

# Boron removal from synthetic hydraulic fracturing wastewaters by hybrid nanofiltration/complexation process

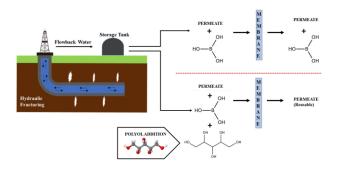
#### Koseoglu H.1\*, and Gonulsuz E.1

<sup>1</sup>Suleyman Demirel University, Faculty of Engineering, Dept. of Environmental Engineering, 32260, Isparta, Turkey Received: 07/07/2022, Accepted: 20/09/2022, Available online: 26/09/2022

\*to whom all correspondence should be addressed: e-mail: hasankoseoglu@sdu.edu.tr

https://doi.org/10.30955/gnj.004339

#### **Graphical abstract**



#### **Abstract**

The primary purpose of this study is to investigate boron removal from synthetic hydraulic fracturing wastewater by membrane processes. The effects of pressure, pH, feed concentration, and polyol concentration on boron removal were determined using a cross-flow, flat-sheet membrane test unit. The nanofiltration membrane was tested within the scope of the experiments. Accordingly, it was determined that the boron removal increased with pressure, pH, and boron concentration. Under the influence of all these variables, the complexing polyol was used in the membrane experiments to remove the boron at a higher level. Xylitol, one of the polyols that forms the most efficient complex with boric acid, was added to the synthetic hydraulic fracturing wastewater at specific molar ratios. In NF membrane tests with polyol addition, >80% boron removal was recorded under specific operating conditions. High-quality permeate water obtained after membrane treatment can be reused as a hydraulic fracturing fluid. It has been proven that the proposed treatment setup can be an effective alternative for boron removal from hydraulic fracturing wastewater.

#### **Keywords**

Boron removal, hydraulic fracturing, membrane, polyol, shale gas

# 1. Introduction

Hydraulic fracturing is a critical technology in the discovery of shale gas, which is defined as an

unconventional gas that has a vital role in meeting energy needs on a global basis (Chen et al., 2015). Increasing wars on a global scale in gas-rich regions of the world in 2022 have been a great motivation for countries to put their own gas reserves into production. In this context, hydraulic fracturing operations have become more important for developed and developing countries. In hydraulic fracturing, the permeability of the rock is increased to produce gas from the source rock, and the reservoir is stimulated with a fracturing network that gives a sufficient surface area to allow production (Speight, 2013). The liquid used in the hydraulic fracturing process is the fracturing fluid. In general, hydraulic fracturing fluids consist of 90% water, 9% proppant, and 1% chemicals, but the amount and ratio of these components vary according to the formation (Koplos et al., 2014). The hydraulic fracturing wastewater (4,000-16,000 m<sup>3</sup>) returning to the surface consists of a mixture of 10-40% of the hydraulic fracturing fluids injected into the well and natural brine from the fractured rock (Jackson et al., 2014). Today, studies looking for solution methods for treating and reusing produced wastewater have increased with regulations and public opinion concerns. The use of membrane-based technologies (pressure-driven membrane processes, membrane distillation, membrane bioreactors, and pervaporation) and advanced oxidation processes (ozonation, Fenton, photocatalysis) has been deemed appropriate for this high-flow wastewater (Silva et al., 2017). Flowback waters from hydraulic fracturing operations, which stand out with their high amount of water consumption, must be treated and recycled within the scope of sustainability. In this context, membrane applications come to the fore. The most important disadvantage of flowback waters is the boron concentration they contain. In order to reuse these waters, which contain much higher boron concentration than the boron concentration of sea waters, it is absolutely necessary to remove the boron effectively and feasibly.

Boron is used as a crosslinker in the hydraulic fracturing fluid and chemically binds the gel polymers, providing the viscosity of the cracking fluid (Stringfellow  $et\ al.$ , 2014). With its boron concentration ( $\cong$ 3-4,000 mg/L), the

hydraulic fracturing wastewater is well above the regulations to re-use the wastewater in the hydraulic fracturing process and its discharge into a receiving environment. Boron concentration at these levels is a significant obstacle to the reuse of wastewater as a hydraulic fracturing fluid. High boron concentrations prematurely cross-link hydroxypropyl guar which affects pumping and cracking (Bu et al., 2018).

It is stated that ion exchange, membrane filtration, and electrocoagulation processes effectively remove boron from wastewater (Karahan *et al.*, 2006). In addition to the filtration system used in membrane processes, combinations with or without pH increase are methods that are effective in boron removal (Geffen *et al.*, 2006). In aqueous environments, boron exists mainly as boric acid and as borate ions according to the decomposition reaction ( $K_a = 6x10^{-10}$ ,  $pK_a = 9.2$ ) shown in the following equation (Power and Woods, 1997):

 $B(OH)_3 + H_3O \square B(OH)_4^- + H^+$ 

Boron exists in an undissociated form (in the form of boric acid) in aqueous solutions at pH values of 7 and lower. Boric acid is a very weak acid with a pKa of 9.2 (Koseoglu et al., 2010; Richards et al., 2010; Yavuz et al., 2013). With the increase in pH value in aqueous solutions, boron turns into dissociated form, that is, borate (Yavuz et al., 2013). Boric acid in molecular form has a small size and is uncharged. Therefore, its removal by NF and RO membranes is low. The dissociated state of the borate ion, on the other hand, has a large radius and is negatively charged. Ions converted from boric acid to borate are highly rejected by negatively charged membranes. For this reason, the removal of the predominant charged form by membrane processes occurs at high levels at pH levels above the pKa value (Kabay, 2015; Güler et al., 2011; Yavuz et al., 2013). Because charged ions are removed mainly by many polymeric membranes such as NF and RO by electrostatic repulsion (Koseoglu et al., 2010). However, effective boron removal from waters with high boron content is quite challenging under high pH conditions (a pH of 10 or higher) where there is a risk of severe membrane clogging with insoluble carbonates, hydroxides, or salts (Geffen et al., 2006; Dydo et al., 2014). For all these reasons, studies using complexing polyols involving borate coupling with polyols with 1,2diol functional groups are available in the literature to eliminate the need for high pH conditions. These complexes are much more stable than monoborate and can be produced under lower pH conditions. With these complexes, boric acid and monoborates can be removed more effectively not only by RO but also by NF membranes (Tu et al., 2013; Dydo et al., 2014).

RO processes are disadvantaged by their high-pressure requirements and low flux generation. Therefore, NF membranes, which stand out with their high flux and low-pressure requirements, were used in our study. In order to overcome the low boron removal problem of NF membranes, polyol complexation was applied to synthetic hydraulic fracturing flowback waters. This study evaluated

boron removal from hydraulic fracturing wastewater returned to the surface due to shale gas production using additional polyols in nanofiltration processes. The experiments carried out within the scope of the study include the filtration of the synthetically prepared hydraulic fracturing wastewater through the NF membrane at various operating pressures, feedwater pH values, and boron concentrations, in the presence and absence of xylitol. The findings obtained in the membrane experiments were evaluated in terms of permeate flux, conductivity removal, and especially boron removal. There are many kinds of research or application projects in the literature on boron removal from wastewaters of various industries. However, boron removal from synthetic hydraulic fracturing flowback water by hybrid nanofiltration/complexation process has not been encountered in the literature to the best of our knowledge. In this way, it was desired to crown the advantages of NF membranes with high boron removal. The findings obtained in this study made significant contributions to the literature.

# 2. Materials and methods

#### 2.1. Membrane test unit

Figure 1 shows the laboratory scale, cross-flow, flat-sheet membrane test unit (SEPA CF II, Osmonics, USA), and the flow chart of the entire system used in the membrane experiments. Since the membrane unit is resistant to pressures up to 69 bar, different membranes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) can be used. The system consists of the high-pressure pump and outlet pressure relief valve, feed tank (37 L capacity), membrane cell, membrane cell carrier, hydraulic hand pump, high pressure regulating valve, and a frequency converter (ABB, Switzerland). It consists of 3 manometers, a permeate-water collection tank, high-pressure-resistant stainless steel, and nylon-seal (Dayco-Imperial) plastic pipes.

19 cm x 14 cm sized membranes (140 cm<sup>2</sup> effective membrane area) are used in the test cell. A frequency converter (ABB ACS-140) integrated into the high-pressure pump (Hydra-Cell G13) provides the desired membrane feed flow. The flow applied in the experiments, and the corresponding cross-flow velocities were 4.8 L/min and approximately 1.2 m/s, respectively. The desired pressure in the membrane cell is adjusted by changing the concentrate flow from the valve in the concentrate line. With this valve, the permeate flow was also controlled. pH, temperature, conductivity (CND), and boron concentrations were measured in feed and permeate streams. Tap water was circulated through the closed space in the entire outer part of the feed tank to ensure that the concentrate recycling, which is heated as a result of high-pressure pumping, does not increase the feed tank's solution temperature and maintains a constant temperature. All experiments were carried out at feed water temperatures of 20 ± 2°C. Alfa Laval NF99 HF, an NF membrane, was used in membrane experiments.

Membrane sheets were obtained from the manufacturers and used as received.

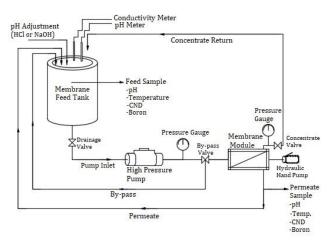


Figure 1. Membrane test unit flow diagram.

# 2.2. Synthetic hydraulic fracturing wastewaters (flowback waters)

In the first stage of the experimental studies, synthetic hydraulic fracturing wastewater was prepared. The composition of synthetic wastewater was determined based on the averages of the compositions of the five fracturing wastewaters listed below: a field from southwest China (Chen et al., 2015), Eagle Ford in Southeast Texas, USA (Sari and Chellam, 2015), Fuling in China (Kong et al., 2017), Denver-Julesburg (DJ) Basin in Colorado, USA (Lester et al., 2015), and Fayetteville Basin in Arkansas, USA (Sardari et al., 2018). While the values of silica (Si), magnesium (Mg), calcium (Ca), sodium (Na), and chlorine (CI) components were constant in all experiments, concentration values of 10 mg/L and 30 mg/L were applied for boron removal tests. Very low or extremely high boron concentrations can occur in hydraulic fracturing and geothermal operations. However, a boron concentration of 10-30 mg/l is generally an average value. There are some studies in the literature on this subject (Kong et al., 2017; Sardari et al., 2018).

The required weighing amounts were calculated for the concentrations determined during the synthetic hydraulic fracturing wastewater preparation. Boron (H<sub>3</sub>BO<sub>3</sub>, Merck), Si (SiO<sub>2</sub>, Aldrich), Mg (MgSO<sub>4</sub>, Aldrich), Ca (CaCO<sub>3</sub>, Merck), Na (NaCl), Merck) and Cl (NaCl, Merck) were weighed on a precision balance (A&D Company Limited FX-300i). After the weighing process, the powdered components were dissolved in 15 liters of deionized water. To ensure the homogeneity of the dissolution process, all synthetic wastewater was divided into three 5-liter glass bottles and mixed at 300 rpm by lka-Werke® (Eurostarpower-b) two-blade mechanical mixer with a PTFE mixing shaft for 24 hours. The characterization of the prepared synthetic hydraulic fracturing wastewater is given in Table 1.

In the first set of membrane tests (first eight experiments), reference synthetic hydraulic fracturing wastewater (without polyol addition) was used as feed water. It is aimed to increase the boron removal by

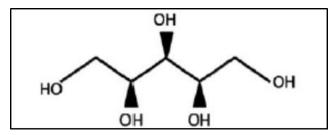
increasing the molecular size of borate ions by adding a complexing polyol to the reference synthetic hydraulic fracturing wastewater in the second set of membrane tests. In aqueous environments, boron exists in the form of boric acid, and boric acid reacts with neutral polyol compounds to form anionic complexes (Geffen *et al.*, 2006).

**Table 1.** Synthetic hydraulic fracturing wastewater characterization

Component	Unit	Value
рН	-	8,5
Conductivity	μS/cm	46,000
Hardness	mg/L CaCO₃	420
Total Dissolved Solids (TDS)	mg/L	32,080
Calcium	mg/L	292
Magnesium	mg/L	63
Sodium	mg/L	4,253
Chloride	mg/L	12,343
Silica	mg/L	17
Boron	mg/L	10 and 30*

<sup>\*:</sup> Two different boron concentrations were applied.

To increase the molecular size of boron, xylitol polyol with five hydroxyl groups was added to the reference synthetic hydraulic fracturing wastewater as a complexing agent. The molecular structure of xylitol polyol is shown in Figure 2. Xylitol contains a 1,2-diol group that can form a chelate complex with boric acid (Dydo *et al.*, 2012). Xylitol has a high equilibrium constant and is harmless to human life (Kim *et al.*, 2015).



**Figure 2.** The molecular structure of xylitol polyol (Park *et al.*, 2015).

Reference synthetic hydraulic fracturing wastewater and xylitol-added synthetic wastewater have the same characterization. The wastewater characterization given in Table 1 is also valid for xylitol-added synthetic wastewater. It was prepared in synthetic wastewater with xylitol in two different boron concentrations, 10 and 30 mg/L. It was aimed to filter the prepared xylitol-added wastewater through the NF process. 1/10 boron/xylitol molar ratio was applied in NF experiments. Preliminary studies were conducted in order to find the optimum dosages for the boron/polyol ratio. 1/10 ratio gave the highest boron removal with the minimum polyol addition. Thus, the 1/10 ratio was chosen.

#### 2.3. Membrane tests

Synthetic hydraulic fracturing wastewater was used as feed water in all membrane tests. The tests were carried out with a total of sixteen experiments, with or without the addition of complexing polyol (xylitol) to the synthetic hydraulic fracturing wastewater. Two different pressure

values of 6.9 and 15.5 bar (100 and 225 psi) were applied with the NF membrane to investigate the effects of operating pressures on membrane performances. Two different pH values (original pH ( $\cong$  8.5) and pH 10) were studied, and pH adjustment was made by adding concentrated NaOH/HCl to keep these values constant in the feeding tank. Term pH org. (original pH) was used to represent that the pH of wastewater in removal tests was not adjusted. During the membrane tests, samples were taken from the feed tank and permeate streams for boron and other measurements at the start,  $2^{nd}$ ,  $4^{th}$ , and  $6^{th}$  hours. In addition, conductivity, TDS, temperature, and pH were measured every hour. The permeate and concentrate flow rates; membrane and pump outlet pressures were calculated and recorded every hour.

In the first eight experiments, reference synthetic hydraulic fracturing wastewater (15 L), prepared without the addition of complexing polyol, was taken into the membrane feeding tank. The membrane, which was kept in deionized water for 24 hours after the preliminary cleaning of the system (pipeline, etc.), was placed in its cell. The first hour of the experiment is called the membrane conditioning period, during which the system is expected to become stable. During this period, measurements were made, but the data of this period were not included in the results. The filtrate and concentrate were fed back into the feed tank throughout the experiment. Each of the experiments lasted for 7 hours without interruption. A new membrane was used for each test. This whole procedure was also applied from the 9th experiment to the 16th experiment with the polyoladded synthetic wastewater. Boron removal (BR) is defined as the ratio of boron that remains in the permeate stream (Cp) over the boron concentration in the feed stream (Cf) and calculated by the formula given below:

BR (%) = (1-Cp/Cf)x100

# 2.4. Analytical measurements

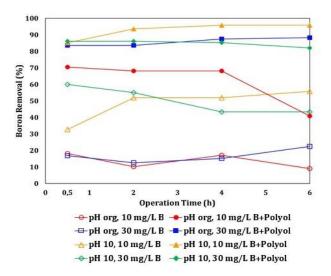
The spectrophotometric carmine method was used for boron analysis. In this method, boron reacts with carminic acid in sulfuric acid solution to obtain a reddish color, and the amount of color is directly proportional to the boron concentration. The measurement wavelength is 605 nm. A spectrophotometer (Hach DR5000) was used to measure absorbances. Conductivity and temperature were measured by the WTW-Inolab-Level-1 device. pH was measured by WTW pH 340i. The chemicals used in the analyses are of analytical purity. Distilled water (DS) was used for stock solutions and dilutions.

#### 3. Results and discussion

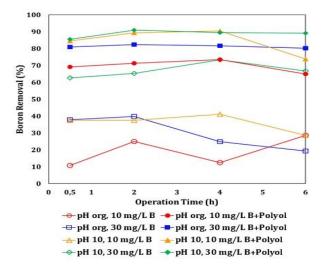
# 3.1. Impact of operating pressure

Figure 3 shows 6.9 bar (100 psi) of feed solution with two different pH values (original pH ( $\sim$ 8.5) & pH 10) using NF membrane, and Figure 4 shows the effect of 15.5 bar (225 psi) pressure on boron removal. While the average boron removal was 13.64% at 6.9 bar pressure, the boron

removal was 19.20% in the experiments where the pressure increased to 15.5 bar. It has been noted that with the increase of the operating pressure, the boron removal in the NF membrane may increase, albeit at a low level. Since the pore size of the NF membranes is large enough for boric acid to pass through, boric acid molecules could not be well retained by the membrane, and the data obtained remained at a low level (Sarp *et al.*, 2008).



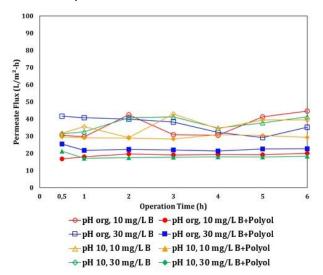
**Figure 3.** Boron removal from synthetic hydraulic fracturing wastewater with NF membrane (operating pressure: 6.9 bar (100 psi); temperature: 20±2°C).



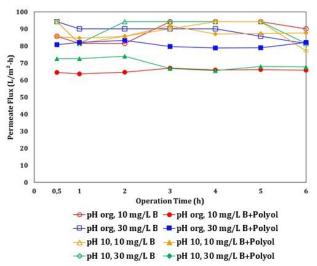
**Figure 4.** Boron removal from synthetic hydraulic fracturing wastewater with NF membrane (operating pressure: 15.5 bar (225 psi); temperature: 20±2°C).

As expected, the permeate fluxes increased with the increase in operating pressure. While the permeate flux was 35.65 L/m².h on average at 6.9 bar pressure (Figure 5), an average of 88.78 L/m².h (Figure 6) was obtained in the experiments where the pressure increased to 15.5 bar. These flux values are concordant with NF membrane tests (Dydo *et al.*, 2005). It was observed that the permeate flux value did not change much over time. This result shows that the membrane conditioning time is sufficient.

The effects of operating pressures on conductivity removal were also investigated. While the conductivity reduction was observed at 18.57% (Figure 7) in the experiments conducted with low pressure, the conductivity removal increased to 21.43% (Figure 8) in the experiments where the pressure was increased. The conductivity removal remained at low levels due to the high monovalent sodium content of the synthetic hydraulic fracturing wastewater filtered through the membrane system.



**Figure 5.** Change of permeate flux in experiments with NF membrane (operating pressure: 6.9 bar (100 psi); temperature: 20±2°C).

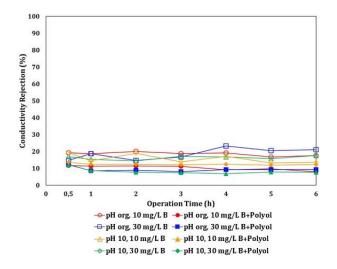


**Figure 6.** Change of permeate flux in experiments with NF membrane (operating pressure: 15.5 bar (225 psi); temperature:  $20\pm2^{\circ}$ C).

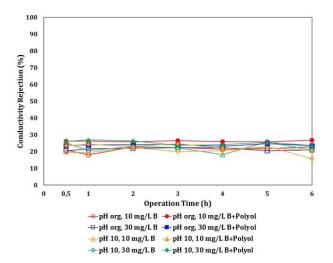
#### 3.2. Impact of water pH

Figures 3 (6.9 bar) and 4 (15.5 bar) show the effect of pH on boron removal. The boron removal, which was recorded as 13.64% at the original pH ( $\sim$ 8.5) under low operating pressure, reached 48.08% by increasing the pH to 10. While 16.96% boron was removed at the original pH at 15.5 bar operating pressure, 36.16% boron removal was obtained by adjusting the pH to 10. The obtained data prove the positive effect of pH value change on boron removal (Dydo *et al.*, 2005; Tu *et al.*, 2011; Tu *et al.*,

2013). With the NF99 membrane, boron removal increased with pH at low pressure (Geffen *et al.*, 2006; Tu *et al.*, 2011; Tu *et al.*, 2013). The number of studies carried out with NF membrane at low pressure is very few in the literature. For this reason, the results obtained are significant as they fill the gap in the literature and constitute a source for future studies. At high operating pressure, with the pH value adjusted to 10, boron removal, which was around 39% until the end of the 4<sup>th</sup> hour, decreased to 29% at the 6th hour, reducing the average boron removal within the scope of the experiment to 36.16%. This highlights the importance of precipitation of calcium carbonate and magnesium salts at high pH values (Sarp *et al.*, 2008).



**Figure 7.** Conductivity removal from synthetic hydraulic fracturing wastewater with NF membrane (operating pressure: 6.9 bar (100 psi); temperature: 20±2°C).



**Figure 8.** Conductivity removal from synthetic hydraulic fracturing wastewater with NF membrane (operating pressure: 15.5 bar (225 psi); temperature: 20±2°C).

A decrease in conductivity removal was noted with increased pH at both pressure values (Figures 7 and 8). This reduction may be due to greater concentration polarization, with the accumulation of larger amounts of inorganic residues on the membrane surfaces at higher pH values. Another possibility is that the sodium ions

resulting from the NaOH solution dosed to increase the pH cannot be retained in the membrane, resulting in an additional conductivity value (Koseoglu *et al.*, 2010). The experiments performed with 6.9 bar operating pressure and permeate fluxes of 35.63 L/m².h, and 37.04 L/m².h were recorded for the original pH and pH 10, respectively (Figure 5). At 15.5 bar pressure, 88.78 L/m².h and 90.61 L/m².h values were obtained (Figure 6). The permeate flux, which changed at a high level with the increase in pressure, did not change to the same extent as the pH increase.

# 3.3. Impact of boron concentration

In experiments carried out with NF membrane at 6.9 bar operating pressure and original pH value, boron removal resulted in 13.64% when the feed solution contained 10 mg/L boron and 16.69% at 30 mg/L boron content. When the pH value was increased to 10, 48.08% (10 mg/L B) and 50.42% (30 mg/L B) boron removal were achieved (Figure 3). The data obtained showed that the boron concentration increased the boron removal at a very low level. Boron concentration increased in the feed solution and likewise increased in the permeate phase (Geffen *et al.*, 2006).

When the feed solution with the original pH value was filtered through the NF99 membrane at 15.5 bar operating pressure, boron removal efficiencies of 19.20% (10 mg/L B) and 30.43% (30 mg/L B) were obtained. These removals were recorded at pH 10 at 36.16% and 67.00%, respectively (Figure 4). At 6.9 bar pressure in the NF membrane, the boron removal, which was slightly increased by the boron concentration, doubled with the increase in pressure. The increase in boron concentration was effective with the increased pressure in the NF membrane. In the data obtained with the NF membrane, the increase in boron concentration in the feed solution did not cause any change in the permeate flux and conductivity removal as in the study of Güler (2021).

# 3.4. Impact of polyol addition

The effect of adding polyol to synthetic wastewater on boron removal was evaluated in terms of operating pressure (6.9-15.5 bar), boron concentration (10-30 mg/L B), and feed solution pH (org. pH-pH 10). In Figure 3, the results of the tests operated with 6.9 bar pressure are given. When the feed solution pH was original and studied at a 10 mg/L, boron removal of 13.64% (without xylitol addition) and 61.93% (with xylitol-added) was obtained. Under the same conditions, by increasing the boron concentration of the feed solution to 30 mg/L, boron removal efficiencies were recorded as 16.69% (without xylitol addition) and 85.74% (with xylitol addition). When the pH of the feed solution containing 10 mg/L boron was adjusted to 10, the boron removal obtained as 48.08% increased to 92.55% with the addition of xylitol. Under the same conditions, 50.42% (without xylitol addition) and 84.83% (with xylitol-added) boron removal were obtained by simply reducing the boron concentration to 30 mg/L.

Figure 4 shows the changes in boron removal with the addition of xylitol at 15.5 bar pressure with the NF

membrane. When working at the original pH value, the boron removal (19.20%) by filtering the feed solution containing 10 mg/L boron through the NF membrane at 15.5 bar pressure increased to 69.68% by adding xylitol to the feed solution. In the tests where the boron concentration of the feed solution was 30 mg/L under the same conditions, the boron removal, which was 30.43% in the absence of xylitol, reached 81.29% when the same test was performed in the presence of xylitol. When the pH of the feed solution containing 10 mg/L boron was adjusted to 10, 36.16% of the boron was removed in the absence of xylitol, and the addition of xylitol was removed 84.52% of the boron. At 30 mg/L boron concentration, 67.00% (without xylitol addition) and 88.77% (with xylitol-added) boron removal were recorded.

The highest boron removal in NF membrane experiments with the addition of xylitol; was 92.55% at 6.9 bar operating pressure, pH 10, and 10 mg/L boron concentration. When the xylitol-added tests are evaluated among themselves, as seen in Figure 3 and Figure 4, boron removal has become more efficient with the increase in pressure and pH with the NF membrane. In general, a significant rise in boron removal was observed with the addition of polyol in all membrane experiments (Geffen et al., 2006; Tu et al., 2013). The increase in boron removal indicates that the formation of ionized boron also increased. Rejection of the ionized complex by NF membranes, as with free borate, increased with increasing pH according to the degree of ionization (Geffen et al., 2006). The complexation reaction has been observed to increase the boron removal at both low and high pH values. In other words, as the solution pH increases, the complexation efficiency increases, and higher boron removal is achieved (Tu et al., 2013). In the tests performed with the NF membrane in the presence of polyol, the boron removal increased with boron concentration (Geffen et al., 2006).

The permeate flux value obtained at an operating pressure of 6.9 bar and in the absence of xylitol at the original pH of 35.63 L/m<sup>2</sup>.h decreased to 18.80 L/m<sup>2</sup>.h with the addition of only xylitol under the same conditions. At pH 10, the permeate flux values of 37.07 L/m<sup>2</sup>.h (without xylitol addition) and 18.19 L/m<sup>2</sup>.h (with xylitol-added) were recorded. Detailed results of these average permeate fluxes are given in Figure 5. With the increase in operating pressure to 15.5 bar, the permeate flux, which was 88.78 L/m<sup>2</sup>.h at the original pH, decreased to 65.38 L/m<sup>2</sup>.h with the addition of xylitol. At pH value of 10, permeate fluxes of 90.61 L/m<sup>2</sup>.h (without xylitol addition) and 69.60 L/m<sup>2</sup>.h (with xylitol-added) were recorded (Figure 6). In tests performed with NF membrane, permeate flux decreased with adding xylitol at two different pressures and pH values (Tu et al., 2013). In NF experiments at 6.9 bar pressure, the decrease in conductivity removal with the addition of xylitol (Figure 7) was reversed at 15.5 bar pressure, and an increase in removal was recorded (Figure 8). In experiments with xylitol addition, conductivity removal increased at both pH values with increased pressure. The highest removal was obtained at the original pH and high pressure.

#### 4. Conclusions

With the applied variables (pressure, pH, and boron concentration), the highest boron removal was 67% in membrane tests. In this case, there is still a boron concentration of 9.9 mg/L in the filtrate. Since the boron concentration in the permeate water is higher than the desired level, boron removal was investigated with a polyol, proving its effectiveness on boron removal in the studies in the literature. With the addition of polyol, boron removal increased up to 92.55%. It has been observed that a high level of boron removal can be achieved with the NF membrane by adding polyol at the original pH. In this context, effective removal can be achieved by adding polyol without changing the pH value. This is especially valuable for the NF process. Boron removal can be high in some RO membranes produced specifically for seawater desalination. However, these membranes can have relatively low flux under high pressure. Energy costs are higher compared to NF membranes. One of the most favorable outcomes of the study is to achieve high boron removal thanks to the addition of polyol, with a pressure value that can be considered low for pressurized membrane processes such as 6.9 bar by using the NF membrane.

Thanks to this treatment setup, which has the potential to be operated with high feasibility, the water with low boron concentration can be reused in hydraulic fracturing operations, thereby increasing the sustainability of operations and relieving the pressure on water resources, which stands out as a valuable and novel perspective that the study brings to the literature. As a result, it has been proven that the proposed treatment setup can be an effective alternative for boron removal from hydraulic fracturing wastewater.

#### References

- Bu T., Chen F., He X., Yang Y., and Wang W. (2018), Researching the complexing conditions of residual boron in produced water from oil & gas fields, *Process Safety and Environmental Protection*, **116**, 254–261.
- Chen G., Wang Z., Nghiem L.D., Li X.M., Xie M., Zhao B., Zhang M., Song J., and He T. (2015), Treatment of shale gas drilling flowback fluids (SGDFs) by forward osmosis: Membrane fouling and mitigation, *Desalination*, **366**, 113–120.
- Dydo P., Nems I., and Turek M. (2012), Boron removal and its concentration by reverse osmosis in the presence of polyol compounds, *Separation and Purification Technology*, **89**, 171–180.
- Dydo P., Turek M., Ciba J., Trojanowska J., and Kluczka J. (2005), Boron removal from landfill leachate by means of nanofiltration and reverse osmosis, *Desalination*, **185**, 131–137.
- Dydo P., Turek M., and Milewski A. (2014), Removal of boric acid,monoborate, and boron complexes with polyols by reverse osmosis membranes, *Desalination*, **334**, 39–46.
- Geffen N., Semiat R., Eisen M.S., Balazs Y., Katz I., and Dosoretz C.G. (2006), Boron removal from water by complexation to polyol compounds, *Journal of Membrane Science*, **286**, 45–51.
- Güler E., Kabay N., Yüksel M., Yavuz E., and Yüksel Ü. (2011), A comparative study for boron removal from seawater by two

- types of polyamide thin film composite SWRO membranes, *Desalination*, **273**, 81–84.
- Güler E. (2021), Effect of geothermal water composition and pretreatment on the product water for boron-sensitive crops, *Journal of Boron*, **6(3)**, 316–325.
- Jackson R.B., Vengosh A., Carey J.W., Davies R.J., Darrah T.H., O'Sullivan F., and Petron G. (2014), The Environmental Costs and Benefits of Fracking, *The Annual Review of Environment and Resources*, **39**, 327–362.
- Kabay N. (2015), Boron removal from geothermal water using membrane processes, Kabay N. (Ed.), Bryjak M. (Ed.), Hilal N. (Ed.), Boron Separation Processes (267–283), Elsevier, 412p, USA.
- Karahan S., Yurdakoc M., Seki Y., and Yurdakoc K. (2006), Removal of boron from aqueous solution by clays and modified clays, *Journal of Colloid and Interface Science*, **293**, 36–42.
- Kim M.K., Eom K.H., Lim J.H., Lee J.K., Lee J.D., and Won Y.S. (2015). Simple boron removal from seawater by using polyols as complexing agents: A computational mechanistic study, Korean Journal of Chemical Engineering, 32, 2330– 2334.
- Kong, F., Chen, J., Wang, H., Liu, X., Wang, X., Wen, X., Chen, C., Xie, Y.F. (2017), Application of coagulation-UF hybrid process for shale gas fracturing flowback water recycling: Performance and fouling analysis. Journal of Membrane Science, 524, 460–469.
- Koplos J., Tuccillo M.E., and Ranalli B. (2014), Hydraulic fracturing overview: How, where, and its role in oil and gas, *Journal American Water Works Association*, **106**, 38–56.
- Koseoglu H., Harman B.İ., Yiğit N.Ö., Güler E., and Kitiş M. (2010), The effects of operating conditions on boron removal from geothermal waters by membrane processes, *Desalination*, 258, 72–78.
- Lester, Y., Ferrer, I., Thurman, E.M., Sitterley, K.A., Korak, J.A., Aiken, G., Linden, K.G. (2015), Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment. Science of the Total Environment, 512–513, 637– 644.
- Park B., Lee J., Kim M., Won Y.S., Lim J.H., and Kim S. (2015), Enhanced boron removal using polyol compounds in seawater reverse osmosis processes, *Desalination and Water Treatment*, **57**, 1–8.
- Power P.P., and Woods W.G. (1997), The chemistry of boron and its speciation in plants, *Plant and Soil*, **193**, 1–13.
- Richards L.A., Vuachere M., and Schafer A.I. (2010), Impact of pH on the removal of fluoride, nitrate, and boron by nanofiltration/reverse osmosis, *Desalination*, **261**, 331–337.
- Sardari, K., Fyfe, P., Lincicome, D., Wickramasinghe, S.R. (2018), Aluminum electrocoagulation followed by forward osmosis for treating hydraulic fracturing produced waters. Desalination, **428**, 172–181.
- Sari, M.A., and Chellam, S. (2015), Mechanisms of boron removal from hydraulic fracturing wastewater by aluminum electrocoagulation. Journal of Colloid and Interface Science, **458**, 103–111.
- Sarp S., Lee S., Ren X., Lee E., Chon K., Choi S.H., Kim S., Kim I.S., and Cho J. (2008), Boron removal from seawater using NF and RO membranes, and effects of boron on HEK 293 human embryonic kidney cell concerning toxicities, *Desalination*, **223**, 23–30.

Silva T.L.S., Morales-Torres S., Castro-Silva S., Figueiredo J.L., and Silva A.M.T. (2017), An overview of exploration and environmental impact of unconventional gas sources and treatment options for produced water, *Journal of Environmental Management*, **200**, 511–529.

- Speight J. (2013), Shale Gas Production Processes, *Gulf Professional Publishing*, 170s, ABD.
- Stringfellow W.T., Domen J.K., Camarillo M.K., Sandelin W.L., and Borglin S. (2014), Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing, *Journal of Hazardous Materials*, **275**, 37–54.
- Tu K.L., Chivas A.R., and Nghiem L.D. (2011), Effects of membrane fouling and scaling on boron rejection by nanofiltration and reverse osmosis membranes, *Desalination*, **279**, 269–277.
- Tu K.L., Chivas A.R., and Nghiem L.D. (2013), Enhanced boron rejection by NF/RO membranes by complexation with polyols: Measurement and mechanisms, *Desalination*, **310**, 115–121.
- Yavuz E., Arar Ö., Yüksel M., Yüksel Ü., and Kabay N. (2013), Removal of boron from geothermal water by RO system-Ileffect of pH, *Desalination*, **310**, 135–139.