8	8.2	7.80	8.2	7.8	6.0–8.5
EC	mS/cm	56.20	6.24	57.60	1.52	57.60	1.45	56.40	2.85	0–3.00
Salt	psu	37.10	3.42	38.50	0.70	38.50	0.70	37.10	1.47	0–1.94[a]
TDS	(g/L)	28.20	3.13	28.80	0.76	28.80	0.72	28.30	1.42	0–2.00
HCO_3^-	(mg/L)	185.8	24.1	206.5	25.4	206.5	22.1	191.7	22.1	0–610
B	(mg/L)	5.30	2.63	5.32	2.17	5.32	2.11	5.37	2.52	0-2.00
Na^+	(mg/L)	12487	1339	13840	311.9	13840	294	13300	704.50	0–920
K^+	(mg/L)	733	81.1	694	22.99	964	19.80	698	54.80	0–2.00
Mg^{2+}	(mg/L)	1258	13.10	1055	0.64	1055	<0.10	1096	<0.10	0–60
Ca^{2+}	(mg/L)	553	2.22	606	1.69	606	1.40	668	2.90	0–400
Cl^-	(mg/L)	23367	2332	22800	487	22800	453	21400	909	0–1065
SO_4^{2-}	(mg/L)	2327	10.7	2326	<0.1	2326	<0.1	2880	<0.1	0–960

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