

1 **Boron Removal from Synthetic Hydraulic Fracturing Wastewaters by Hybrid**
2 **Nanofiltration/Complexation Process**

3
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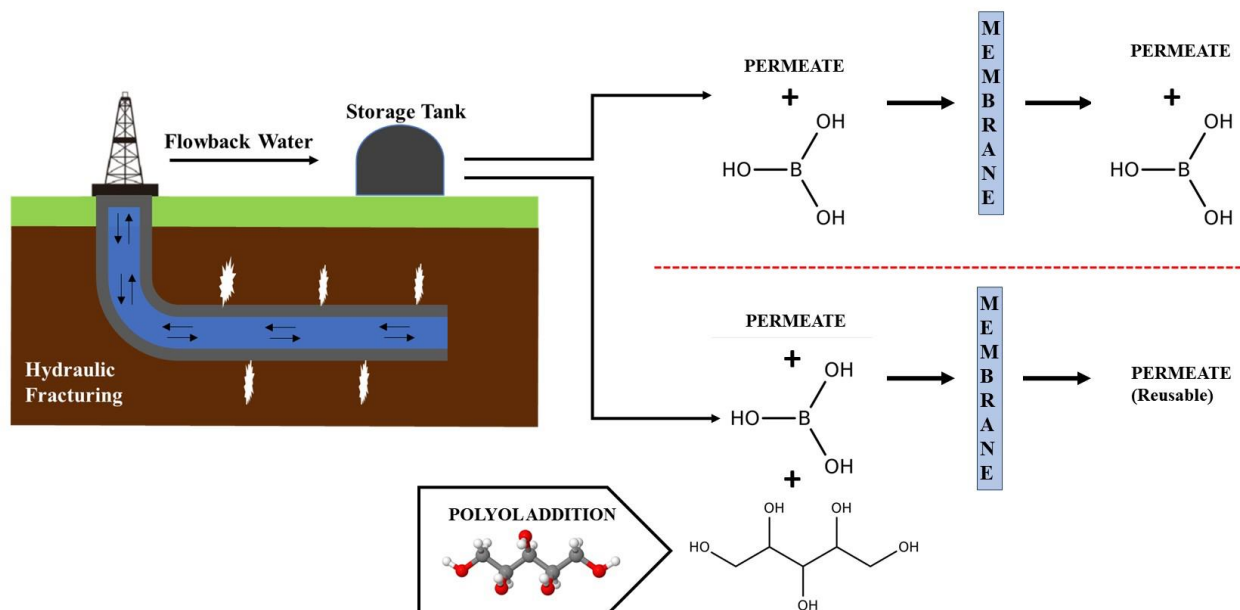
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13 **ABSTRACT**

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

26

27 **Keywords:** Boron removal, hydraulic fracturing, membrane, polyol, shale gas

28 **1. Introduction**

29 Hydraulic fracturing is a critical technology in the discovery of shale gas, which is defined as an
30 unconventional gas that has a vital role in meeting energy needs on a global basis (Chen et al., 2015).

31 Increasing wars on a global scale in gas-rich regions of the world in 2022 have been a great motivation
32 for countries to put their own gas reserves into production. In this context, hydraulic fracturing
33 operations have become more important for developed and developing countries. In hydraulic
34 fracturing, the permeability of the rock is increased to produce gas from the source rock, and the
35 reservoir is stimulated with a fracturing network that gives a sufficient surface area to allow
36 production (Speight, 2013). The liquid used in the hydraulic fracturing process is the fracturing fluid.

37 In general, hydraulic fracturing fluids consist of 90% water, 9% proppant, and 1% chemicals, but the
38 amount and ratio of these components vary according to the formation (Koplos et al., 2014). The
39 hydraulic fracturing wastewater (4,000-16,000 m³) returning to the surface consists of a mixture of
40 10–40% of the hydraulic fracturing fluids injected into the well and natural brine from the fractured
41 rock (Jackson et al., 2014). Today, studies looking for solution methods for treating and reusing
42 produced wastewater have increased with regulations and public opinion concerns. The use of
43 membrane-based technologies (pressure-driven membrane processes, membrane distillation,
44 membrane bio-reactors, and pervaporation) and advanced oxidation processes (ozonation, Fenton,
45 photocatalysis) has been deemed appropriate for this high-flow wastewater (Silva et al., 2017).
46 Flowback waters from hydraulic fracturing operations, which stand out with their high amount of
47 water consumption, must be treated and recycled within the scope of sustainability. In this context,
48 membrane applications come to the fore. The most important disadvantage of flowback waters is the
49 boron concentration they contain. In order to reuse these waters, which contain much higher boron
50 concentration than the boron concentration of sea waters, it is absolutely necessary to remove the
51 boron effectively and feasibly.

52 Boron is used as a crosslinker in the hydraulic fracturing fluid and chemically binds the gel polymers,
53 providing the viscosity of the cracking fluid (Stringfellow et al., 2014). With its boron concentration

54 ($\cong 3\text{-}4,000$ mg/L), the hydraulic fracturing wastewater is well above the regulations to re-use the
55 wastewater in the hydraulic fracturing process and its discharge into a receiving environment. Boron
56 concentration at these levels is a significant obstacle to the reuse of wastewater as a hydraulic
57 fracturing fluid. High boron concentrations prematurely cross-link hydroxypropyl guar which affects
58 pumping and cracking (Bu et al., 2018).

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



66 Boron exists in an undissociated form (in the form of boric acid) in aqueous solutions at pH values
67 of 7 and lower. Boric acid is a very weak acid with a pK_a of 9.2 (Koseoglu et al., 2010; Richards et
68 al., 2010; Yavuz et al., 2013). With the increase in pH value in aqueous solutions, boron turns into
69 dissociated form, that is, borate (Yavuz et al., 2013). Boric acid in molecular form has a small size
70 and is uncharged. Therefore, its removal by NF and RO membranes is low. The dissociated state of
71 the borate ion, on the other hand, has a large radius and is negatively charged. Ions converted from
72 boric acid to borate are highly rejected by negatively charged membranes. For this reason, the removal
73 of the predominant charged form by membrane processes occurs at high levels at pH levels above the
74 pK_a value (Kabay, 2015; Güler et al., 2011; Yavuz et al., 2013). Because charged ions are removed
75 mainly by many polymeric membranes such as NF and RO by electrostatic repulsion (Koseoglu et
76 al., 2010). However, effective boron removal from waters with high boron content is quite
77 challenging under high pH conditions (a pH of 10 or higher) where there is a risk of severe membrane
78 clogging with insoluble carbonates, hydroxides, or salts (Geffen et al., 2006; Dydo et al., 2014). For
79 all these reasons, studies using complexing polyols involving borate coupling with polyols with 1,2-

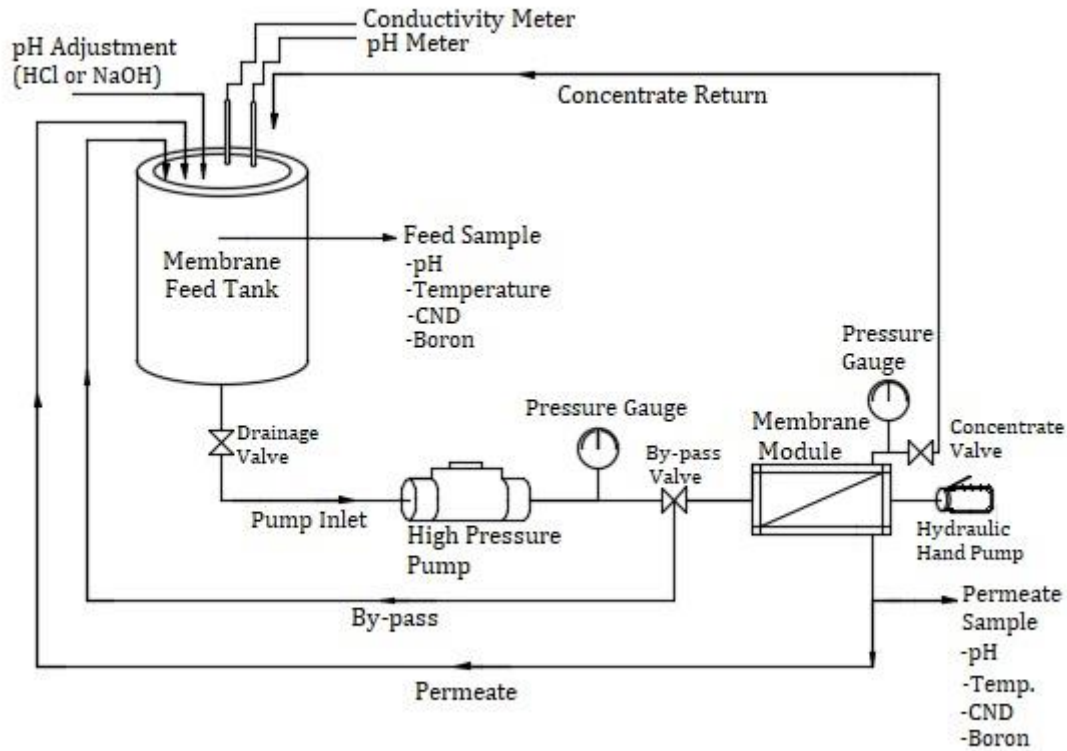
80 diol functional groups are available in the literature to eliminate the need for high pH conditions.
81 These complexes are much more stable than monoborate and can be produced under lower pH
82 conditions. With these complexes, boric acid and monoborates can be removed more effectively not
83 only by RO but also by NF membranes (Tu et al., 2013; Dydo et al., 2014).
84 RO processes are disadvantaged by their high-pressure requirements and low flux generation.
85 Therefore, NF membranes, which stand out with their high flux and low-pressure requirements, were
86 used in our study. In order to overcome the low boron removal problem of NF membranes, polyol
87 complexation was applied to synthetic hydraulic fracturing flowback waters. This study evaluated
88 boron removal from hydraulic fracturing wastewater returned to the surface due to shale gas
89 production using additional polyols in nanofiltration processes. The experiments carried out within
90 the scope of the study include the filtration of the synthetically prepared hydraulic fracturing
91 wastewater through the NF membrane at various operating pressures, feedwater pH values, and boron
92 concentrations, in the presence and absence of xylitol. The findings obtained in the membrane
93 experiments were evaluated in terms of permeate flux, conductivity removal, and especially boron
94 removal. There are many kinds of research or application projects in the literature on boron removal
95 from wastewaters of various industries. However, boron removal from synthetic hydraulic fracturing
96 flowback water by hybrid nanofiltration/complexation process has not been encountered in the
97 literature to the best of our knowledge. In this way, it was desired to crown the advantages of NF
98 membranes with high boron removal. The findings obtained in this study made significant
99 contributions to the literature.

100 **2. Materials and methods**

101 *2.1. Membrane test unit*

102 Figure 1 shows the laboratory scale, cross-flow, flat-sheet membrane test unit (SEPA CF II,
103 Osmonics, USA), and the flow chart of the entire system used in the membrane experiments. Since
104 the membrane unit is resistant to pressures up to 69 bar, different membranes such as reverse osmosis
105 (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) can be used. The system

106 consists of the high-pressure pump and outlet pressure relief valve, feed tank (37 L capacity),
107 membrane cell, membrane cell carrier, hydraulic hand pump, high pressure regulating valve, and a
108 frequency converter (ABB, Switzerland). It consists of 3 manometers, a permeate-water collection
109 tank, high-pressure-resistant stainless steel, and nylon-seal (Dayco-Imperial) plastic pipes.
110 19 cm x 14 cm sized membranes (140 cm² effective membrane area) are used in the test cell. A
111 frequency converter (ABB ACS-140) integrated into the high-pressure pump (Hydra-Cell G13)
112 provides the desired membrane feed flow. The flow applied in the experiments, and the corresponding
113 cross-flow velocities were 4.8 L/min and approximately 1.2 m/s, respectively. The desired pressure
114 in the membrane cell is adjusted by changing the concentrate flow from the valve in the concentrate
115 line. With this valve, the permeate flow was also controlled. pH, temperature, conductivity (CND),
116 and boron concentrations were measured in feed and permeate streams. Tap water was circulated
117 through the closed space in the entire outer part of the feed tank to ensure that the concentrate
118 recycling, which is heated as a result of high-pressure pumping, does not increase the feed tank's
119 solution temperature and maintains a constant temperature. All experiments were carried out at feed
120 water temperatures of $20 \pm 2^\circ\text{C}$. Alfa Laval NF99 HF, an NF membrane, was used in membrane
121 experiments. Membrane sheets were obtained from the manufacturers and used as received.



122
123 **Figure 1.** Membrane test unit flow diagram

124 *2.2. Synthetic hydraulic fracturing wastewaters (flowback waters)*

125 In the first stage of the experimental studies, synthetic hydraulic fracturing wastewater was prepared.
126 The composition of synthetic wastewater was determined based on the averages of the compositions
127 of the five fracturing wastewaters listed below: a field from southwest China (Chen et al., 2015),
128 Eagle Ford in Southeast Texas, USA (Sari and Chellam, 2015), Fuling in China (Kong et al., 2017),
129 Denver-Julesburg (DJ) Basin in Colorado, USA (Lester et al., 2015), and Fayetteville Basin in
130 Arkansas, USA (Sardari et al., 2018). While the values of silica (Si), magnesium (Mg), calcium (Ca),
131 sodium (Na), and chlorine (Cl) components were constant in all experiments, concentration values of
132 10 mg/L and 30 mg/L were applied for boron removal tests. Very low or extremely high boron
133 concentrations can occur in hydraulic fracturing and geothermal operations. However, a boron
134 concentration of 10-30 mg/l is generally an average value. There are some studies in the literature on
135 this subject (Kong et al., 2017; Sardari et al., 2018).

136 The required weighing amounts were calculated for the concentrations determined during the
 137 synthetic hydraulic fracturing wastewater preparation. Boron (H_3BO_3 , Merck), Si (SiO_2 , Aldrich),
 138 Mg ($MgSO_4$, Aldrich), Ca ($CaCO_3$, Merck), Na ($NaCl$, Merck) and Cl ($NaCl$, Merck) were weighed
 139 on a precision balance (A&D Company Limited FX-300i). After the weighing process, the powdered
 140 components were dissolved in 15 liters of deionized water. To ensure the homogeneity of the
 141 dissolution process, all synthetic wastewater was divided into three 5-liter glass bottles and mixed at
 142 300 rpm by Ika-Werke[®] (Eurostarpower-b) two-blade mechanical mixer with a PTFE mixing shaft
 143 for 24 hours. The characterization of the prepared synthetic hydraulic fracturing wastewater is given
 144 in Table 1.

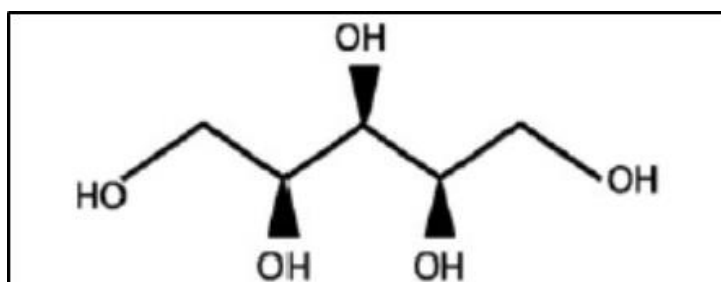
145 Table 1. Synthetic hydraulic fracturing wastewater characterization

Component	Unit	Value
pH	-	8,5
Conductivity	$\mu S/cm$	46,000
Hardness	mg/L $CaCO_3$	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*

146 *: Two different boron concentrations were applied.

147 In the first set of membrane tests (first eight experiments), reference synthetic hydraulic fracturing
 148 wastewater (without polyol addition) was used as feed water. It is aimed to increase the boron removal
 149 by increasing the molecular size of borate ions by adding a complexing polyol to the reference
 150 synthetic hydraulic fracturing wastewater in the second set of membrane tests. In aqueous
 151 environments, boron exists in the form of boric acid, and boric acid reacts with neutral polyol
 152 compounds to form anionic complexes (Geffen et al., 2006).

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



158

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

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

167 2.3. Membrane tests

168 Synthetic hydraulic fracturing wastewater was used as feed water in all membrane tests. The tests
169 were carried out with a total of sixteen experiments, with or without the addition of complexing polyol
170 (xylitol) to the synthetic hydraulic fracturing wastewater. Two different pressure values of 6.9 and
171 15.5 bar (100 and 225 psi) were applied with the NF membrane to investigate the effects of operating
172 pressures on membrane performances. Two different pH values (original pH (\cong 8.5) and pH 10) were
173 studied, and pH adjustment was made by adding concentrated NaOH/HCl to keep these values
174 constant in the feeding tank. Term pH org. (original pH) was used to represent that the pH of
175 wastewater in removal tests was not adjusted. During the membrane tests, samples were taken from

176 the feed tank and permeate streams for boron and other measurements at the start, 2nd, 4th, and 6th
177 hours. In addition, conductivity, TDS, temperature, and pH were measured every hour. The permeate
178 and concentrate flow rates; membrane and pump outlet pressures were calculated and recorded every
179 hour.

180 In the first eight experiments, reference synthetic hydraulic fracturing wastewater (15 L), prepared
181 without the addition of complexing polyol, was taken into the membrane feeding tank. The
182 membrane, which was kept in deionized water for 24 hours after the preliminary cleaning of the
183 system (pipeline, etc.), was placed in its cell. The first hour of the experiment is called the membrane
184 conditioning period, during which the system is expected to become stable. During this period,
185 measurements were made, but the data of this period were not included in the results. The filtrate and
186 concentrate were fed back into the feed tank throughout the experiment. Each of the experiments
187 lasted for 7 hours without interruption. A new membrane was used for each test. This whole procedure
188 was also applied from the 9th experiment to the 16th experiment with the polyol-added synthetic
189 wastewater. Boron removal (BR) is defined as the ratio of boron that remains in the permeate stream
190 (C_p) over the boron concentration in the feed stream (C_f) and calculated by the formula given below:
191

$$BR (\%) = (1 - C_p / C_f) \times 100$$

193 2.4. Analytical measurements

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

201 3. Results and Discussion

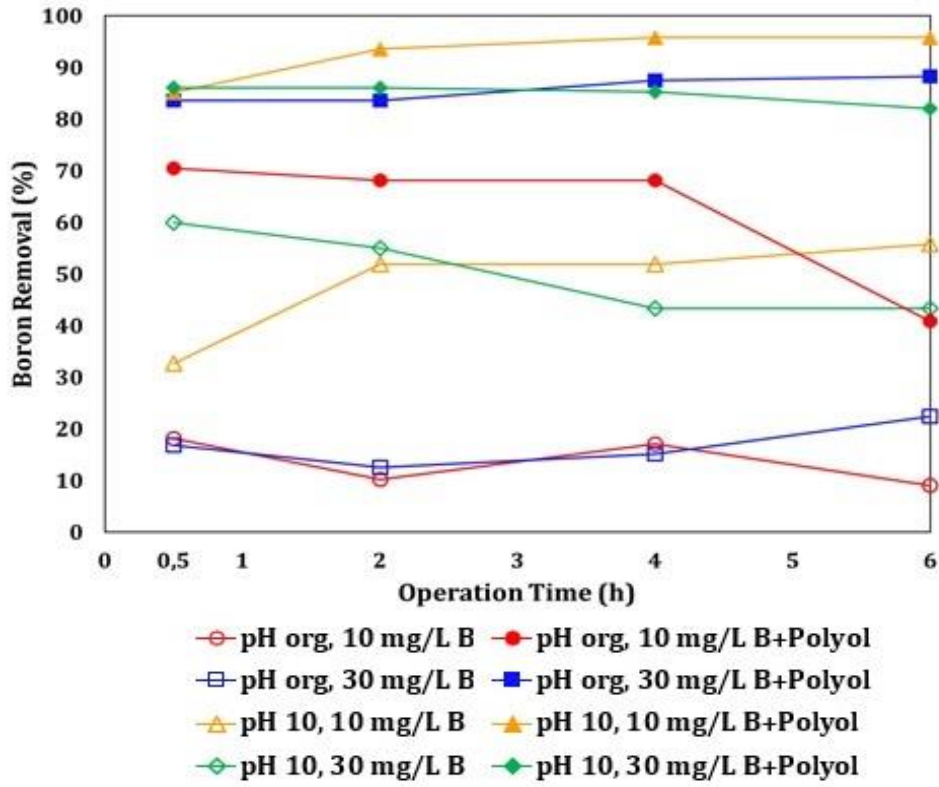
202 3.1. Impact of operating pressure

203 Figure 3 shows 6.9 bar (100 psi) of feed solution with two different pH values (original pH (~8.5) &
204 pH 10) using NF membrane, and Figure 4 shows the effect of 15.5 bar (225 psi) pressure on boron

205 removal. While the average boron removal was 13.64% at 6.9 bar pressure, the boron removal was
206 19.20% in the experiments where the pressure increased to 15.5 bar. It has been noted that with the
207 increase of the operating pressure, the boron removal in the NF membrane may increase, albeit at a
208 low level. Since the pore size of the NF membranes is large enough for boric acid to pass through,
209 boric acid molecules could not be well retained by the membrane, and the data obtained remained at
210 a low level (Sarp et al., 2008).

211 As expected, the permeate fluxes increased with the increase in operating pressure. While the
212 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
213 (Figure 6) was obtained in the experiments where the pressure increased to 15.5 bar. These flux values
214 are concordant with NF membrane tests (Dydo et al., 2005). It was observed that the permeate flux
215 value did not change much over time. This result shows that the membrane conditioning time is
216 sufficient.

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

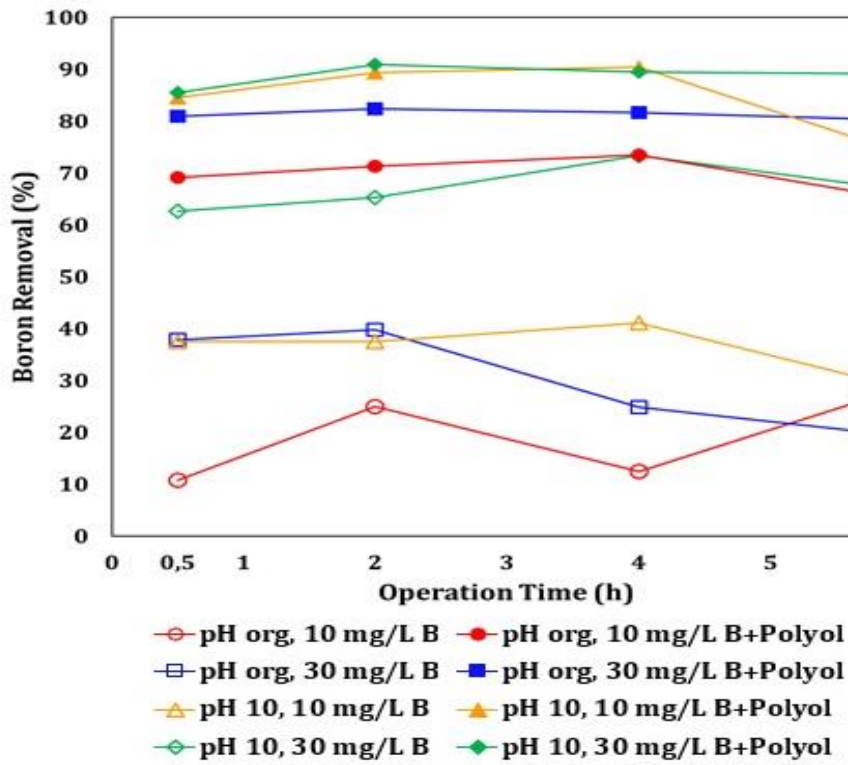


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Figure 3. Boron removal from synthetic hydraulic fracturing wastewater with NF membrane (operating pressure: 6.9 bar (100 psi); temperature: 20±2°C)



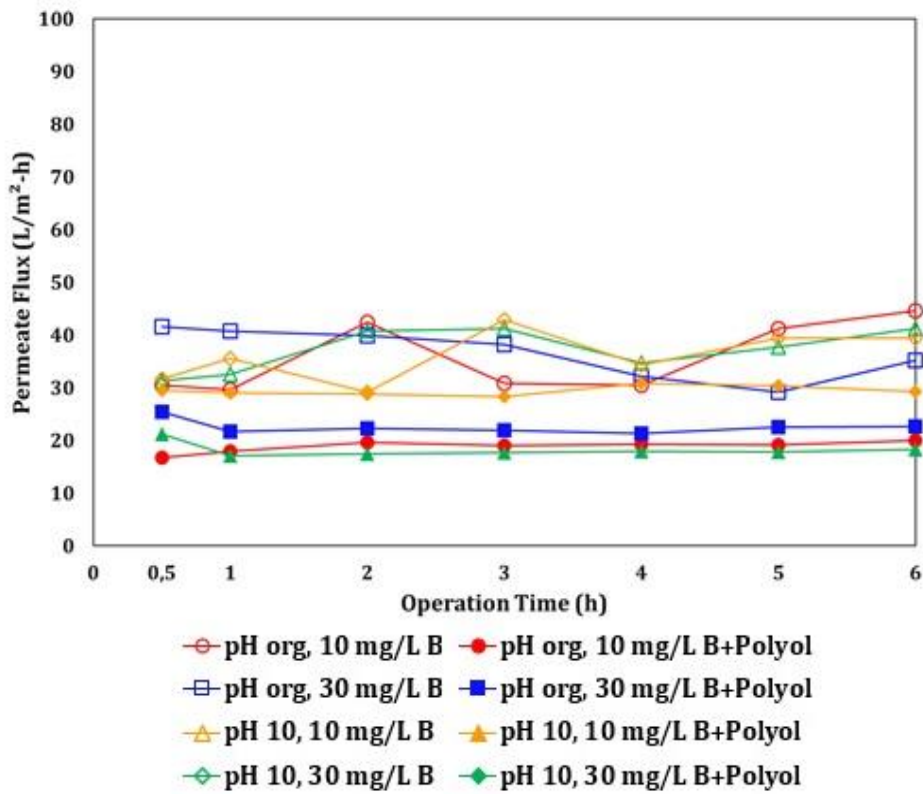
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Figure 4. Boron removal from synthetic hydraulic fracturing wastewater with NF membrane (operating pressure: 15.5 bar (225 psi); temperature: 20±2°C)

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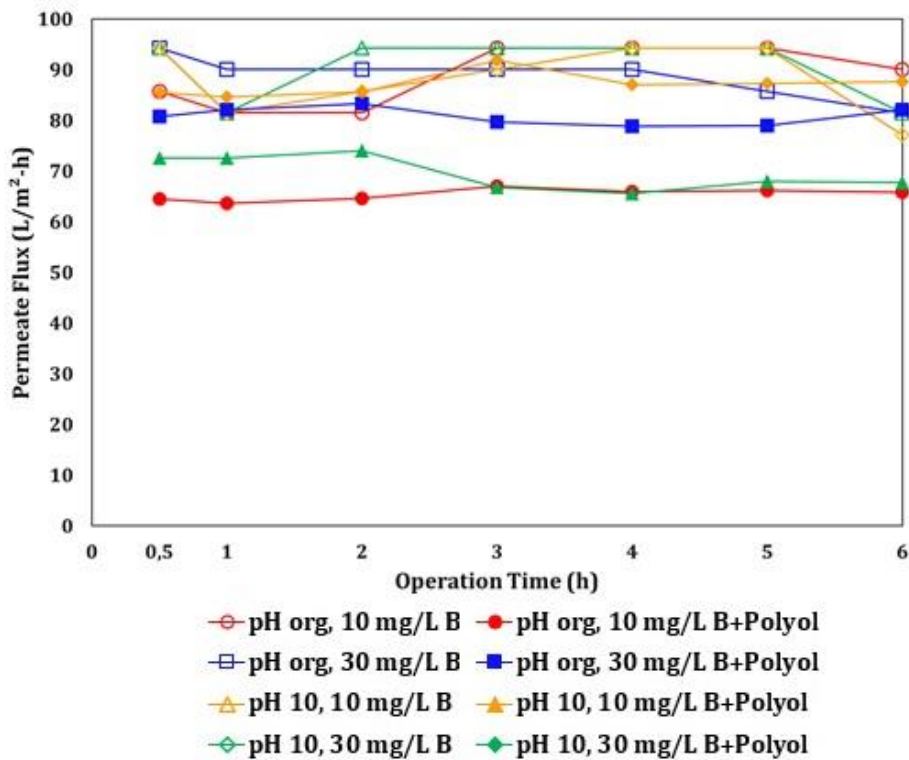


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Figure 5. Change of permeate flux in experiments with NF membrane (operating pressure: 6.9 bar (100 psi); temperature: $20 \pm 2^\circ\text{C}$).



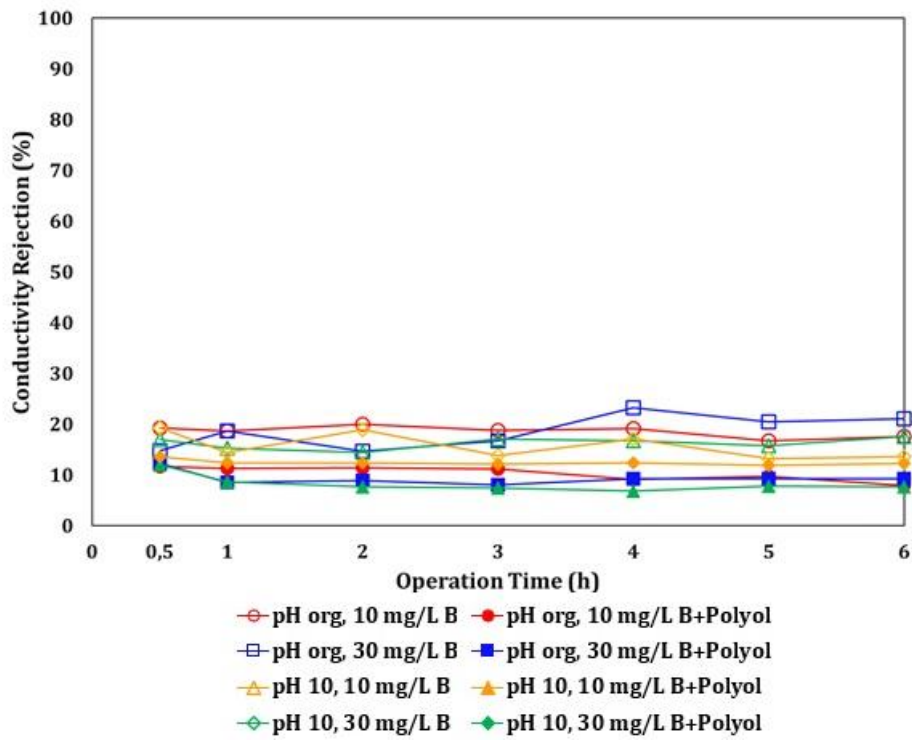
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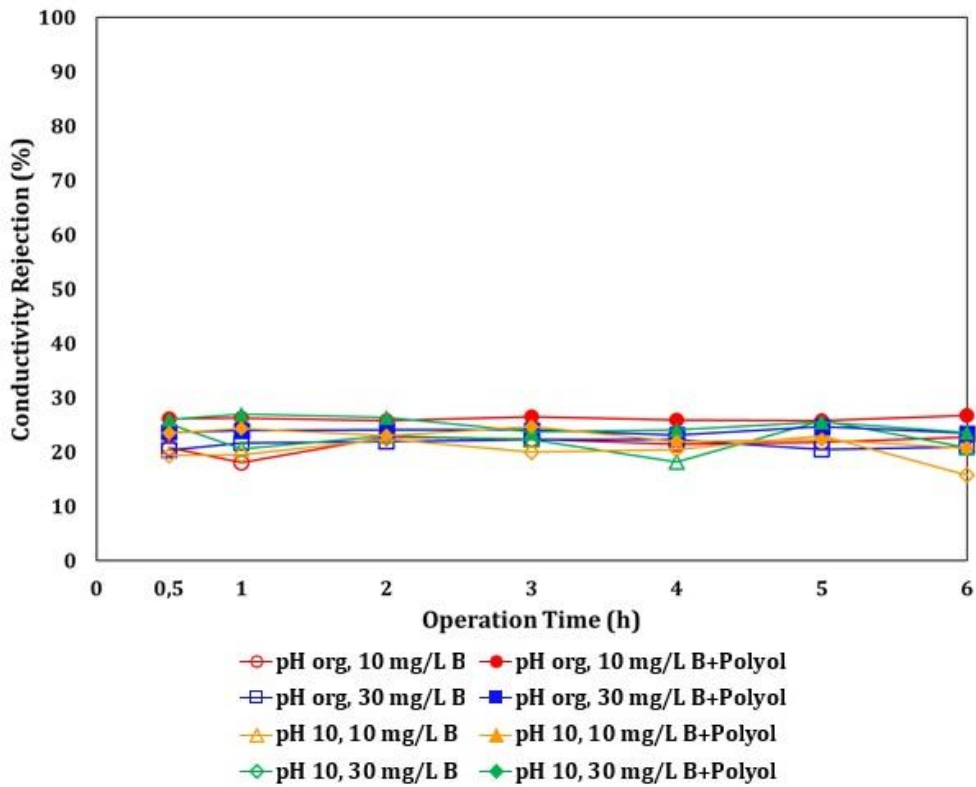
Figure 6. Change of permeate flux in experiments with NF membrane (operating pressure: 15.5 bar (225 psi); temperature: $20 \pm 2^\circ\text{C}$)

236



237

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



240

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

243

244 3.2. Impact of water pH

245 Figures 3 (6.9 bar) and 4 (15.5 bar) show the effect of pH on boron removal. The boron removal,
246 which was recorded as 13.64% at the original pH (~ 8.5) under low operating pressure, reached
247 48.08% by increasing the pH to 10. While 16.96% boron was removed at the original pH at 15.5 bar
248 operating pressure, 36.16% boron removal was obtained by adjusting the pH to 10. The obtained data
249 prove the positive effect of pH value change on boron removal (Dydo et al., 2005; Tu et al., 2011; Tu
250 et al., 2013). With the NF99 membrane, boron removal increased with pH at low pressure (Geffen et
251 al., 2006; Tu et al., 2011; Tu et al., 2013). The number of studies carried out with NF membrane at
252 low pressure is very few in the literature. For this reason, the results obtained are significant as they
253 fill the gap in the literature and constitute a source for future studies. At high operating pressure, with
254 the pH value adjusted to 10, boron removal, which was around 39% until the end of the 4th hour,
255 decreased to 29% at the 6th hour, reducing the average boron removal within the scope of the
256 experiment to 36.16%. This highlights the importance of precipitation of calcium carbonate and
257 magnesium salts at high pH values (Sarp et al., 2008).

258 A decrease in conductivity removal was noted with increased pH at both pressure values (Figure 7-
259 Figure 8). This reduction may be due to greater concentration polarization, with the accumulation of
260 larger amounts of inorganic residues on the membrane surfaces at higher pH values. Another
261 possibility is that the sodium ions resulting from the NaOH solution dosed to increase the pH cannot
262 be retained in the membrane, resulting in an additional conductivity value (Koseoglu et al., 2010).
263 The experiments performed with 6.9 bar operating pressure and permeate fluxes of 35.63 L/m².h, and
264 37.04 L/m².h were recorded for the original pH and pH 10, respectively (Figure 5). At 15.5 bar
265 pressure, 88.78 L/m².h and 90.61 L/m².h values were obtained (Figure 6). The permeate flux, which
266 changed at a high level with the increase in pressure, did not change to the same extent as the pH
267 increase.

268 *3.3. Impact of boron concentration*

269 In experiments carried out with NF membrane at 6.9 bar operating pressure and original pH value,
270 boron removal resulted in 13.64% when the feed solution contained 10 mg/L boron and 16.69% at

271 30 mg/L boron content. When the pH value was increased to 10, 48.08% (10 mg/L B) and 50.42%
272 (30 mg/L B) boron removal were achieved (Figure 3). The data obtained showed that the boron
273 concentration increased the boron removal at a very low level. Boron concentration increased in the
274 feed solution and likewise increased in the permeate phase (Geffen et al., 2006).

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

283 *3.4. Impact of polyol addition*

284 The effect of adding polyol to synthetic wastewater on boron removal was evaluated in terms of
285 operating pressure (6.9-15.5 bar), boron concentration (10-30 mg/L B), and feed solution pH (org.
286 pH-pH 10). In Figure 3, the results of the tests operated with 6.9 bar pressure are given. When the
287 feed solution pH was original and studied at a 10 mg/L, boron removal of 13.64% (without xylitol
288 addition) and 61.93% (with xylitol-added) was obtained. Under the same conditions, by increasing
289 the boron concentration of the feed solution to 30 mg/L, boron removal efficiencies were recorded as
290 16.69% (without xylitol addition) and 85.74% (with xylitol addition). When the pH of the feed
291 solution containing 10 mg/L boron was adjusted to 10, the boron removal obtained as 48.08%
292 increased to 92.55% with the addition of xylitol. Under the same conditions, 50.42% (without xylitol
293 addition) and 84.83% (with xylitol-added) boron removal were obtained by simply reducing the boron
294 concentration to 30 mg/L.

295 Figure 4 shows the changes in boron removal with the addition of xylitol at 15.5 bar pressure with
296 the NF membrane. When working at the original pH value, the boron removal (19.20%) by filtering

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

305 The highest boron removal in NF membrane experiments with the addition of xylitol; was 92.55% at
306 6.9 bar operating pressure, pH 10, and 10 mg/L boron concentration. When the xylitol-added tests
307 are evaluated among themselves, as seen in Figure 3 and Figure 4, boron removal has become more
308 efficient with the increase in pressure and pH with the NF membrane. In general, a significant rise in
309 boron removal was observed with the addition of polyol in all membrane experiments (Geffen et al.,
310 2006; Tu et al., 2013). The increase in boron removal indicates that the formation of ionized boron
311 also increased. Rejection of the ionized complex by NF membranes, as with free borate, increased
312 with increasing pH according to the degree of ionization (Geffen et al., 2006). The complexation
313 reaction has been observed to increase the boron removal at both low and high pH values. In other
314 words, as the solution pH increases, the complexation efficiency increases, and higher boron removal
315 is achieved (Tu et al., 2013). In the tests performed with the NF membrane in the presence of polyol,
316 the boron removal increased with boron concentration (Geffen et al., 2006).

317 The permeate flux value obtained at an operating pressure of 6.9 bar and in the absence of xylitol at
318 the original pH of 35.63 L/m².h decreased to 18.80 L/m².h with the addition of only xylitol under the
319 same conditions. At pH 10, the permeate flux values of 37.07 L/m².h (without xylitol addition) and
320 18.19 L/m².h (with xylitol-added) were recorded. Detailed results of these average permeate fluxes
321 are given in Figure 5. With the increase in operating pressure to 15.5 bar, the permeate flux, which
322 was 88.78 L/m².h at the original pH, decreased to 65.38 L/m².h with the addition of xylitol. At pH

323 value of 10, permeate fluxes of 90.61 L/m².h (without xylitol addition) and 69.60 L/m².h (with xylitol-
324 added) were recorded (Figure 6). In tests performed with NF membrane, permeate flux decreased
325 with adding xylitol at two different pressures and pH values (Tu et al., 2013). In NF experiments at
326 6.9 bar pressure, the decrease in conductivity removal with the addition of xylitol (Figure 7) was
327 reversed at 15.5 bar pressure, and an increase in removal was recorded (Figure 8). In experiments
328 with xylitol addition, conductivity removal increased at both pH values with increased pressure. The
329 highest removal was obtained at the original pH and high pressure.

330 **4. Conclusions**

331 With the applied variables (pressure, pH, and boron concentration), the highest boron removal was
332 67% in membrane tests. In this case, there is still a boron concentration of 9.9 mg/L in the filtrate.
333 Since the boron concentration in the permeate water is higher than the desired level, boron removal
334 was investigated with a polyol, proving its effectiveness on boron removal in the studies in the
335 literature. With the addition of polyol, boron removal increased up to 92.55%. It has been observed
336 that a high level of boron removal can be achieved with the NF membrane by adding polyol at the
337 original pH. In this context, effective removal can be achieved by adding polyol without changing
338 the pH value. This is especially valuable for the NF process. Boron removal can be high in some RO
339 membranes produced specifically for seawater desalination. However, these membranes can have
340 relatively low flux under high pressure. Energy costs are higher compared to NF membranes. One of
341 the most favorable outcomes of the study is to achieve high boron removal thanks to the addition of
342 polyol, with a pressure value that can be considered low for pressurized membrane processes such as
343 6.9 bar by using the NF membrane.

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

348 that the proposed treatment setup can be an effective alternative for boron removal from hydraulic
349 fracturing wastewater.

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