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Enhanced boron removal using polyol compounds in seawater reverse osmosis processes

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ABSTRACT

The removal of boron is a very important issue in desalination using seawater reverse osmosis (SWRO). A novel approach using polyol compounds to remove boron is introduced in this study. Polyols are compounds possessing multiple hydroxyl groups and they can combine with uncharged boric acid by generating anionic complexes. As a result, a large molecule is formed and it can be easily rejected by SWRO membrane at seawater pH. Lab-scale SWRO tests were performed to investigate the effect of polyol on the boron removal using different types of polyol (xylitol, glycerol, and D-mannitol). The polyol–boron reaction occurs in seawater condition with low boron concentration and various ion compounds, which leads to two important findings that boron-polyol reaction occurs with low boron and polyol concentrations, and there are no significant inhibitors for the reaction in seawater. The boron-polyol reaction rate is so fast that it can be easily applied to full-scale SWRO processes. The boron removal rate increases at higher polyol concentrations and at larger numbers of hydroxyl groups of polyol.

Keywords: Seawater reverse osmosis (SWRO); Boron removal; Polyol; Hydroxyl group

1. Introduction

Average earth crust concentration of boron element is low (equal to 10 mg/kg only), and boron compounds are naturally found in various soluble forms with concentration ranging from 4 to 5 mg/L in seawater [1]. Solubility of boron are likely to be high, and borate complex is formed with 76% of $B(OH)_3$, 13% of $B(OH)_4^-$, and 11% of metal ion at a temperature of about 25˚C, pH of 8.2 and salinity of 34.8‰ [2]. Boron is referred to as essential nutrients for the growth of animals and plants. However, high intake of boron in amount a bit greater than required can be

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toxic. Symptoms of boron poisoning in humans include nausea, vomiting, diarrhea, dermatitis, and lethargy. It also can cause damage to growth of plants and crops [3,4].

In the guidelines for Drinking Water Quality published in 1993, the World Health Organisation (WHO) recommended that the maximum boron concentration be set to 0.3 mg/L. In 1998, this value was relaxed to 0.5 mg/L because of the technical limitations to remove boron. In 2011, WHO guideline of allowable value of boron concentration in drinking water was revised again to 2.4 mg/L due to the lack of data about toxicity for human health [5]. Although WHO guideline has been relaxed up to the present, each country has different standard of boron removal for drinking water and agricultural country or country mainly taking legumes and vegetables rich in boron maintain rigorous standard as shown in Table 1 [6].

Boron in seawater can be removed by various methods such as coagulation and flocculation using mineral cluster [3], pH adjustment followed by reverse osmosis (RO) process [7,8], and ion exchange process [6]. Boron removal can be increased up to 87.4% in pre-treatment using mineral cluster as a coagulant [3]. At pH below 8, most of boron compounds are present as a form of neutral $B(OH)_3$, and an anionic form of $B(OH)_4^-$ increases at higher pH as shown in Eq. (1).

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \tag{1}$$

Table 1
Boron concentration guideline for drinking water [6]

Region	Maximum boron concentration (mg/L)
South Korea	0.3 → 1.0 in 2009
State of Minnesota (USA)	0.6
State of Florida (USA)	0.63
European Union (EU)	1.0
Abu Dhabi	1.5
Saudi Arabia	0.5
WHO	0.3 → 0.5 in 1998 → 0.5 to 2.4 in 2011

Thus, most of boron compounds in seawater (pH 8) are electrically neutral and have small molecular size, which is the reason why it is difficult to remove boron by RO process [7]. Increasing pH up to 11 (i.e. alkali is injected into permeate flow of the first stage as shown in Fig. 1) can be a good solution for this problem because $B(OH)_4^-$ has larger size than $B(OH)_3$ and negatively charged, leading enhanced rejection by negatively charged RO membrane surface [8]. However, it has potential problem of scaling by calcium and magnesium ions due to high pH [4]. This method has operational complexity that feed water passes through RO membrane twice and needs additional chemical and capital costs (i.e. second pass RO should be installed and operated.). In another way, boron can be removed by anion-exchange resin [6], but it is rarely acceptable because only a small amount of boron ion is present in seawater (i.e. 4–5 mg/L) compared to other anions.

Polyol is a generic term of compounds with multiple alcohol polymers. Polyol with over two hydroxyl (–OH) groups creates complex compound (called the borate complex) in tetrahedral shape followed by ester reaction with boron in nature (Eq. (2), where *R* is hydrocarbon group.) [6,9,10]. Electrically charged complex compounds and large-sized molecule can improve boron rejection, which may lead to simplify the process compared to pH adjustment method followed by second pass RO.

$$B(OH)_3 + 3ROH \leftrightarrow B(OR)_3 + 3H_2O \tag{2}$$

The stability of the borate complex strongly depends on the type of diol used. A strong complex is formed when the diol used involves the hydroxyl groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally coordinated boron [9]. For example, a stable complex is formed by the reaction of boron with compounds possessing cis-diol system such as D-mannitol, D-sorbitol, and D-ribose [6]. In this case, stable borate complex, cis-diol monoborate ester, or bis-diol borate complex is formed (Fig. 2).

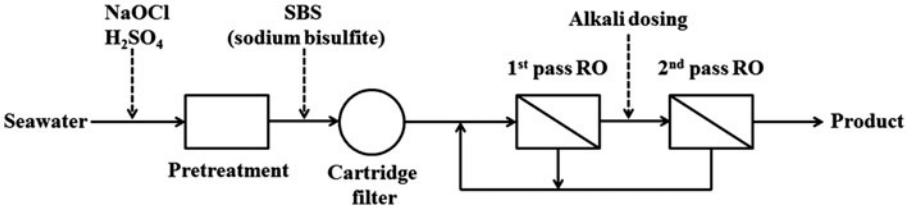


Fig. 1. Boron removal by pH adjustment followed by second pass RO process.

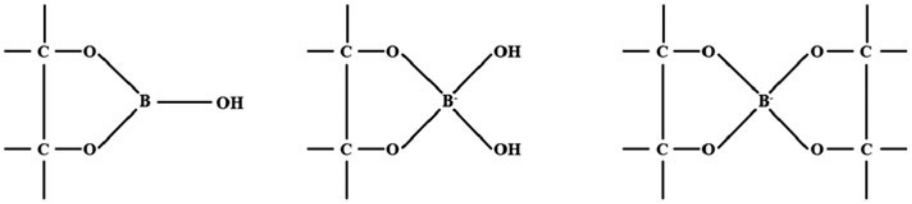


Fig. 2. Schematic drawings of the neutral *cis*-diol monoborate ester, the monoborate complex, and the bis(diol) borate complex [9].

Thus, boron removal rate can be increased by using polyol and dense membrane (e.g. RO membrane) with smaller pore size than complex compound of boron mannitol [1,10–12]. Dydo et al. [1] reported that boron removal rate was 50–99.7% as a function of pH (ranged from 7 to 11). In their tests, boron concentration was 70 mg/L, and D-mannitol, N-methyl D-glucamine, and D-gluconate were used as polyol. Geffen et al. [10] found that boron removal can be increased up to 97% with D-Mannitol when boron concentration was 7 and 32 mg/L at various pH (6–9.6). Dydo et al. [11] reported that the boron removal rate was a function of permeate flux and boron concentration. The removal rate increased at higher flux and boron concentration with N-methyl-d-glucamine, D-mannitol, and sodium D-gluconate as polyol at pH ranged from 7 to 11. According to Tu et al. [12], combination of boron with polyol are unstable, and creation of its complex compound can be effectively rejected by NF. In their experiment using D-mannitol, glycerol and sorbitol, NF and RO membranes were used, and pH was controlled in a range from 6 to 10. Feed water was prepared with 10 mM NaCl, 1 mM $CaCl_2$, and 1 mM $NaHCO_3$, and boron concentration was 1 and 4.6 mg/L.

As discussed above, there are several researches on the enhancement of boron removal by polyol in RO process. But, there are few references on the use of polyol for boron removal in seawater-like conditions (i.e. 4–5 mg/L B, 35,000 mg/L as total dissolved solids concentration, and pH 8), which motivates this study. Thus, the main objective of this study is to investigate boron removal enhancement by polyol in seawater reverse osmosis (SWRO) process in the seawater-like condition.

2. Materials and methods

2.1. Lab-scale RO test

Boron removal tests were carried out using a cross-flow lab-scale RO system described elsewhere [13]. RO membrane was provided by Toray Chemical Korea, Inc. The feed channel dimensions in the RO cell are 11 cm in length, 6 cm in width, and 1 mm in height. Membrane surface and cross-sectional flow areas are then 6.6×10^{-3} m^2 and 6.0×10^{-5} m^2, respectively. A recirculating chiller is used to maintain a constant temperature and stir boron with polyol in the feed tank.

At the beginning of each RO test, deionized (DI) water is filtered through RO membrane for 16–24 h at constant pressure of 50 bars and temperature of 20˚C, respectively, to allow for membrane compaction and other unknown causes of flux decline inherent to lab-scale recirculation systems. After a stable flux was obtained, the DI water in the feed tank is replaced by salt solution with boron. Then, polyol is spiked with a desired concentration if necessary. The mixture in the feed tank is stirred by recirculating chiller. During the boron removal experiments, feed water temperature, applied pressure and cross-flow velocity were maintained at 20˚C, 50 bar, and 0.42 m/s, respectively. Boron concentration in feed (C_f) and permeate (C_p) solutions were measured to calculate boron removal rate (R) such as:

$$R = 1 - \frac{C_p}{C_f} \tag{3}$$

The salt rejection rates were also calculated using the same procedure to obtain boron removal rate as shown in Eq. (3).

2.2. Reagents

In order to remove the effect of membrane fouling on boron removal, artificial seawater was prepared for the boron removal test. A scientific grade marine salt mix (Coralife, Franklin, Wisconsin, USA) was used to simulate clean seawater without any foulants. Comparison of the prepared artificial and natural seawater is shown in Table 2. Boron concentration for the artificial and natural seawater was 4.73 and 4.87 mg/L, respectively. Boric acid with extra pure grade

Table 2
Comparison of artificial seawater and seawater

Element	Artificial seawater	Natural seawater[a]
pH	8.42 ± 0.18	8.43 ± 0.04
Conductivity (mS/cm)	47.26 ± 3.17	47.04 ± 2.06
Specific gravity	1.028 ± 0.015	1.032 ± 0.044
B (ppm)	4.73 ± 0.21	4.87 ± 0.06

[a] Taken in a coastal area in Gijang-gun, Busan, South Korea.

(Daejung chemical & metals, Co., Ltd, Korea) was used to control boron concentration to a desired value.

Polyols tested for this study were D-mannitol, xylitol, and glycerol with extra pure grade (Daejung Chemical & Metals, Co., Ltd, Korea) as shown in Table 3. According to material safety data sheet provided by their manufactures, these compounds are nontoxic and suitable for drinking water.

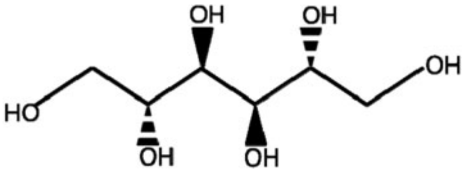
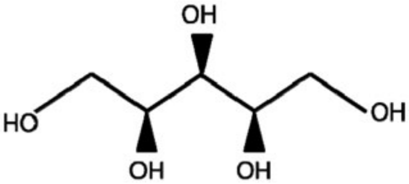
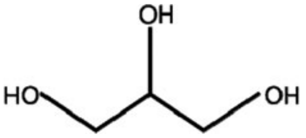
2.3. High-concentration boron removal test

In order to analyze boron removal rate at high concentration, boron concentration of 200 mg/L is added to DI water to produce feed water. Lab-scale RO test was carried out with this feed water, and xylitol was added to set the molar ratio of boron to polyol at 1:2. Boron concentration with high level (e.g. 20–400 mg/L) was analyzed using Atomic Absorption Spectrophotometer (AA-7000F, Shimadzu, Japan). Feed water pH was adjusted from 7 to 10 during the test.

2.4. Boron removal test in seawater-like condition

Feed water was prepared using the artificial seawater with boron concentration of 4.73 mg/L as discussed in Section 2.2. AA-7000F for measuring concentration of boron cannot analyze boron concentration less than 20 mg/L, which is the reason why another method to analyze low-concentration boron. Carmine method using DR3900 (Hach, Germany) was used for measuring low-concentration boron and it is suggested by Standard Methods for the Examination of Water and Wastewater (4500-B) [14], where boron concentration is measured by its reaction with carminic acid in the presence of sulfuric acid to produce reddish color to bluish one by forming complex compound as shown in Fig. 3. The boron reagents for this measurement were prepared by dissolving powder pillows (BoroVer®3 Boron Reagent, Hach Co., Ltd, USA) and sulfuric acid with ACS grade (Hach Co., Ltd, USA). The intensity of color is directly proportional to boron concentration. Average value of multiple measurements of the intensity of color is used for the analysis.

Table 3
Characteristic polyol used in experiment

Chemical name	Chemical formula	Molecular weight (g/mol)	Molecular structure
D-mannitol	$C_6H_{14}O_6$	182.172	
Xylitol	$C_5H_{12}O_5$	152.15	
Glycerol	$C_3H_8O_3$	92.09	

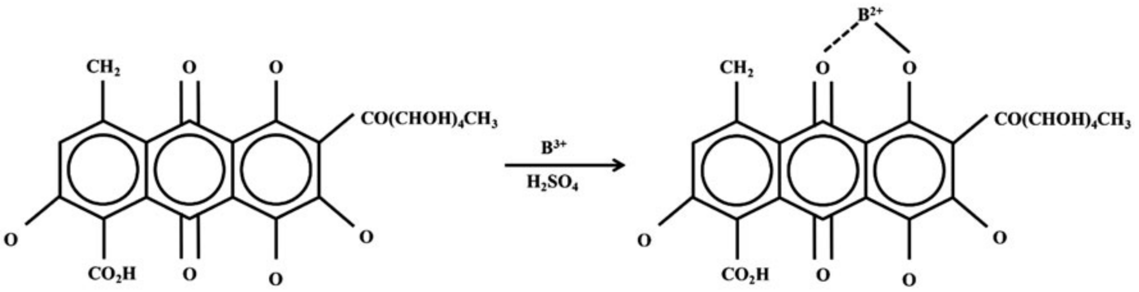


Fig. 3. Reaction of boron with carmine [15].

3. Results and discussions

3.1. Verification of boron concentration measurements

AA-7000F and carmine method for high- and low-concentration boron analysis were verified using boron solutions of known concentrations. In case of AA-7000F for high-concentration boron, it is found that AA-7000F measurement data are well correlated with the input values obtained at every five points (20, 50, 100, 200, and 400 mg/L) as shown in Fig. 4(a), and the coefficient of determination (R^2) was 0.9932. The verification of carmine method was carried out with two different ways. For the first verification, DI water was used as solvent with boron concentrations of 1–12 mg/L, where the measured data agree pretty well to the known concentrations ($R^2 = 0.9961$) as shown in Fig. 4(b). The second verification method for carmine method was carried out with artificial seawater as solvent. Boron concentrations were set to 4.73, 5.73, 6.73, and 7.73 mg/L, which were prepared by adding boron of 0, 1, 2, and 3 mg/L to the artificial seawater as given in Table 2. The measured data followed the known concentration (Fig. 4(c)) with the coefficient of determination (R^2) was 0.9424, which means the accuracy of boron concentration measurement with carmine method in seawater was lower than that in DI water ($R^2 = 0.9932$). This might be caused from an inhibition effect of other ion compounds in seawater. However, this measurement accuracy ($R^2 = 0.9424$) was acceptable in this work because the objective of boron concentration measurement is not to obtain its exact concentration, but to find out the effect of polyol–boron reaction on the boron removal efficiency in seawater.

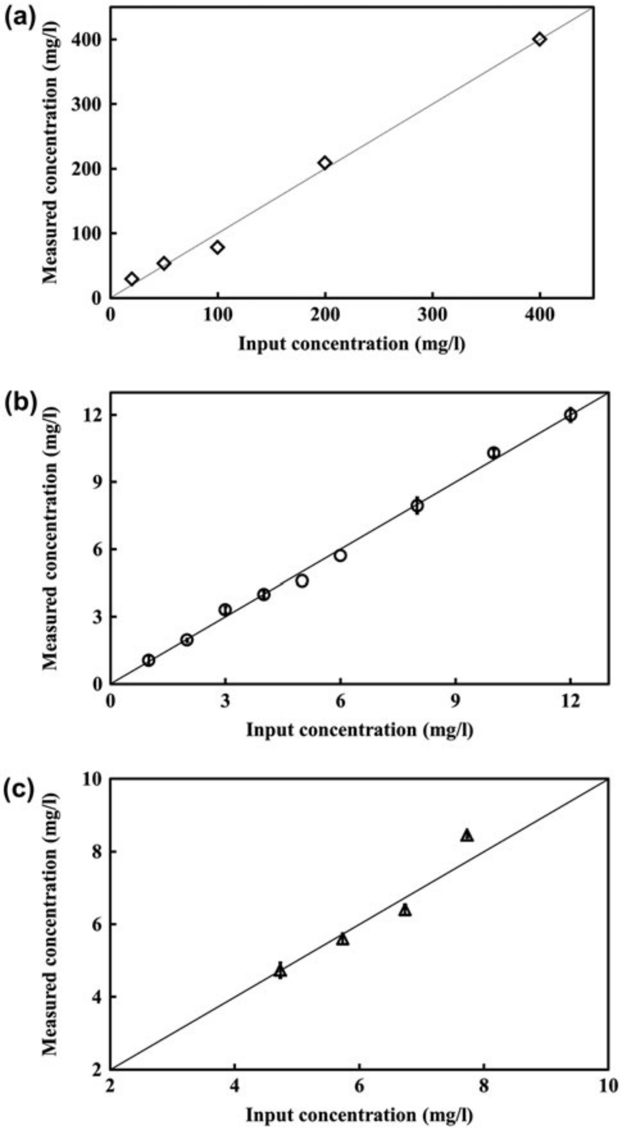


Fig. 4. The verifications of (a) AA-7000F to measure high-concentration boron in DI water; (b) carmine method to measure low boron concentration in DI water; and (c) carmine method to measure low boron concentration in seawater condition.

3.2. High-concentration boron removal in DI water: effects of pH and polyol on boron removal

As discussed earlier, boron removal rate increases at higher pH values because the portion of borate increases as pH increases. The reaction between boric acid and polyol also increases the boron rejection, and the reaction occurs more vigorously as pH increases, which induces higher boron removal at higher pH values as reported elsewhere [12]. Fig. 5 clearly shows this tendency in a lab-scale RO test, where a high boron concentration of 200 mg/L was injected into DI water, and both feed and permeate boron concentrations were measured using AA-7000F. The boron removal rate increased from 62.93% to 75.02% as pH increased without addition of any polyol. When xylitol was injected with molar ratio of 1:2 (boron:xylitol) the boron removal rate was enhanced compared to the case with no polyol addition. For example, the boron removal at pH 8 (commonly known as seawater pH) increased from 60.42% to 75.25% thanks to the addition of xylitol, and this enhanced removal rate exceeds the removal rate of pure boron solution at pH 10, which means boron removal can be enhanced without pH adjustment in SWRO processes.

3.3. Boron removal in seawater: effect of polyol concentration on boron removal

The boron removal enhancement by polyol results from the reaction between polyol and boron. The reaction rate is governed by the concentrations of polyol and boron and the presence of any inhibitors. In SWRO processes, boron concentration is rather small (i.e. 4–5 mg/L) and seawater contains a lot of ionic compounds (e.g. Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^+, Cl^-, SO_4^{2-}, HCO_3^-, and so on) which may inhibit the polyol–boron reaction. Most of previous researches, however, did not cover the effect of seawater condition on the polyol–boron reaction.

Fig. 6 shows the results of low-concentration boron removal test in seawater condition. The boron removal rate increases from 52.4% (no polyol addition) to 79.9% with addition of xylitol, which means that the polyol–boron reaction rate in seawater condition was high enough to induce the enhanced boron removal. During the experiment at a constant pH of 8.4, salt rejection was about 96% while permeate flux was maintained at a constant value of 20.9 LMH at 50 bars of applied pressure. As expected, the boron removal rate increased at higher polyol concentrations (Fig. 6) because the polyol–boron reaction rate increases as polyol concentration increases.

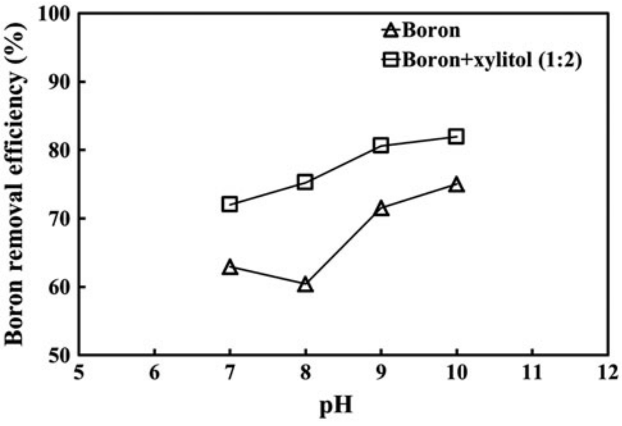


Fig. 5. Effects of pH and polyol on boron removal.

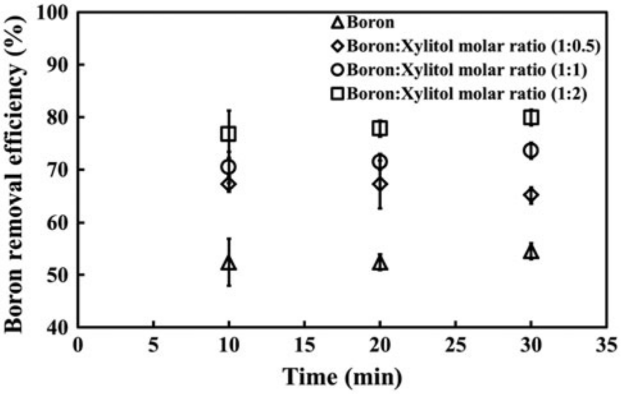


Fig. 6. Effect of polyol concentration on boron removal efficiency in seawater.

The one more thing which should be focused on the results in Fig. 6 is that the boron removal rate did not change after 10 min from the injection of xylitol, which means that the polyol–boron reaction reached the steady state in a short time less than 10 min. Unfortunately, 10 min is the minimal time to obtain enough amount of sample to measure boron concentration. The polyol–boron reaction rate was too fast to measure the time necessary to reach the steady state in a lab-scale test. This can be a very important factor for the real-field application because retention time for the polyol–boron reaction could be ignored, which makes the simple injection of polyol to enhance boron removal in real-field SWRO applications.

3.4. Boron removal in seawater: effect of polyol types on boron removal

Three different types of polyols (e.g. D-mannitol, xylitol, and glycerol) were tested to enhance boron removal in the lab-scale SWRO experiments. The injected polyol concentration was determined with the boron to polyol molar ratio of 1:2. Xylitol showed the highest performance, and glycerol exhibited the least enhancement in boron removal (Fig. 7(a)). During the

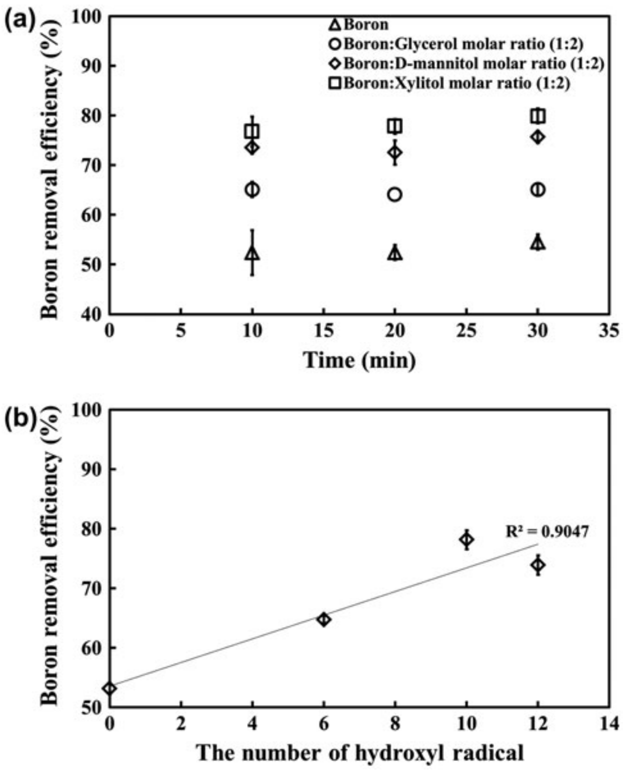


Fig. 7. Effects of (a) polyol types and (b) the number of hydroxyl groups in polyol on boron removal efficiency.

experiment at a constant pH of 8.4, salt rejection was about 95.8% while permeate flux was maintained at a constant value of 20.3 LMH at 50 bars of applied pressure.

As discussed earlier, the polyol–boron reaction occurs due to hydroxyl groups in polyol, which may lead to the assumption that the reaction rate is a function of the number of hydroxyl groups in polyol. D-mannitol, xylitol, and glycerol have 6, 5, and 3 hydroxyl groups, respectively (Table 3). A regression analysis revealed that boron removal and the number of hydroxyl groups in polyol are correlated with reliable coefficient of determination ($R^2 = 0.9047$) (Fig. 7(b)). However, xylitol showed better performance than D-mannitol although D-mannitol has one more hydroxyl group than xylitol. This result reveals that there might be other factors except the number of hydroxyl groups affecting polyol–boron rejection.

4. Conclusions

It is already known that addition of polyol can improve the boron removal efficiency due to the polyol–boron reaction, which enlarges boron-polyol complex to be rejected by RO membrane. However, there are few data about whether boron removal rate can be controlled specifically in seawater condition, where boron exists at a low concentration (less than 5 mg/L). Therefore, this work is conducted to investigate the effect of polyol on the boron removal in seawater condition. The new findings are listed as follows:

1. The polyol–boron reaction occurs in seawater condition with low boron concentration and various ion compounds, which leads to two important findings that boron-polyol reaction occurs with low boron and polyol concentrations and there are no significant inhibitors for the reaction in seawater.
2. The polyol–boron reaction rate was too fast to measure the time necessary to reach the steady state in a lab-scale test, which makes the simple injection of polyol to enhance boron removal in real-field SWRO applications.
3. Boron removal rate showed increasing tendency with one exception as the number of hydroxyl groups increases. The number of hydroxyl groups seems like one of the most influencing factor for boron removal enhancement by polyol, but there might be more factors affecting the polyol–boron reaction leading to the boron removal.

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