



Research Paper

Reclamation of Reverse Osmosis Permeate and Concentrate of Geothermal Water Using Novel Chelating Resins by Hybrid Method Coupling Adsorption and Ultrafiltration

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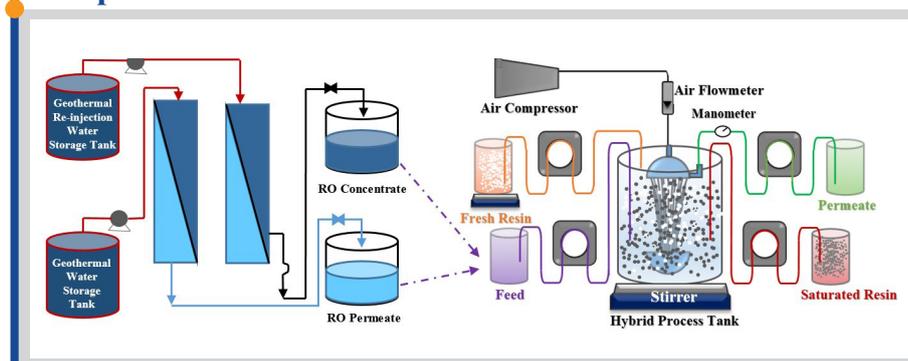
Chelating resin

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Hybrid method coupling adsorption and ultrafiltration

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Graphical abstract



Highlights

- RO process was integrated with adsorption-membrane filtration hybrid method for reclamation of geothermal water.
- Novel chelating resins were employed in adsorption-membrane filtration hybrid method.
- Boron was removed from the RO permeate of geothermal water
- Both boron and arsenic were separated from the RO concentrate of the geothermal water.

Abstract

Management of the concentrated brine with high ion concentrations after reverse osmosis (RO) filtration of geothermal water is a serious environmental problem. In addition to the concentrated brine, the RO permeate of geothermal water is also problematic in terms of boron concentration as it is usually above the permissible limit value stated by WHO for drinking and irrigation water. In our present work, the RO process was integrated with hybrid method combining adsorption with ultrafiltration to remove boron from the geothermal water RO permeate (GW-ROP) while boron and arsenic removals from the geothermal re-injection water RO concentrate (GRIW-ROC). In this sense, novel chelating resins such as novel N-methyl-D-glucamine (NMDG) based resins (1JW and 2JW) along with boron selective core-shell based chelating resin (2PTN) were employed. According to the data obtained, the 2JW resin achieved 81.7% and 95.8% of boron removals from GW-ROP and GRIW-ROC solutions, respectively. The 2JW resin achieved a good success in the removal of boron compared with commercial Dowex XUS 43594.00 resin. In case of arsenic removal from GRIW-ROC, the 2JW resin showed a better performance than Dowex XUS 43594.00 resin at the same resin concentration. Boron removals from the GW-ROP were 72.0% with 1JW resin and 65.8% with 2PTN resin by achieving the permissible boron level set for drinking water. On the other hand, 2PTN resin could not reduce the boron concentration in the GRIW-ROC below the permissible values.

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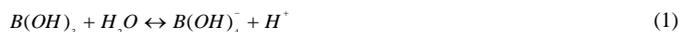
1. Introduction

Water scarcity is still a major problem all over the world due to the high consumption of available water sources, poor water management, industrialization, and the increase in the global population. In this manner, sustainable and eco-friendly treatments of salty underground water resources

are required [1]. The most common method is the RO process which enables the rejection of colloidal or dissolved solids from water. On the other hand, it is not easy to eliminate small neutral molecules such as boric acid utilizing RO [2]. Generally, the character of boron species is based on the pH of water.

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According to the equilibrium reaction given in Equation 1, boron exists in the form of boric acid (H_3BO_3) at lower pH values while it turns into the charged form of borate ions ($B(OH)_4^-$) at higher pH. The charged and fully hydrated form of boron as $B(OH)_4^-$ is highly rejected by the RO membranes owing to their larger size. Additionally, the elimination of boron by RO membranes depends on the salinity of feed, temperature, pressure, and initial boron concentration in the solution [3].



Since higher pH values are needed for the high rejection of boron by RO membranes in the single-pass RO operation, alkali addition is required to increase pH [4]. However, this can cause calcium carbonate and magnesium hydroxide precipitations when the pH value is equal to or higher than 10.5. Thus, the alkali consumption and hardness bring about scaling problems in the single-pass RO system [4]. Usually, 40-50% of boron rejection is obtained by a conventional single-pass RO unit in seawater desalination, but the boron concentration obtained in the product water still exceeds the allowable level for irrigation water [5]. To face that problem, a second RO pass or alternative techniques are selected to reduce the negative effect of pH increase on the scaling problem of RO membranes.

Several combinations of distinctive separation processes were applied considering the boron removal from the RO permeate (ROP). For this purpose, the ion exchange method with boron selective chelating resins, a hybrid method combining adsorption by boron selective chelating resins and membrane filtration, and electrodialysis (ED) following the RO process were tested. By using the seawater RO membranes pursued by the boron selective ion exchange resin, the boron concentration in the seawater ROP was decreased below the permissible level with 99.0-99.9% of percent removal [8]. This combined process was not affected by temperature variations [8-10]. While boron selective ion exchange resins showed remarkable performance in boron removal, the RO process achieved a good salt rejection. For instance, the RO process was integrated with a hybrid method for the desalination of seawater and also for boron removal from seawater. The hybrid system was analyzed with short and long-term studies by using MF and UF membranes [11]. It was observed that the boron removal was accomplished with a certain resin concentration by using both membranes. Moreover, the final boron concentration in permeate was found lower than the legal amount for irrigation water.

The other challenge in the RO operation is the management of the concentrated brine generated after the process. As a result of the poor management of concentrate, ecosystems can be adversely affected by the uncontrolled discharge of brine. These environmental problems are due to the high salinity of the concentrate and high concentrations of inorganics accumulated in the RO concentrate (ROC) [6]. Many studies have addressed the properties of pollutants that may present in the ROC or the treatment options that can be applied to minimize the associated pollutants [1, 6-7]. Considering the significant effects of the toxic and persistent organic pollutants, innovative and cost-effective treatment technologies are needed to struggle with the RO concentrate [6].

The higher amount of boron present in geothermal water causes serious environmental problems if it is utilized for irrigation in agricultural areas. Besides affecting the character of the soil, heavy metals can form complexes with boron in geothermal waters. Consequently, boron removal methods have to be developed for the elimination of these complexes [12]. One of the attempts to rejection of salt, boron, and silica from the geothermal water was the use of four different membranes in the laboratory-scale cross-flow RO system [13]. It was indicated that the efficiencies of the RO membranes could be improved by increasing the applied pressure. Yavuz et al. [14] initiated their consecutive studies by investigating the influence of the membrane configuration and the operational pressure for boron removal from the geothermal water in a mini-pilot scale plant. They reported that only 49% of boron removal was achieved by running a single pass brackish water RO (BWRO) membrane at 15 bar of the operating pressure. The final boron concentration in permeate (4.7 mg/L) did not meet the allowable level for the irrigation water. They investigated the effect of pH as well as other operational parameters on boron removal [15]. Although the most suitable product water in terms of boron concentration was obtained at a pH value of 10.5, they concluded that further increase in pH can be a problem for the RO membranes at high pH. Finally, the seawater RO membrane, (SWRO) was employed for the treatment of the geothermal water [16]. They concluded that the SWRO membrane was more efficient in the rejection of boron than the BWRO membrane without pH adjustment.

Besides the RO membranes, boron selective chelating resins have been employed for the removal of boron from geothermal water and ROP of the geothermal water. In this regard, Samatya et al. [17] investigated the boron

removal from ROP of geothermal water comprised of 5.40 mg B/L by using monodisperse porous poly(glycidyl methacrylate) resin containing NMDG. They found that the obtained resins were more effective in terms of boron removal from the ROP compared to commercial boron selective Dowex (XUS 43594.00) resin. In similar research, Samatya et al. [18] investigated the effect of boron removal from the ROP by monodisperse porous poly(vinylbenzylchloride) based chelating resins having NMDG as a ligand. They reported that the obtained results were highly promising.

Elsewhere, Şen et al. [19] worked on the removal of boron from the ROP of the geothermal water. They have also studied boron and arsenic removal from the ROC of the geothermal water in a batch mode using novel core-shell-based chelating resins (1PTN and 2PTN). It was reported that 2PTN resin could compete with the commercial boron selective chelating resin Diaion CRB 05 resin for both boron and arsenic removals.

An integrated process combining RO and adsorption-ultrafiltration hybrid method was suggested by Kabay et al. [20] for boron separation from geothermal water. The ROP having a boron content of 4.75-5.15 mg/L was fed to the hybrid system where the boron selective commercial Dowex resin was employed for the boron removal. It was mentioned that the resin concentration and its replacement rate should be optimized to fulfill the boron standard for irrigation water [20].

Elsewhere, a similar hybrid study was carried out with poly(glycidyl methacrylate) or poly(vinyl benzoyl chloride) based monodisperse particles functionalized with NMDG [21] to eliminate boron from the geothermal water. It was shown that the reduction of boron concentration from 11 mg/L to 1 mg/L took place within 20-30 min.

In our previous study, novel boron selective chelating resins 1JW, 2JW, and 2PTN were investigated to determine their sorption performances for the separation of boron and arsenic from geothermal water using the hybrid system [22]. Some operational parameters such as the resin type, the resin concentration, and its rate of replacement were studied to determine their influences on boron removal from geothermal water. As a continuation of our previous work, in this study, a hybrid method combining adsorption and ultrafiltration was operated to remove boron from the ROP of geothermal water as well as boron and arsenic from the ROC of the geothermal water by using novel NMDG resins I and II (1JW, 2JW, and 2PTN).

2. Experimental

2.1. Water Samples

A laboratory-scale cross-flow membrane system (SEPA CF II GE-Osmonics) was employed for the filtration of the geothermal water (GW) obtained from a well in the geothermal area of Izmir Geothermal Company. The properties of related geothermal water were detailed previously [22]. In order to collect the RO permeate sample (GW-ROP), the DOW XLE BWRO membrane was produced by Dow Film Tech. was employed under 20 bar of pressure [13-15]. The GW-ROP solution obtained was used as a feed solution in the hybrid tests.

The RO concentrate sample (GRIW-ROC) was collected from a pilot-scale RO unit established at Geothermal Heating Center by collecting the spent geothermal water before its re-injection to the well (GRIW) as the feed solution. In this system, a spiral-wound BW30 (FilmTech) RO membrane was used under an operational pressure of 25 bar with a 60% of water recovery. General properties GW, GW-ROP obtained by SEPA CF II GE-Osmonics membrane test system, GRIW to be injected, and GRIW-ROC were summarized in Table 1.

Table 1
Properties of GW, GW-ROP, GRIW, and GRIW-ROC

Parameter	Unit	GW	GW-ROP	GRIW	GRIW-ROC
pH	-	8.40	6.25	8.40	8.93
Conductivity	µS/cm	1721	41.80	1836	4580
Total Dissolved Solid	mg/L	-	19.56	-	2390
B	mg/L	10.94-9.95	4.54	5.7	17.7
As	µg/L	160	<10	80	250

2.2. Chelating Resins

The production of novel NMDG resins I (1JW and 2JW) and NMDG resin II (2PTN) containing NMDG groups were previously reported by Wolska et al. [23, 24] and Cyganowski et al. [25], respectively. Also, the characteristics of novel NMDG resins and their syntheses were simply

described in our previous study along with the characteristics of commercially available boron-selective Dowex resin [22]. While the average size of the particles of novel NMDG resins I (1JW and 2JW) is 40 μm of, the respective value is 600 μm for novel NMDG resin II (2PTN). The Dowex resin has 20 μm of average particle size after grinding.

2.3. Hybrid system

In the hybrid studies, a submerged membrane module having ultrafiltration membranes in a hollow fiber configuration was used for filtration of the ion exchange resins used as adsorbent. As the solutions, both GW-ROP and GRIW-ROC were employed separately in the vessel containing a defined concentration of ion exchange resin while the fresh resin suspension in the pure water was delivered to the vessel continuously during the operation. A constant airflow was provided to the UF module at a feed rate of 4 mL/min using a compressor to minimize the collection of resin particles on the surface of membranes. The flow chart and details about the hybrid system were described previously [22].

2.4. Experimental methods

In the study with GW-ROP solution, the resin concentration (C_r) was provided as 1 g/L for Dowex and 2JW resins while the respective value was 2 g/L for 1JW and 2PTN resins. These values were optimum amounts based on the preliminary batch adsorption results.

The experiments carried out using GRIW-ROC solution were performed by arranging the C_{resin} as 2 and 3 g/L for Dowex resin, 3 g/L for 2JW resin, and 8 and 16 g/L in terms of 2PTN resin. The flow rates of permeate drawn from the UF membrane module (Q_{per}) and the fresh solution fed to the vessel were equally adjusted to 5 mL/min. The feed flow rate of the fresh resin suspension toward the vessel and the resin replacement rate (Q_{sat}) were kept at the same level of 6 mL/min. The hybrid experiments were run for 3 h by taking the permeate samples at certain time intervals (0, 5, 10, 15, 30, 45, 60, 90, 120, 150, and 180 min).

The boron concentrations in the solutions were determined by the spectrophotometric curcumin method [26] with Jasco V-530 UV/visible spectrophotometer operated at 543 nm of λ_{max} . The boron measurements were carried out as two parallels with 3.0-4.0% of relative standard deviation (RSD). On the other hand, arsenic concentrations in solutions were measured by using Shimadzu AA 7000 model atomic absorption spectrophotometer. The relative standard deviation for arsenic measurement was determined as 1.8-5.0%.

3. Results and discussion

Although the concentration of arsenic in GW-ROP solution was below the maximum permissible value (10 $\mu\text{g As/L}$), it was noted that boron concentration was still above the allowable level for both drinking water (<2.4 mg B/L) and irrigation water (<1 mg B/L). In this context, it was decided to use a hybrid method to reduce the boron concentration in the GW-ROP solution. The boron-selective resins used in the hybrid system were Dowex, 1JW, 2JW, and 2PTN.

Fig. 1 shows the changes in boron concentrations in the permeate samples versus the time for each resin during the hybrid tests.

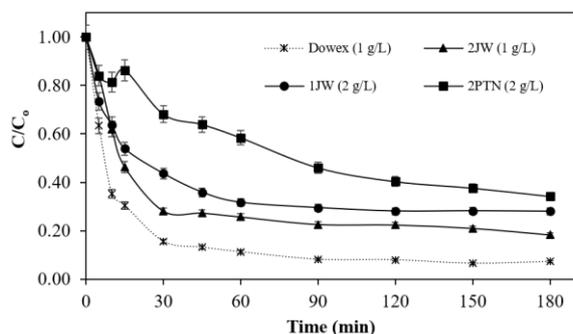


Fig. 1. C/C_0 vs time plots for boron removal obtained with GW-ROP solution employed in AMFH tests ($Q_{\text{per}} = 5$ mL/min and $Q_{\text{sat}} = 6$ mL/min)

According to Fig. 1, Dowex resin (1 g/L) decreased the initial boron concentration of 5.24 mg B/L below the permissible level for irrigation water within the first 30 min of the process. After reaching 84.4% of boron removal, the final boron concentration was found to be 0.34 mg B/L. In 150 min of the process, the boron removal was 93.5%.

Regarding 2JW resins with 1 g/L of C_{resin} , the initial boron concentration was lowered to 0.94 mg B/L after 150 min getting a 79.9% of boron removal and the obtained value agreed well with the permissible level of boron in irrigation water [5].

The reason why the Dowex resin reduced the boron concentration faster than that with 2JW resin was its relatively smaller particle size (20 μm) compared to the novel 2JW resin having an average particle size of 40 μm . This can be explained by, the reduced resin particle size enhancing the contact area of the resin, which led to an improvement in boron removal performance by lowering the boron concentration in the permeate [27].

On the other hand, both novel 1JW and 2PTN resins gave lower boron removals even for their doubled resin concentration (2 g/L). As a result of the study, the maximum boron removals of 72.0% and 65.8% were obtained after 180 min for 1JW and 2PTN resins offering the allowable boron concentration value for drinking water rather than for irrigation water.

In the study by Güler et al. [11], a similar hybrid system with a UF membrane module was tested for Dowex resin for the boron removal of the ROP of seawater. They operated the hybrid system with 3 mL/min of Q_{sat} and 10 mL/min of Q_{per} as well as an initial boron concentration of 1.95 mg B/L. According to their results, the boron concentrations in the ROP decreased to nearly zero (0.05-0.08 mg B/L) with approximately 97.0% of boron removal when C_{resin} was 1 g/L. It should be noted that the differences in the initial boron concentration and operational parameters can affect the boron removal performance of this resin.

In another study, Dowex resin was tested in boron removal from the GW-ROP solution by a similar hybrid system. The effect of the resin concentration and its replacement rate were investigated by keeping Q_{per} at 10 mL/min. It was observed that the boron removal increased with an increase in the resin concentration and the resin replacement rate [20]. When 1 g/L of C_{resin} , 6 mL/min of Q_{sat} , and 10 mL/min of Q_{per} were adjusted, the maximum boron removal by Dowex resin reached the level of 90.6%. In this study, maximum boron removal was obtained as 93.5% when Q_{per} was 5 mL/min while C_{resin} and Q_{sat} were as same as in the previous work [20]. We can say that a certain decrease in the Q_{per} positively affected the boron removal performance.

As explained before, both boron and arsenic concentrations in the GW-ROC solution are higher than their concentrations in the geothermal water. In order to reinject the RO concentrate safely underground, it should be either blended with geothermal water and/or treated with chelating resins to remove both boron and arsenic which exist at high concentrations in the RO concentrate before reinjection. For this purpose, the removal of boron and arsenic from the RO concentrate of geothermal re-injection water (GRIW-ROC) was investigated using the novel boron selective resins (2JW and 2PTN) and Dowex resin in the hybrid method.

The Dowex resin decreased the boron concentration in the RO concentrate of the geothermal water to 1.79 mg B/L (boron removal: 90.5%) when 2 g/L of resin concentration was used (Fig. 2). Since the final boron concentration was still higher than the permissible level for the irrigation water, C_{resin} was raised to 3 g/L. According to obtained results, the decrease in the boron concentration below the permissible level of boron was observed after 30 min. The continuation of the operation allowed us to reach a higher boron removal of 96.3% and to obtain the product water with a boron concentration of 0.72 mg B/L.

In the experiment run with the 2JW resin by using a C_{resin} of 3 g/L, the amount of boron dropped to 1.74 mg B/L in 45 min. Then, the boron removal reached 95.8% after 180 min of the process (Fig. 2). Thus, the boron concentration at the end of the experiment was obtained as 0.79 mg B/L which meets the standards stated by WHO [5]. Compared to Dowex resin, the 2JW resin gave almost similar boron removal after 180 min. However, Dowex resin could decline the boron concentration to a value below 1 mg B/L about 30 min earlier than the 2JW resin. As explained before, the reason for such fast removal was because Dowex resin has a smaller particle size.

The NMDG II (2PTN) resin was also tested for boron removal from the GRIW-ROC solution. In this case, 8 g/L of C_{resin} was used in the hybrid test. According to Fig. 2, the boron concentration in the GRIW-ROC solution was dropped till the end of the experiment (180 min) to 9.08 mg/L which was much higher than the permissible value of boron for both drinking and irrigation water. When the C_{resin} was raised to 16 g/L, the boron removal by the 2PTN resin was enhanced to 79.6% after 180 min but the remaining boron concentration in the product water (4.71 mg/L) was still higher than the permissible levels. The lowest boron removal performance of the 2PTN resin was explained by its larger particle size considering that of Dowex resin and the boron sorption with its epidermis layer only [22].

Along with boron, the arsenic removal performances of Dowex, 2JW, and 2PTN resins from the GRIW-ROC solution used in the hybrid system were also obtained. The obtained results for each resin were illustrated in Fig. 3.

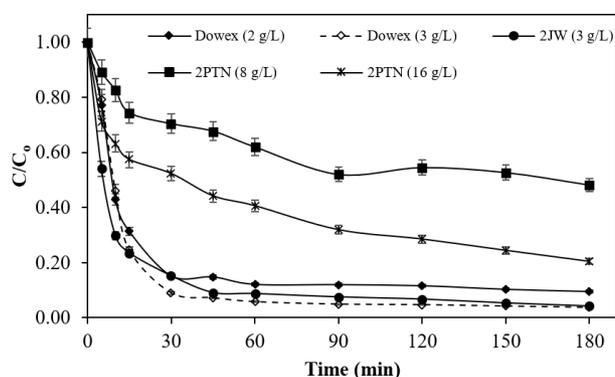


Fig. 2. C/C_0 vs time plots for boron removal obtained with GRIW-ROC solution in AMFH tests ($Q_{per}= 5$ mL/min and $Q_{sat}= 6$ mL/min)

As shown in Fig. 3, a gradual decrease in the arsenic concentration appeared with the Dowex resin used with a concentration of 3 g/L in the hybrid system. The maximum arsenic removal was 30.3% after 180 min.

For the case of the 2JW resin, arsenic concentration was dropped till 15 min and then a gradual decrease was seen until the end of the experiment. The maximum arsenic removal obtained with the 2JW resin (3 g/L) was 42.0% at the end of 3 h. Compared to Dowex resin, the 2JW resin performed greater arsenic removal from the GRIW-ROC solution at the same resin concentration (3 g/L).

Concerning 2PTN resin which has 8 g/L of C_{resin} , the arsenic concentration gradually decreased with the highest arsenic removal of 39.5% in 180 min. As seen in Fig. 3, the arsenic removal from the GRIW-ROC solution did not increase although the amount of 2PTN resin used for the experiment was doubled to 16 g/L.

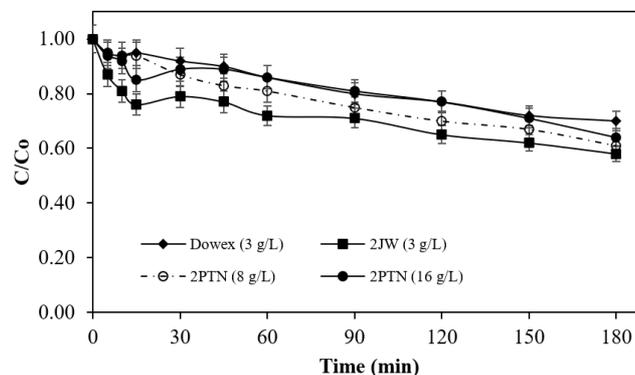


Fig. 3. C/C_0 vs time plots for arsenic removal from GRIW-ROC solution employed in AMFH tests ($Q_{per}= 5$ mL/min and $Q_{sat}= 6$ mL/min)

The results were given in Table 2. Among the novel chelating resins tested, the 2JW resin was an alternative resin to the commercial boron selective Dowex resin in terms of boron removal from GW-ROP and the GRIW-ROC solutions. While Dowex and 2JW resins achieved decreased boron concentration in GW-ROP solution below the limit for irrigation water, 1JW and 2PTN resins gave promising results for the allowable boron level in drinking water.

In the experiment with the GRIW-ROC solution, apart from the Dowex resin, the 2JW resin was the resin to obtain a suitable boron concentration (0.79 mg B/L) in the product water using a resin concentration of 3 g/L.

Table 2

Summary table for boron and arsenic removals from GW-ROP and GRIW-ROC solutions using commercial and novel boron selective resins by hybrid system

Resin	C_{resin} (g/L)	Solution	Q_{sat} (mL/min)	Q_{per} (mL/min)	$[B]_{initial}$ (mg/L)	$[B]_{final}$ (mg/L)	$[As]_{initial}$ (μ g/L)	$[As]_{final}$ (μ g/L)	Max. removal (%)	
									B	As
Dowex	1	GW-ROP	6	5	5.24	0.34	X	X	93.5	X
2JW	1				3.84	0.82	X	X	81.7	X
1JW	2				4.46	1.25	X	X	72.0	X
2PTN	2				4.47	1.31	X	X	65.8	X
Dowex	2	GRIW-ROC	6	5	18.83	1.79	X	X	90.5	X
Dowex	3				19.63	0.72	232	161	96.3	30.3
2JW	3				19.05	0.79	274	159	95.8	42.0
2PTN	8				18.85	9.08	271	164	51.8	39.5
2PTN	16				23.14	4.71	231	148	79.6	35.9

$[B]_{initial}$: Boron concentration at $t=0$; $[B]_{final}$: The minimum boron amount in permeate; $[Q_{sat}]$: Resin replacement rate (fresh and saturated resins); $[Q_{per}]$: Flow rate of permeate; $[As]_{initial}$: Arsenic concentration at $t=0$; $[As]_{final}$: The minimum arsenic amount in permeate; $[C_{resin}]$: Resin concentration; X: Not determined.

4. Conclusions

Novel chelating ion exchange resins were used in the hybrid system combining adsorption with ultrafiltration for the removal of boron from GW-ROP and GRIW-ROC solutions. To lower the concentration of boron to the permissible level for both drinking and irrigation water standards, process conditions should be optimized. The hybrid tests for arsenic separation from GRIW-ROC are still ongoing. For this, arsenic selective ion exchange resins will be employed due to the lower performance of novel boron selective resins for arsenic separation using a hybrid method.

CRedit authorship contribution statement

E. Çermikli: Investigation; Writing original draft

F. Şen: Investigation

J. Wolska: Investigation

P. Cyganowski: Investigation

Y. Abdullahi Jarma: Investigation; Methodology

E. Altok: Investigation; Methodology

M. Arda: Project administration; Formal analysis

M. Bryjak: Supervision; Resources; Project administration

N. Kabay: Supervision; Resources; Writing-review & editing; Project administration.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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