Evaluation of removing monovalent and divalent ions of brackish water in Qom Province using membrane processes of nanofiltration, reverse osmosis and hybrid system

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\textbf{Abstract}

The water shortage in the Middle East and North Africa, especially in Iran, and overuse of groundwater resources, are serious problems in the world. For this reason, the desalination of brackish water is essential for clean water demand. In Iran, Qom Province is one of the areas which faces drought and water shortage, therefore using membrane desalination can be a solution to resolve the water crisis in this area. In this study, the desalination process was performed by nanofiltration (NF), reverse osmosis (RO) and hybrid NF/RO membranes. Then, the percentage of monovalent and divalent ions removal in the three processes; NF, RO, and hybrid NF/RO membranes were compared. This study also used the reverse osmosis system analysis (ROSA) simulation model to find the effect of pressure change on the performance of the three membrane processes and the change in membranes to NF90-4040 and BW 30-4040. The results of the pilot study, software ROSA and comparison of NF, RO, and hybrid NF/RO membrane processes were characterized in terms of water production quality and ion removal by the above two methods. The percent of monovalent and divalent ions in software ROSA were calculated at 91.25% and 99.5%, which is close to 100% and therefore is considered as purified drinking water.

\textbf{Keywords:} Brackish water; Desalination; Nanofiltration; Reverse osmosis; Hybrid processes; ROSA simulated model

\section{1. Introduction}

According to a UN statement, the entire world is facing a shortage of safe drinking water due to an increasing population and limited supply networks. The countries in the Middle East and North Africa are located in an area facing climate changes and hot climates. In addition, there is drought and lack of precipitation in these areas [1,2].

Due to these changes and environmental destruction, water resources have been reduced and water shortage is
becoming a major problem. Due to the lack of water, the residents of these areas are facing an unstable distribution of water resources. Therefore, in order to solve the problem of unstable freshwater distribution, the UN Department of Construction has proposed the use of desalination in the Middle East to distribute freshwater, especially in urban areas [3–5].

In Iran, since it is located in the Middle East, water resources play an important role in economic development, and due to climate change, the expansion of industries and increasing population, high-quality water supply is less than the demand. Desalination technologies have been proposed in order to cope with the water crisis and the poor quality of water resources [6,7].

Qom Province is one of the provinces located in the central desert of Iran and groundwater around Qom and Aliabad is used for the water supply network. Groundwater levels in the province have declined in recent years. The decline in the province is due to the overuse of these resources. Therefore, groundwater wells in these areas are rich in dissolved solids and salt [8–10].

The membrane desalination industry has become a common technology for the water supply network in Iran [11–13]. Several studies have been conducted to develop a healthy water supply network in Iran and it is recommended desalination facilities be used for drinking water supplies. Most desalination facilities in Iran and elsewhere in the world use reverse osmosis (RO) membranes with a polyamide nanocomposite structure. These membranes are used in household and commercial desalination devices [14–17].

According to the results of recent studies in Iran, it has been suggested that nanofiltration (NF) membranes of the NF90 series are used to remove polyvalent ions from brackish water [18,19]. Also, in a study by Talaeipour et al. [20,21], physicochemical parameters have been removed by NF and RO membranes.

The purpose of this study is to evaluate the performance of NF, RO and hybrid NF/RO membranes for removing monovalent and divalent ions from brackish water in Qom Province. In addition, comparing the performance of these membranes with different pressures and application of software reverse osmosis system analysis (ROSA) is an important point of this study.

2. Materials and methods

For achieving the study objective, the amount of mono and divalent ions removed by the membranes’ processes were evaluated in the three phases as follows:

2.1. At first, Qom Province was chosen as the study area

2.1.1. Explanatory investigation and characteristics of the study area

In Iran, most water resources contain chloride (Cl\(^{-1}\)), sulfate (SO\(_{4}\))\(^{-2}\), magnesium (Mg\(^{2+}\)), calcium (Ca\(^{2+}\)), and sodium (Na\(^{+}\)) ions. Qom Province and City are located in the watershed of the central desert of Iran and between the Salt Lake and the desert. Most of the water resources in this area include groundwater resources account for most of the water resources in this area Fig. 1. Qom aquifer consists of 21 brackish water wells in Qom City and 13 brackish water wells in Aliabad Plain. Qom City is located on the alluvium fan made of the coarse-grained permeable sediment and Aliabad wells are located on the thick alluvium plain. All the wells in the study area have been contaminated by the urban and industrial sewerage and penetration of the ions because of drought, lack of precipitation, and permeable sediment aquifer. In this area, the main source of water supply is provided by the brackish underground water with the electrical conductivity (EC) of 2,500–6,500 µmoh/cm, which is accessible in 24 m of wells’ water table and a maximum of 12 million m\(^3\)/y water volume. Then, the water parameters were selected to run the experimental test [22–24].

2.2. Tested samples

All 312 samples were collected in this applied-descriptive study from the brackish groundwater in the wells present in Qom Province with a pre-sterilizer amount of 100–200 mL in a glass bottle by simple random sampling. After, collection of all the samples, they were sent to the Qom Central Water and Wastewater Laboratory to perform the experimental test. An experimental test was done every week for one year (2017–2018). Afterwards, the concentrations of positive and negative anion and cation monovalent and divalent ions were tested before entering the device as the feed water and after crossing the membranes as the flux.

In the final phase, the membranes installed on the LUNA100 gallon per day desalination device were the TW30-1821-100 (RO of tap water), NF90-2540, and NF/RO hybrid under control of 5 bar pressure driving force according to the guidelines of the Luna Water Corp., (33 Coates Crescent, Richmond Hill, ON L4E2L9, Canada) and Dow Chemical Company, (Data Privacy Director, 2211 H.H. Dow Way, Midland, Michigan 48674).

The membrane structure is made of a thin film nanocomposite polyamide made by Dow Chemical Company, (Data Privacy Director, 2211 H.H. Dow Way, Midland, Michigan 48674) [25,26].

2.3. Used equipment

2.3.1. Chemical ions analyses

The changes in the chloride ion (Cl\(^{-1}\)) concentration was measured by the Titrette Class A precision with the telescoping filling tube of 170–330 mm purchased from the GMBH Company (Germany). The changes in the concentration of sodium (Na\(^{+}\)) and potassium (K\(^{+}\)) monovalent ions were calculated by a Jenway industrial flame photometer FP7 purchased from the Bibby Scientific Ltd., (UK). The content of sodium Ion (Na\(^{+}\)) was measured in the amount of 1,000 ppm (parts per million) with special cell in the range of 0–40 ppm and a radiation wave of 589 nm for yellow emitted ion. Also, potassium concentration was measured by the cell in the range of 0–20 ppm with 766 nm of radiation wave and violet emitted ion.

The changes in the concentration of divalent ions of calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) were measured by applying a portable Multiparameter Meter (HQ40D, Hach
Co., Laser House, Ground Floor, Suite B Waterfront Quay, Salford Quays, GB – Manchester, M50 3XW, UK) with a confidence interval of 95% ± 0.5% [27]. The changes in the sulfate ion (SO$_4^{2-}$) content was calculated by the photometer 7,100 with 420 nm of radiation wave purchased by the Wagtech Company, (UK).

2.3.2. Statistical analysis and software

In this study, we used ROSA simulated effects. Software ROSA is used to determine the optimum operating conditions of RO and NF membranes.

ROSA simulated model with BW30-4040 (brackish water reverse osmosis) and NF90-4040 membranes was used to study the effect of pressure on the membrane’s performance and ion removal.

Software ROSA has been used specifically on BW30-4040 reverse osmosis membranes. ROSA version 8.0.3 was released in March 2012 [28,29].

All the measurements and laboratory tests were statistically carried out by the independent-samples $t$-test and Bonferroni test to determine the effect of treatment by the membrane processes. For comparing the results of three membranes within one year, a linear mixed model, as a part of the advanced one-way analysis of variance test was performed.

Moreover, the normal distribution of all the data was confirmed by the Kolmogorov–Smirnov test. All the statistical analyses were performed by the SPSS statistical software (version 25; IBM, Armonk, NY). A $p$-value of <0.05 was considered statistically significant.

3. Results

After sampling over a year, the changes in the content of each ion were calculated in the RO, NF, and the membranes integrated as hybrid NF/RO on desalination plan. As shown in Table 1, the concentration of the monovalent ions of chloride (Cl$^-$), sodium (Na$^+$), and potassium (K$^+$), and bivalent sulfate (SO$_4^{2-}$), calcium (Ca$^{2+}$) and magnesium (Mg$^{2+}$) was reduced by the NF, RO, and hybrid NF/RO processes with respect to their concentration in milligrams per liter obtained as a consequence of removal in the feed water are shown in Table 1.

Also, as shown in Table 1, the results of monovalent and divalent ions removal statistical test $p < 0.001$ calculations with a 95% confidence interval show that the removal

Table 1
Study of separation ions and analyzed concentration ions in mg/L; through NF90, RO (TW30) and hybrid NF/RO membranes

<table>
<thead>
<tr>
<th>Ions</th>
<th>Feedwater</th>
<th>Flux (mg/L)</th>
<th>Flux (mg/L)</th>
<th>Flux (mg/L)</th>
<th>$P$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Nanofiltration</td>
<td>Reverse osmosis</td>
<td>Hybrid nanofiltration/</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(NF90-2540)</td>
<td>(tabwater) TW30-1821-100</td>
<td>reverse osmosis (NF/RO)</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1,223.4 ± 54.6</td>
<td>965.4 ± 48</td>
<td>696.4 ± 42.6</td>
<td>451.5 ± 31.2</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>900.5 ± 41.1</td>
<td>40.5 ± 6.1</td>
<td>25.3 ± 3.6</td>
<td>14.5 ± 2.9</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>686.4 ± 35.3</td>
<td>438.3 ± 6.1</td>
<td>312.9 ± 20.9</td>
<td>199.7 ± 20.1</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>K$^+$</td>
<td>13.62 ± 1.18</td>
<td>6.33 ± 1.32</td>
<td>4.37 ± 1.06</td>
<td>3.56 ± 1.06</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>270.2 ± 17.3</td>
<td>88.7 ± 10.1</td>
<td>53.1 ± 5.6</td>
<td>24.5 ± 3.5</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>156.1 ± 7.6</td>
<td>47.1 ± 3.3</td>
<td>32.9 ± 2</td>
<td>17.3 ± 1.5</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

*Results are shown as mean and standard deviation.
rate of ions in the three processes of NF, RO, and hybrid membranes was not the same and statistically significant. Figs. 2 and 3 show the changes in the concentration of monovalent and divalent ions as feed water from the membrane processes in the pilot and simulated ROSA. In this study, the ROSA simulator was used to increase the removal rate of ions in membrane processes. In this software, the quality of produced water and the inlet pressure (NF with 6.96 bar pressure, RO with 13.45 bar pressure) and the hybrid with 13.87 bar pressure are software inputs, resulting in concentration changes as output data shown in Tables 2 and 3.

4. Discussion

In the present study, the concentrations of ions and their removal rate were tested by NF, RO and hybrid NF/RO process membranes at 5 bar pressure using the pilot method. In order to determine the removal rate at varying pressures, we used ROSA software at 6.96 bar pressures using the NF membrane, 13.45 bar using RO membranes and at 13.87 bar pressures using the hybrid NF/RO system. The monovalent and divalent ions were compared in three membrane processes with constant and varying pressures.

4.1. Removal of ions in NF membranes

The removal rate of monovalent ions by NF90-2541 NF membranes at 5 bar pressure included 258/10 mg/L for chlorine ion (Cl\(^{-1}\)), 34/10 mg/L for sodium ion (Na\(^{+1}\)), and 7.26 mg/L for potassium ion (K\(^{+1}\)), in addition to removal of divalent ions, included 181.6 mg/L for calcium (Ca\(^{+2}\)), 1.09 mg/L for magnesium (Mg\(^{+2}\)) and 860 mg/L for sulfate (SO\(_4\)^{2-}\) in Table 1, and Figs. 2 and 3 show the highest and lowest ion removal percentages, by the NF process in the pilot and ROSA software, respectively as follows.

\[ \text{SO}_4^{2-} > \text{Mg}^{+2} > \text{Ca}^{+2} > \text{K}^{+1} > \text{Na}^{+1} > \text{Cl}^{-1} \]

The percentage of rejection ions in NF, RO in addition to hybrid NF/RO membranes is calculated by the following Eq. (1) [30].

\[ R = 100 \times \frac{C_{\text{permeable}}}{C_{\text{feed}}} \]

where \( R \) is the percentage of salt and ions rejection, \( C_{\text{permeable}} \) is the concentration ions in permeable or flux water and \( C_{\text{feed}} \) is the concentration ions in the feed water.

The removal rate of monovalent chloride ion at 21% showed the lowest removal percentage. Also, the divalent sulfate ion at 95.5% and magnesium at 68% showed the highest removal percentages. In a study by Shahi [31] in New Mexico, with NF90 and low-pressure membranes, the rate of chloride ion removal was 21.8%, sulfate 95% and sodium 55%, which is similar to the present study [31].

In the present study, NF90-2541 and NF90-4040 series NF membranes were used. The results showed that divalent ions were removed more than monovalent ions. According to reports of Wang et al. [33] and Juholin et al. [32] the rate of removal and concentration of ions and especially the removal of divalent ions by NF90 series membranes is higher than that of NF270. In this study, for this reason NF90 series
Fig. 3. Ions rejection ratio for membranes (NF, RO, hybrid NF/RO) by simulated ROSA software.

Table 2
Effect of pressure on permeate ions concentration in nanofiltration and reverse osmosis; membranes by ROSA software

<table>
<thead>
<tr>
<th>Content of ions</th>
<th>Feed water (mg/L)</th>
<th>Permeate in nanofiltration (NF90-4040) mg/L with pressure 6.96 bar</th>
<th>Permeate in brackish water reverse osmosis (BW30-4040) mg/L with pressure 13.45 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻¹</td>
<td>1,223.4</td>
<td>101.31</td>
<td>10.52</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>900.5</td>
<td>11.54</td>
<td>3.37</td>
</tr>
<tr>
<td>Na⁺¹</td>
<td>686.4</td>
<td>67.53</td>
<td>7.74</td>
</tr>
<tr>
<td>K⁺¹</td>
<td>13.62</td>
<td>1.14</td>
<td>0.13</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>270.2</td>
<td>5.08</td>
<td>1.14</td>
</tr>
<tr>
<td>Mg⁺²</td>
<td>156.1</td>
<td>3.06</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 3
Effect of pressure on permeate ions concentration in hybrid NF/RO

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Pressure driving force 13.87 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid NF/RO</td>
<td>Hybrid nanofiltration and reverse osmosis (NF/RO) in reverse osmosis system analysis (ROSA) software, feedwater = permeable of nanofiltration</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ions</th>
<th>Permeable NF used as feedwater of hybrid (mg/L)</th>
<th>Permeable (rejection of hybrid) mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻¹</td>
<td>101.31</td>
<td>0.8</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>11.54</td>
<td>0.04</td>
</tr>
<tr>
<td>Na⁺¹</td>
<td>67.53</td>
<td>0.56</td>
</tr>
<tr>
<td>K⁺¹</td>
<td>1.14</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>5.08</td>
<td>0.02</td>
</tr>
<tr>
<td>Mg⁺²</td>
<td>3.06</td>
<td>0.01</td>
</tr>
</tbody>
</table>
membranes were used. And the result is similar to the above studies.

4.2. Removal of ions by RO membranes

The study results showed that the reduced concentration of monovalent ions by RO membranes was 527 mg/L for chloride ion (Cl⁻), 376.6 mg/L for sodium ion (Na⁺), 8.89 mg/L for potassium (K⁺), and the reduced concentration of divalent ions was 875.2 mg/L for sulfate ion (SO₄²⁻), 123.2 mg/L for magnesium ion (Mg²⁺), and 217.2 mg/L for calcium ion (Ca²⁺) as shown in Table 1.

The removal rate of using TW30-1821-100 RO membrane was about 70% which was more than the removal rate of using the NF membrane Fig. 2. The membranes used had polyamide structures with thin composite film with less than 0.3 nm pores. These membranes have the ability to remove compounds, pollutants and ions in water with a molecular weight of less than 150 Da [34,35].

In the present study, the levels of removal and reduction in sulfate ion concentration in the three processes; NF, RO, and hybrid membrane processes at both pressures 5 and 13.87 bar are nearly the same.

The percentage of sulfate ion removal in all membranes is justified by the Donan phenomenon and dielectric repulsivity and the divalent ions in the NF membrane due to the polyamide structure of the membranes and the negative electric charge on the surface of the membranes [36,37].

In a study by Cappelle [38] on the rate of ion removal using NF90 series NF membrane, the removal percentage of magnesium ion (90.1%) was the highest after sulfate ion (97.6%), and the removal percentage of chloride ion removal (37.2%) was reported as the lowest removal percentage.

In the present study, by changing the NF membrane model to NF90-4040 and increasing the pressure from 5 to 6.96 bar, the percentage of removal of ions was changed from the range of 91.16% to 98.5% by ROSA software, indicating that the monovalent ion removal rate reaches up to 91.16% and the divalent ion removal rate reaches up to 98.5%. In studies by Farsi et al. [39] and Madsen [40], the percentage of ion removal due to increased pressure reached more than 96.5%, and it has been reported that the removal of bivalent ions was higher than that of monovalent ions. They also suggested the use of a combination of NF and RO membranes to increase the removal of ions.

In studies by Farsi et al. [39] and Madsen [40], the percentage of ion removal due to increased pressure reached more than 96.5%, and it has been reported that the removal of bivalent ions was higher than that of monovalent ions. They also suggested the use of a combination of NF and RO membranes to increase the removal of ions.

In Iran, the conducted studies have also reported the rate of removal of ions by the NF90 membrane at 4–7 bar pressure over 95%, which is similar to the present study [18,19].

4.3. Results of ion removal by the hybrid NF/RO process

The reduced concentration of ions by the hybrid process was 10.6 mg/L for potassium (K⁺), 456.8 mg/L for sodium (Na⁺), 772 mg/L for chloride (Cl⁻), 245.7 mg/L for calcium (Ca²⁺), 138.8 mg/L for magnesium (Mg²⁺) and 886.10 mg/L for sulfate (SO₄²⁻) as shown in Table 1. In this study, using ROSA software we evaluated and compared hybrid desalination system performance by increasing the pressure from 5 to 13.87 bar. The increased efficiency of the hybrid NF/RO process by the NF membrane as a pre-treatment in ROSA software was evaluated in terms of milligrams per liter (mg/L) for removal of the monovalent and bivalent ions as shown in Table 3 and compared with the results of the hybrid NF/RO in the pilot which is illustrated in Fig. 4. The results showed that by increasing the pressure and using the NF membrane as a pre-treatment the concentration of ions was very low and reached 0.01–1 mg/L and removal percentage reached 78.65%–99.5% (zero discharge desalination) that shown in Figs. 2–4.

In a study by Altaee and Hilal (2015), and Ramaswami (2018) using NF, RO and hybrid NF/RO processes, 80% removal was reported that is similar to the hybrid NF/RO results in the present pilot study [41,42].

In studies by Kong et al. [43] and Park et al. [44], by combining NF90 and RO membranes, the ion removal rate reached above 99%.

Also, the study results of Kaya et al. [45] and Fini et al. [46] showed that by increasing the pressure and the combination of the two NF and RO membranes, the percentage of removal of ions and salt increased dramatically, which was close to 100% (zero discharge desalination).

In the present study, in the hybrid NF/RO system, and by increasing the pressure in ROSA software, the removal of ions reached near 100%, which is similar to the study’s results of the researches mentioned above [43–46].

5. Conclusion

The study results show the evaluation of the performance of the three processes; NF, RO, and NF/RO hybrid membrane at constant and different pressures and membranes.

Fig. 4. Variation of different ions flux under condition types (pressure and internal concentration) in hybrid NF/RO processes.
The results of the reduction in concentration and absorption of ions at the constant pressure of 5 bar by three membrane processes on the tab water scale were compared with membranes on the brackish water scale at various pressures by ROSA software.

In general, according to the results, using NF, RO, and hybrid membranes showed that the percentage of ion removal in the hybrid process is increased. Also, in the desalination process by the NF membranes, the divalent ions are better removed than the monovalent ions of potassium, sodium, and chloride. However, in the hybrid desalination system and RO membranes, all ions are better removed. In the hybrid system, by increasing the pressure through ROSA simulation, the percentage of ions removal is increased to about 100%. Furthermore, according to the results of ROSA software, it can be concluded that in addition to increasing pressure using NF membranes as RO membrane pre-treatment in the hybrid system water treatment, desalination reached zero discharge desalination. Moreover, the percent removal of ions in ROSA software was higher than the results of the pilot method.

To sum up, although the hybrid NF/RO process improved the system of desalination and performance of treatment, the other hybrid systems integrated in addition to the hybrid NF/RO need to be further investigated.

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