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Process optimization of boron and hardness removal from boron mining wastewater using mixed-bed ion exchange resin by response surface Methodology (RSM)

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ABSTRACT

The treatment of boron mine wastewater containing high concentrations of boron and hardness is critically important due to its environmental impact and reuse limitations. In this study, the simultaneous removal of boron and total hardness from boron mining wastewater was investigated using a mixed-bed ion exchange resin (Tulsion® MB-115). The process was modeled and optimized by response surface methodology (RSM) based on central composite design (CCD) to evaluate the effects of pH (6–10), solid/liquid ratio (S/L) (20–60 g L^{-1}), and temperature (T) (15–35 °C). Maximum hardness removal of 98.6% was achieved at pH 8.5, S/L 45.5 g L^{-1}, and 25°C, while maximum boron removal of 73.2% was obtained at pH 9.2, S/L 60 g L^{-1}, and 22°C. Under optimized simultaneous conditions (pH 10, S/L 52.8 g L^{-1}, 15 °C), removal efficiencies reached 97.5% for hardness and 71.1% for boron. Analysis of variance (ANOVA) confirmed the statistical significance of the quadratic models ($R^2 = 85.26\%$ for hardness; $R^2 = 98.57\%$ for boron). The S/L was the most influential factor for hardness removal, whereas boron removal was significantly influenced by pH, solid/liquid ratio, and temperature.

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KEYWORDS
Boron removal; hardness removal; mixed-bed resin; optimization; response surface methodology; RSM

Introduction

Contemporary environmental pollution has emerged as a critical global challenge, largely attributable to accelerated population growth, industrialization, and anthropogenic activities.[1] Boron is widely used in various industries, including glass and porcelain industry, photography, medicine, electronics, military applications, fuel, nuclear technology, semiconductors and related industries.[2–4] Boron is also an essential element for plant growth; however, it has a narrow acceptable concentration range in irrigation water.[5–8] Boron removal from contaminated waters is essential due to its antiseptic and toxic effects on living organisms.[9] The direct discharge of boron to seawater and surface waters at high concentration causes ecological problems.[10] Recent studies have highlighted the environmental and health implications of elevated boron concentrations in water resources, particularly in regions influenced by industrial and mining activities. Advanced analytical and treatment approaches have been explored to improve monitoring and removal efficiency under complex environmental conditions.[11–13] These findings highlight the need for efficient and optimized treatment strategies for industrial wastewaters containing high boron levels.

Turkey holds 61% of the world's boron minerals and produces boric acid, borax, colemanite, and ulexite.[14] One of Turkey's major boron deposits is located in the Bigadiç region.[15] Colemanite minerals extracted at the Bigadiç mine are kept in water and then washed to purify the colemanite.[16] In addition, the plant generates large volumes of wastewater originating from groundwater in open-pit mines. This groundwater contains approximately 150 mg L^{-1} of boron,[17] as well as high total hardness concentrations, which may alter the ecological characteristics of groundwater and surface waters in the event of discharge or infiltration.

A portion of the groundwater is used in washing process. The excessive groundwater and waste washing water are transferred to Çamköy Dam in the mine region.[16,17] The dam water is not suitable for irrigation as the concentration range of boron in irrigation use is very narrow, impacting both useful and toxic effects in plants.[14] It is essential to treat and discharge excess wastewater into nature in order to reduce both the capacity requirement of the wastewater dam and potential ecological risk.

Several processes can be employed to remove or limit the boron concentration from drinking water, groundwater, irrigation water, and wastewater.[18] Some of

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these methods are adsorption, ion exchange, chemical precipitation, electrocoagulation, electrodialysis, reverse osmosis, membrane processes, ultrafiltration, and solvent extraction.[19,20] Adsorption, ion exchange, and membrane processes are among the most commonly employed methods for boron removal from water.[21–26] On the other hand, ultrafiltration,[27] nanofiltration,[28] adsorption,[29,30] electrocoagulation,[31–34] reverse osmosis [17,35] are used for hardness removal from water and wastewaters. Also, ion exchange is widely employed for softening hard waters, treating polyvalent cations, and industrial water treatment.[36–42]

Synthetic resins and zeolites are commonly used as ion exchange materials.[9,43,44] Mixed resins provide the simultaneous removal of both anions and cations from aqueous solutions.[38]

In the treatment of boron-containing wastewater, membrane-based techniques such as membrane filtration, reverse osmosis, and ultrafiltration may lead to issues including surface deposition and membrane fouling. Therefore, appropriate pretreatment processes, such as precipitation and ion exchange, are generally required to minimize operational limitations and enhance overall process performance.

This study aimed to investigate the removal of boron and hardness from colemanite mine wastewater using a mixed-bed resin, with process optimization performed through response surface methodology (RSM) using Minitab 19.0. Simultaneous and separate removal conditions of boron and total hardness by ion exchange were investigated so that the results could be used as a pre-treatment method of membrane filtration unit or as a private treatment method. The main contributions of this study are summarized as follows:

- Industrial wastewater with high concentrations of boron and hardness, which has not been extensively studied in the literature, was used.
- A mixed-bed resin (Tulsion MB-115), capable of removing both anions (boron) and cations (hardness), was selected, although it has not been previously applied to such wastewater.
- RSM-based optimization was performed, offering advantages in terms of time, cost, and labor efficiency for the treatment of wastewater from these and similar plants.

Despite the extensive literature on boron removal, most studies have focused either on selective boron removal from synthetic solutions or on hardness removal as an independent process. Limited research has addressed the simultaneous treatment of real industrial wastewater containing high concentrations of both boron and hardness, particularly in boron mining applications. The coexistence of elevated hardness may significantly influence ion exchange performance, competitive interactions, and process optimization; however, these interactions have not been systematically evaluated in the literature. Furthermore, the application of mixed-bed ion exchange resins for the simultaneous removal of contaminants in such complex wastewater matrices remains underexplored. Previous optimization studies have predominantly focused on single-response optimization rather than assessing different operational targets within the same experimental framework. Accordingly, the present study aims to address these gaps by investigating the simultaneous and separate removal of boron and total hardness from real colemanite mine wastewater using a mixed-bed ion exchange resin. RSM was applied to statistically model the system and determine optimal operational conditions for different treatment priorities, thereby providing a practical basis for both pretreatment and direct treatment applications in boron-rich industrial wastewater management.

Materials and methods

Materials

The used wastewater was supplied from Çamköy dam in Bigadiç colemanite mine in Turkey and the characterization of colemanite mine wastewater was as follows: boron 537 mg L^{-1}, total hardness 727 mg $CaCO_3$ L^{-1}, calcium hardness 210 mg $CaCO_3$ L^{-1}, sulfate 713 mg L^{-1}, pH 8.6, conductivity 2137 µS cm^{-1}, and suspended solids 9 mg L^{-1}.

TULSION MB-115 mixed resin obtained from Thermax company was used in the study. TULSION MB-115 is a mixture of strong acid cation exchange resin Tulsion T-46 (H) and strong base anion exchange resin Tulsion A-33 (OH) in 1:1.5 volumetric ratio. The characteristics of the resin are given in Table 1.

Sodium hydroxide and hydrochloric acid solutions were used for pH adjustment. The chemicals used are of analytical purity.

Methods

Experimental method

In order to determine the equilibrium time, an adsorption study was carried out with 10 g resin at natural pH (8.6) using 100 mL wastewater in a batch reactor. At predetermined time intervals, wastewater were taken, and total hardness was determined by the 2340 C EDTA titrimetric method,[45] while boron was

Table 1. The characteristics of the TULSION MB-115 mixed resin.

	Tulsion T-46	Tulsion A-33
Type	Strong acid cation exchange resin	Strong base anion exchange resin
Matrix Structure	Cross linked polystyrene	Cross linked polystyrene
Functional Group	Sulfonic acid	Quaternary ammonium Type I
Physical Form	Moist spherical beads	Moist spherical beads
Ionic form supplied	Hydrogen	Hydroxide
Screen Size U.S.mesh(wet)	16 to 50	16 to 50
Particle Size	0.3 to 1.2 mm	0.3 to 1.2 mm
Fines Content	Less than 2% passing through 40 U.S. mesh	Less than 2% passing through 40 U.S. mesh
Total exchange capacity	1.8 meq mL^{-1} minimum of 99% in hydrogen form	1.0 meq mL^{-1} minimum of 90% in OH form and less than 1% in Cl form
pH range	0 to 14	0 to 14
Temperature stability	120°C	80°C
Solubility	Insoluble in all common solvents	Insoluble in all common solvents
Organic leachables	Less than 0.2 mg $KMNO_4$ per ml of wet resin	Less than 0.2 mg $KMNO_4$ per ml of wet resin
Backwash settled density	Approx.750 $gm.liter^{-1}$	
Impurities	Fe = 50 mg L^{-1}(max) Cu = 50 mg L^{-1} (max) Pb = 50 mg L^{-1} (max)	Fe = 50 mg L^{-1} (max) Cu = 50 mg L^{-1} (max) Pb = 50 mg L^{-1} (max)
Bead strength	Avg. not less than 500 g $bead^{-1}$ by Chatillon test	Avg. not less than 300 g $bead^{-1}$ by Chatillon test

analyzed by the potentiometric method.[46] All experiments were conducted in triplicate under identical conditions. The reported values represent the mean of three independent measurements. Experimental repeatability was further supported by replicated center points included in the CCD design.

Response surface methodology (RSM) optimization

The RSM was first introduced by Box and Wilson [47] The RSM is formed from mathematical and statistical analysis approaches.[48] In RSM, the optimum conditions are attempted to be determined by using certain design parameters. The effects of process factors on the response and their interactions with each other are taken into consideration. The method is based on the creation of an empirical model for evaluating the relationship between controllable experimental factors and the results obtained.[49] RSM is important in fields where complex systems with many variables affect process performance. The method is evaluated as technological planning for developing processes, optimization of process performance, formulation, and design of products.[50–52]

Using the Minitab 19 program, the experimental design was performed with the CCD method. The total number of experiments required for the CCD was determined based on its standard structural formulation. For a system with n independent variables, the total number of runs (N) is given by Equation (1).

$$N = 2n + 2n + nc \qquad (1)$$

where n represents the input factors, 2n corresponds to the axial (star) points, and n_c denotes the replicated center points.[53]

Considering three independent variables (pH, S/L, and T), each examined at five levels with six center-point replications, a total of 20 experimental runs were designed based on the CCD.

During the design, pH, S/L, and T were designated as independent variables, while hardness and boron removal efficiencies were identified as dependent variables. The factors and levels determined for the design are given in Table 2.

100 mL of wastewater was taken and placed in a polyethylene bottle, and experiments were carried out in a temperature-controlled shaker under the conditions determined in the experimental design during the equilibrium period. At the end of the equilibrium period, samples were taken and analyzed for boron and hardness. Boron concentration calculations were calculated according to Equation (2), and hardness concentrations were calculated according to Equation (3)

$$\text{Boron}(\text{mg/L}) = \frac{(V_1 - V_2) \times 0.21627 \times 1000 \times Sf}{V_3} \qquad (2)$$

Here, V_1 is KOH consumption (mL), V_2 is KOH consumption for pure water, f is standardized factor, V_3 is taken solution volume (mL).

$$\text{Hardness}\left(\frac{\text{mg}\,\text{CaCO}_3}{\text{L}}\right) = \frac{A \times B \times 1000}{V} \qquad (3)$$

Table 2. Experimental design factors and levels.

Factors	−2	−1	0	+1	+2
A- pH	6	7	8	9	10
B-Solid/Liquid (S/L) (g L^{-1})	20	30	40	50	60
C-Temperature (T) (°C)	15	20	25	30	35

Here, A is the consuming EDTA solution (mL), B is the equivalent of 1 mL EDTA solutionas mgCaCO$_3$.The independent variable removal efficiency (%) was calculated according to Equation (4).[54

$$\text{Removal Efficiency}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (4)$$

Here C$_0$ is the initial concentration (mg L^{-1}), C$_e$ is the equilibrium concentration (mg L^{-1}). The calculation of the equilibrium adsorbed amount (q$_{ads}$,mg g^{-1}) for boron and total hardness was determined utilizing Equation (5).[55,56]

$$q_{ads} = \frac{(C_0 - C_e)V}{m} \quad (5)$$

Here, q$_{ads}$ represents the capacity of adsorbed boron or total hardness (mg g^{-1}), C$_0$ and Ce represent the initial and equilibrium concentrations of boron or total hardness in milligrams per liter (mg L^{-1}).

Result and discussions

Determination of equilibrium time

In order to determine the equilibrium time, experiments were conducted using wastewater samples obtained from the boron processing plant under the following conditions: pH 8.6 (natural), 100 mL sample volume, 10 g resin, 25°C, and 150 rpm. TULSION MB-115 mixed resin was used for boron and hardness removal from boron mine wastewater. The results are given in Fig. 1. As can be seen in Fig. 1, a time span of 30 min was enough for equilibrium in hardness and boron.

RSM optimization for hardness and boron removal

RSM is a statistical tool employed to optimize processes in which multiple independent input variables influence a dependent output variable, referred to as the response. It is useful to relate the factor and response in a mathematical model such as the response function.[53,57,58]

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \quad (6)$$

In the given Equation (6), Y represents the predicted response, with b$_0$ as the constant coefficient. Other coefficients b$_i$, b$_{ii}$, and b$_{ij}$ are derived from the polynomial equation, corresponding to the linear, quadratic and interaction coefficient and X$_i$, X$_j$ are coded values of the independent variables, respectively.[59,60]

Central composite design (CCD), which is one of the important components of RSM, is a five-level experimental design that includes axial and factorial points in the design of experimental studies, unlike Box Behnken and other models in RSM. Process optimization in CCD was found to be important in determining the factor values at which the response is maximized. A significant benefit is that it requires only a limited number of experimental runs to ascertain the optimal experimental conditions.[53,61]

The optimization of hardness and boron removal by TULSION MB-115 mixed resin was studied by CCD analysis taking into consideration of full quadratic approach at 30 min of equilibrium time, 150 rpm conditions. The experimental design matrix and the hardness and boron removal efficiency percentages calculated from the experiments performed according to these conditions are given in Table 3.

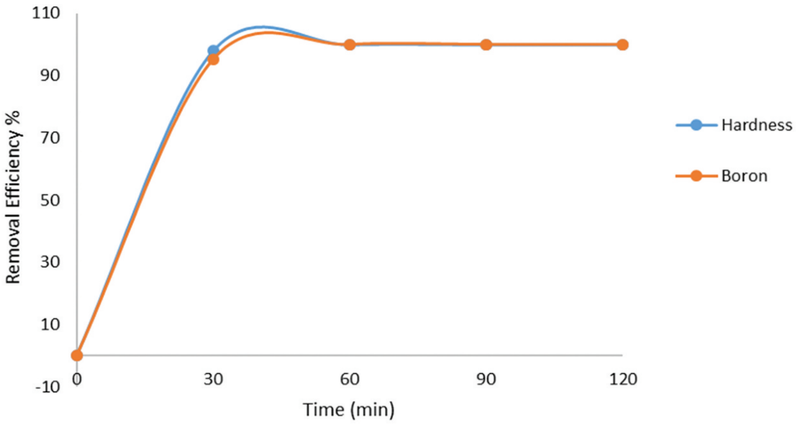


Figure 1. Effect of contact time on hardness and boron removal (initial boron concentration: 537 mg L^{-1}; total hardness: 727 mg CaCO$_3$ L^{-1}; pH: 8.6; resin dosage: 10 g per 100 mL; temperature: 25°C; agitation speed: 150 rpm).

The quadratic model equation obtained from CCD for hardness and boron removal efficiency in terms of input factors are given in Equation 7 and Equation 8, respectively. By using Equation 7 and Equation 8, responses can be obtained for different levels of the parameters.

$$\begin{aligned} \mathit{Hardness\ Removal}(\%) = {} & 40.6 + 6.67pH + 0.829(S/L) + 1.005T \\ & - 0.331pH^2 - 0.00984(S/L)^2 - 0.00249T^2 \\ & + 0.0185(pH)(S/L) - 0.0980(pH)(T) \\ & - 0.00140(S/L)(T) \end{aligned} \tag{7}$$

$$\begin{aligned} \mathit{Boron\ Removal}(\%) = {} & -382.2 + 75.4pH - 0.09(S/L) + 6.87T \\ & - 2.671pH^2 - 0.00359(S/L)^2 - 0.1005T^2 \\ & - 0.082(pH)(S/L) - 0.961(pH)(T) \\ & + 0.1076(S/L)(T) \end{aligned} \tag{8}$$

R-Squared (R-Sq) values of 85.26% (with an adjusted R-Squared of 71.99%) were computed for hardness removal, while the values for boron removal were R-Sq 98.57% (with an adjusted R-Squared of 97.28%).

ANOVA was used to analyze the statistical validation and predictive quality of the resulting model. The p values (probability constants) were used as a control parameter to check the reliability of the developed statistical model, individual and interaction effects of the parameters.[62] A model term is considered significant if the *p*-value is less than 0.05, while an insignificant model is indicated by a lack of fit value exceeding 0.05.[63]

The ANOVA results for hardness removal are presented in Table 4. The quadratic model was found to be statistically significant (F = 6.43, $p = 0.004$). Among the investigated factors, only the S/L ratio showed significant linear and quadratic effects ($p < 0.001$), identifying resin dosage as the primary factor governing hardness removal. In contrast, pH, temperature, and interaction terms were not statistically significant ($p > 0.05$), indicating limited parameter interdependence within the studied range. This finding aligns with ion-exchange theory, where removal efficiency is predominantly controlled by the availability of active exchange sites.

Although the lack of fit was statistically significant (F = 194.19, $p < 0.001$), the consistently high removal efficiencies and low pure error indicate strong experimental repeatability. Therefore, the model was considered acceptable for optimization within the investigated experimental range. The pareto chart graph showing the effectiveness of the parameters on hardness removal is given in Fig. 2. The Pareto chart of standardized effects provides a visual assessment of term significance. The vertical dashed line at 2.228 represents the critical *t*-value corresponding to the 95% confidence level. The S/L ratio (B) exceeded the significance threshold and was identified as the most influential parameter in the hardness removal process. The quadratic term S/L*S/L (BB) was also statistically significant. In contrast, pH, T and the remaining interaction and quadratic terms did not exceed the critical limit and were therefore considered insignificant within the investigated experimental range.

The ANOVA results for boron removal are presented in Table 5. The quadratic model was found to be highly significant ($p < 0.001$), with a high F-value confirming strong explanatory power. The model exhibited an R^2 of 98.57% and an adjusted R^2 of

Table 3. Central composite design (CCD) experimental matrix and corresponding hardness and boron removal efficiencies (equilibrium time: 30 min; agitation speed: 150 rpm).

Run Order	pH	Solid/Liquid ($g\ L^{-1}$)	Temperature (°C)	Hardness Removal (%)	Boron Removal (%)
1	7	30	20	96.27	20.03
2	9	30	20	96.80	38.05
3	7	50	20	97.60	41.85
4	9	50	20	99.20	59.72
5	7	30	30	96.97	0.93
6	9	30	30	95.87	2.86
7	7	50	30	98.35	47.40
8	9	50	30	97.66	42.93
9	6	40	25	98.62	16.64
10	10	40	25	95.74	42.83
11	8	20	25	90.10	5.07
12	8	60	25	99.04	72.89
13	8	40	15	97.20	44.72
14	8	40	35	99.31	16.01
15	8	40	25	98.62	39.70
16	8	40	25	98.62	41.13
17	8	40	25	98.35	42.38
18	8	40	25	98.62	36.11
19	8	40	25	98.62	38.26
20	8	40	25	98.62	38.62

Table 4. ANOVA analysis of hardness removal using TULSION MB-115 mixed resin.

Source	DF	Adj SS	Adj MS	F-Value	p-Value
Model	9	68.574	7.619	6.43	0.004
Linear	3	40.854	13.618	11.48	0.001
pH	1	1.836	1.836	1.55	0.242
S/L	1	38.378	38.378	32.37	0.000
T	1	0.640	0.640	0.54	0.479
Square	3	25.486	8.495	7.16	0.007
pH*pH	1	2.755	2.755	2.32	0.158
S/L*S/L	1	24.321	24.321	20.51	0.001
T*T	1	0.098	0.098	0.08	0.780
2-Way Interaction	3	2.234	0.745	0.63	0.613
pH*S/L	1	0.274	0.274	0.23	0.641
pH*T	1	1.921	1.921	1.62	0.232
S/L*T	1	0.039	0.039	0.03	0.859
Error	10	11.858	1.186		
Lack-of-Fit	5	11.797	2.359	194.19	0.000
Pure Error	5	0.061	0.012		
Total	19	80.431			

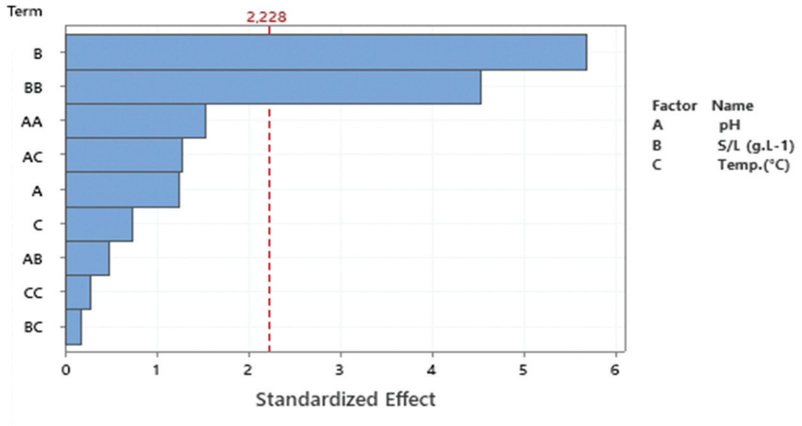


Figure 2. Pareto chart for hardness removal using TULSION MB-115 mixed resin.

97.28%, indicating excellent agreement between predicted and experimental values and demonstrating high predictive capability. As indicated by the *p*-values ($p < 0.05$) in Table 5, the statistically significant model terms are pH, S/L, T, pH*pH, T*T, pH*T and S/L*T. The pareto chart graph showing the effectiveness of the parameters on boron removal is given in Fig. 3. As shown in Fig. 3, the vertical dashed line at 2.23 represents the critical *t*-value corresponding to the 95% confidence level. The S/L ratio (B) was identified as the most influential parameter in the boron removal process. Other

Table 5. ANOVA analysis of boron removal using TULSION MB-115 mixed resin.

Source	DF	Adj SS	Adj MS	F-Value	p-Value
Model	9	6524.06	724.90	76.51	0.000
Linear	3	5815.43	1938.48	204.61	0.000
pH	1	459.35	459.35	48.49	0.000
S/L	1	4411.28	4411.28	465.62	0.000
T	1	944.79	944.79	99.73	0.000
Square	3	287.00	95.67	10.10	0.002
pH*pH	1	179.33	179.33	18.93	0.001
S/L*S/L	1	3.25	3.25	0.34	0.571
T*T	1	158.80	158.80	16.76	0.002
2-Way Interaction	3	421.63	140.54	14.83	0.001
pH*S/L	1	5.36	5.36	0.57	0.469
pH*T	1	184.61	184.61	19.49	0.001
S/L*T	1	231.66	231.66	24.45	0.001
Error	10	94.74	9.47		
Lack-of-Fit	5	70.05	14.01	2.84	0.139
Pure Error	5	24.69	4.94		
Total	19	6618.80			

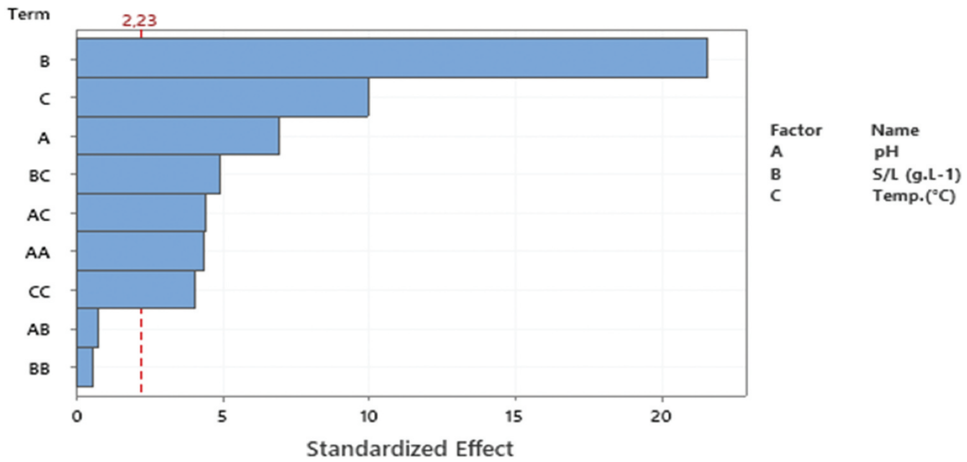


Figure 3. Pareto chart for boron removal using TULSION MB-115 mixed resin.

statistically significant parameters affecting boron removal are; temperature (C), pH (A), S/L*T (BC), pH *T (AC), pH*pH (AA), and T*T(CC), respectively.

Response surface plots for variables

Response surface plots for hardness removal by TULSION MB-115 mixed resin

The surface plots showing the binary interactions of the parameters on the removal efficiency in hardness removal from wastewater with TULSION MB-115 mixed resin are given in Fig. 4. Fig. 4(a) shows the binary interactions of pH and S/L, keeping the temperature constant at 25°C; Fig. 4(b) shows the binary interactions of S/L ratio constant at 40 g L^{-1}, pH and temperature; Fig. 4(c) shows the binary interactions of S/L and T parameters on hardness removal, keeping pH 8 constant. As seen in Fig. 4(a,c), an increase in pH and temperature does not lead to a significant change in removal efficiency, whereas an increase in the S/L ratio results in improved removal efficiency. In Fig. 4, it is evident that an increase in the S/L (20–60 g L^{-1}) ratio leads to a corresponding increase in removal efficiency (90–100%). The graphs presented in Fig. 4 are consistent with Table 4 and Fig. 2.

Response surface plots for boron removal by TULSION MB-115 mixed resin

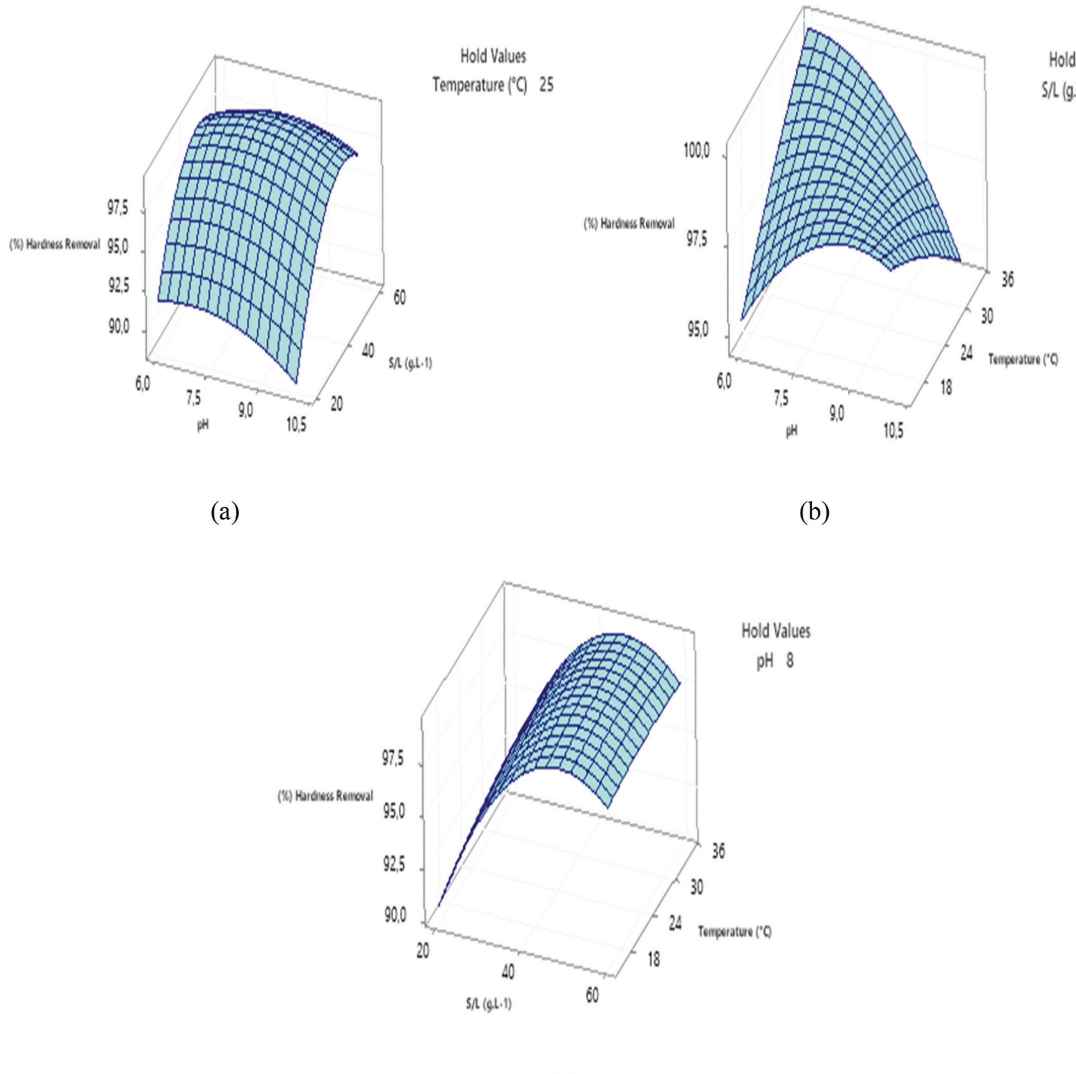
Figure 5 presents surface plots illustrating the binary interactions of parameters influencing the removal efficiency in boron removal from wastewater using TULSION MB-115 mixed resin. Fig. 5(a) illustrates the binary interactions between S/L and pH, with the temperature maintained at a constant 25°C. In Fig. 5(b), the binary interactions are presented with the S/L ratio held constant at 40 g L^{-1}, focusing on the interplay between pH and temperature. Fig. 5(c) depicts the binary interactions of S/L and temperature parameters in relation to boron removal, with pH held constant at 8. In Fig. 5(a), an increase in pH and S/L ratio is observed to enhance boron removal efficiency. Fig. 5(b) shows that higher boron removal efficiencies are achieved under high pH and low temperature conditions. In Fig. 5(c), it is evident that boron removal efficiency increases when the S/L value exceeds 30 g L^{-1} for all temperature values. Fig. 5 shows that boron removal will be above 60% at S/L ratio (55–60 g L^{-1}), pH (7–10) and temperature (15–35 °C) operating conditions.

Process optimization

The study investigated conditions where the removal efficiency was maximized with RSM for three different scenarios in industrial wastewater containing hardness and boron: hardness, boron, and simultaneous removal of both hardness and boron.

The optimizations of the processes were carried out using Minitab 19.0 software with 95% reliability level. The mean of the three replicate validation experiments carried out under the optimal conditions determined by RSM is in accordance with the experimental results predicted by the program.

In the removal of industrial wastewater containing hardness and boron using mixed resin, optimization was performed with RSM to determine the conditions where exclusively hardness removal is maximized. Table 6 presents the conditions that maximized hardness removal (pH 8.5, 45.5 g L^{-1}, 25°C). As a result of the experiment conducted under the conditions presented in Table 6, hardness removal efficiency of 98.6% was achieved.



(a)

(b)

(c)

Figure 4. Response surface plots for hardness removal showing the interaction effects of (a) pH and S/L, (b) pH and temperature, and (c) S/L and temperature at 30 min equilibrium time and 150 rpm agitation.

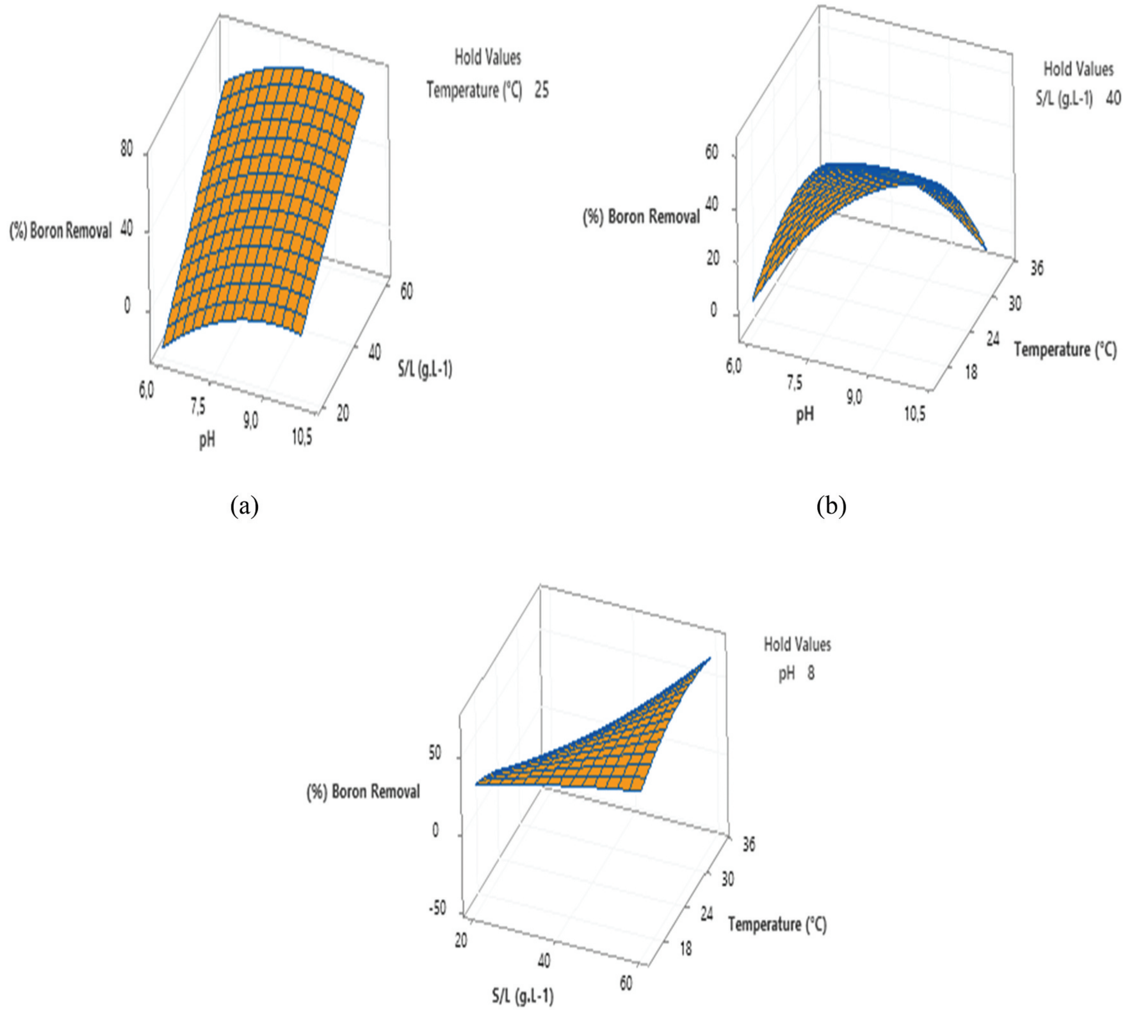
Boonpanaid and Piyamongkala studied with tap water containing an initial hardness concentration of 109.8 ± 20.56 mg L^{-1}, achieving removal efficiencies of 46% with Amberlite resin and 82.45% with Nuosep resin.[64] Pentamwa et al. investigated the possibility of using waste plastics as synthetic resin to remove hardness in groundwater. They achieved a removal efficiency of 43.49% at an initial hardness concentration of 440 mg L^{-1}.[65] Apell and Boyer aimed to purify groundwater containing an average of 275 mg L^{-1} hardness using magnetically enhanced anion and cation exchange resins, achieving removal efficiencies exceeding 55%.[66]

In this study, ion exchange occurred between the hardness-forming cations (M^{2+}) present in industrial wastewater and the Tulsion T-46 cation exchange resin, which exhibits strong acidic properties due to the sulfonic groups present in the mixed-bed resin TULSION MB-115, as shown in Equation 9. A removal efficiency of 98.6% was achieved for industrial wastewater with an initial total hardness concentration of 727 mg L^{-1}.

$$2(R - SO_3^- H^+) + M^{2+} \rightarrow (R - SO_3^-)_2 M^{2+} + 2H^+ \tag{9}$$

The comparison of hardness removal studies using different resins is summarized in Table 7.

Optimization using RSM was performed in the treatment of industrial wastewater containing hardness and boron with mixed resin, aiming to identify the conditions that exclusively maximize boron removal. Table 8 displays the conditions that maximized boron removal (pH 9.2, 60 g L^{-1}, 22°C). The experiments conducted under the conditions given in Table 8 resulted in achieving a boron removal efficiency of 73.2%.



(a) (b)

(c)

Figure 5. Response surface plots for boron removal illustrating the interaction effects of (a) pH and S/L, (b) pH and temperature, and (c) S/L and temperature under 30 min equilibrium time and 150 rpm agitation.

Table 6. Optimum conditions for hardness removal efficiencies.

Optimum Experiment Conditions				
pH	S/L (g L^{-1})	Temperature (°C)	Hardness Removal RSM Model Prediction (%)	Hardness Removal Experimental Result (%)
8.5	45.5	25	95.97–100.00	98.6

Table 7. Comparison of total hardness removal efficiencies using different resin.

Resin Name	Initial Total Concentration (mg L^{-1})	Total Hardness Removal Efficiency (%)	Ref.
Amberlite, NuoSep	109.8 ± 20.56	46, 82.45	[64]
A synthetic resin	440	43.49	[65]
Magnetically enhanced anion and cation exchange resins	275	<55	[66]
TULSION MB-115	727	98.6	This study

Table 8. Optimum conditions for boron removal efficiencies.

Optimum Experiment Conditions				
pH	S/L (g L^{-1})	Temperature (°C)	Boron Removal RSM Model Prediction (%)	Boron Removal Experimental Result (%)
9.2	60	22	62.87–81.03	73.2

As seen in Table 8, pH 9.2 was found to maximize boron removal. In similar studies, Öztürk and Köse reached maximum boron removal at pH 9, Korkmaz et al. at pH 8.5, Boncukcuoğlu et al. at pH 9.5.[4,14,67] It is seen that the increase in S/L ratio increases the boron removal efficiency. This can be explained by the increase in resin surface area in proportion to the amount of resin.

In aqueous solutions, boron typically exists as boric acid and various borate species, with their forms depending on the pH of the solution, temperature and the concentration of boron.[22,67,68] Boric acid exhibits relatively weak Lewis acidity, with a pKa of 9.2 at 25°C, as indicated by Equation 10.[22]

$$B(OH)_3 + OH^- \rightarrow B(OH)_4^- \qquad (10)$$

As seen in Fig. 6, if the pH of the solution is below 9.2, boric acid predominates; if the pH is above 9.2, borate ion predominates.[22,68] In addition, $B(OH)_3$ and $B(OH)_4^-$ are predominantly found at low concentrations (<216 mg L^{-1}). At high concentrations (>290 mg L^{-1}), boron solutions contain numerous boron species such as $B_2O(OH)_6^{2-}$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^{2-}$.[22]

At an initial boron concentration of 537 mg L^{-1}, experiments were conducted within pH (6–10) and temperature (15–35 °C) ranges. Due to high concentrations and elevated pH ranges, borate ions predominate in the solution. As pH increases, borate anions, which bind to hydroxide groups on the resin, increase, resulting in enhanced removal efficiency.

In this study, boron present in industrial wastewater was removed through ion exchange using the Tulsion A-33 anion exchange resin, which exhibits strong basic properties due to the presence of quaternary ammonium functional groups in the mixed-bed resin TULSION MB-115, as described in Equation (11). As a result, a removal efficiency of 73.2% was achieved for industrial wastewater with an initial boron concentration of 537 mg L^{-1}.

$$\begin{aligned} &R - N^+(CH_3)_3OH^- + B(OH)_4^- \\ &\quad \rightarrow R - N^+(CH_3)_3B(OH)_4^- + OH^- \end{aligned} \qquad (11)$$

Table 9 presents a comparison of studies on boron removal using various resins.

An examination of the studies presented in Table 9 indicates that boron-specific resins are commonly employed for boron removal. In contrast, a lower-cost mixed-bed resin was used in the present study. The selectivity order of conventional anion exchange resins for sulfate and boron is reported as $SO_4^{2-} > NO_3^- > PO_4^{3-} > C_2O_4^{2-} > Cl^- > B(OH)_4^-$.[74] Due to the high boron concentration in the industrial wastewater used in this study, it was anticipated that boron removal by anion exchange functional groups might occur in competition with sulfate, as high boron complexes can

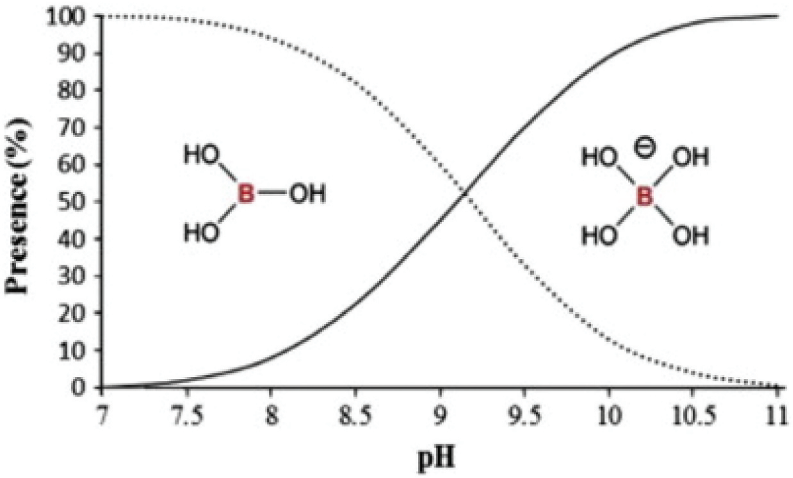


Figure 6. Diagram illustrating the distribution of boric acid and borate ions in solution across different pH values[22].

Table 9. Comparison of boron removal efficiencies using different resin.

Resin Name	Initial Boron Concentration (mg L^{-1})	Boron Removal Efficiency (%)	Ref.
Dowex 2 × 8	600	33.3–55	[4]
P(VbNMDG) resin, Diaion CRB02	10.25, 11	98, 85	[69]
Amberlite IRA 743	19	99	[70]
Diaion CRB 02	30	98.1	[71]
Amberlite IRA 743	500	44.9	[72]
Diaion CRB, Diaion WA 30	20	63.1, 64.3	[73]
Purolite S108	400	100	[14]
TULSION MB-115	537	73.2	This study

form depending on pH.[22] In addition, the complex matrix structure resulting from the presence of various ions and components in the water, due to its nature as real industrial wastewater, may have contributed to the limited boron removal efficiency.

In the removal of industrial wastewater containing hardness and boron using mixed resin, optimization was performed with RSM to determine the conditions under which hardness and boron removal is maximum at the same time. Table 10 provides the conditions (pH 10, 52.8 g L^{-1}, 15°C) that simultaneously maximize hardness and boron removal. Removal efficiencies of 97.5% for hardness and 71.1% for boron were obtained under optimum conditions. Under optimal conditions, a low temperature offers convenience by eliminating the need for additional operational processes. Under simultaneous optimization conditions, the adsorption capacities were determined as 13.4 mg g^{-1} for hardness and 7.2 mg g^{-1} for boron, respectively.

Experiments were conducted for hardness and boron removal under randomly selected conditions within the working range of the parameters. These experimental results were compared with the results calculated using Equations 7 and 8 obtained from RSM and are presented in Table 11. The agreement between the calculated and experimental results indicates that the model operates reliably within the confidence interval.

The proposed mixed-bed ion exchange process presents several advantages compared to alternative treatment technologies. Unlike membrane-based systems such as reverse osmosis and nanofiltration, ion exchange does not require high operating pressures and is less susceptible to performance decline caused by membrane fouling under high hardness conditions. Additionally, the simultaneous removal of cations and anions using a mixed resin simplifies the treatment scheme and may reduce the need for separate softening and boron-selective units.

However, certain limitations should also be considered. Ion exchange resins require periodic regeneration, leading to secondary waste generation. Furthermore, highly selective boron-specific resins reported in the literature may achieve higher boron removal efficiencies under controlled conditions, although they are generally more expensive and often tested in synthetic solutions rather than complex industrial wastewaters.

Therefore, the proposed approach offers a practical and operationally simple alternative, particularly as a pretreatment step prior to advanced membrane systems, where hardness removal is essential to minimize scaling and fouling risks.

Table 10. Optimum conditions for hardness removal efficiencies and boron removal efficiencies.

Optimum Experiment Conditions						
pH	S/L (g L^{-1})	Temperature (°C)	Hardness Removal RSM Model Prediction (%)	Hardness Removal Experimental Result (%)	Boron Removal RSM Model Prediction(%)	Boron Removal Experimental Result (%)
10	52.8	15	93.32–100.00	97.5	52.28–84.07	71.1

Table 11. The experimental and predicted hardness and boron removal efficiencies for different parameter levels selected within the studied range.

Selected Experiment Conditions						
pH	S/L (gL^{-1})	Temperature (°C)	Hardness Removal RSM Model Prediction (%)	Hardness Removal Experimental Result (%)	Boron Removal RSM Model Prediction(%)	Boron Removal Experimental Result (%)
6.5	42	17	96.96	96.68	20.95	20.01
8.5	55	22	98.68	98.85	64.64	63.22
9.5	35	32	95.38	95.02	3.5	3.29

Conclusions

In this study, the modeling and optimization of hardness and boron removal from boron mining wastewater using the ion exchange method were investigated in a batch system through RSM.

- Equations for calculating hardness and boron removal efficiencies have been obtained. Additionally, surface plots illustrating the impact of binary parameter interactions on removal efficiency have been generated. In ANOVA analyses, it was observed that the effective parameter for hardness removal efficiency is the S/L ratio, while pH and temperature were found to be ineffective. In the case of boron removal, it has been determined that the effective parameters are, in sequence, S/L ratio, temperature, and pH.
- Under the conditions where maximum hardness removal efficiency was targeted (pH 8.5, S/L 45.5 g L^{-1}, 25°C), experiments achieved a 98.6% removal efficiency.
- Under the conditions where maximum boron removal efficiency was targeted (pH 9.2, S/L 60 g L^{-1}, 22°C), experiments achieved a 73.2% removal efficiency.
- Under conditions aimed at achieving simultaneous maximum hardness and boron removal (pH 10, S/L 52.8 g L^{-1}, 15°C), a hardness removal efficiency of 97.5% and a boron removal efficiency of 71.1% were achieved.

The study demonstrates the effectiveness of TULSION MB-115 resin in treating wastewater obtained from the boron mining industry, which contains high concentrations of boron and hardness, and achieving high removal efficiencies. Another advantage of the resin is its usability over a wide pH range (0–14). The proximity of the optimal conditions obtained from RSM to the natural conditions of the wastewater will provide advantages in the application of ion exchange treatment processes. It is observed that this resin is effective in boron removal and can also be preferred as a pretreatment method before treatment methods such as membrane or reverse osmosis.

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All authors of the present paper contributed to the study conception, design, and analysis. All authors read and approved the final manuscript.

Author contributions

CRediT: **Elif Özmetin:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – review & editing; **Elif Calgan:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft; **Yeliz Süzen:** Conceptualization, Funding acquisition, Investigation, Methodology, Software, Validation, Writing – original draft.

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No potential conflict of interest was reported by the author(s).

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Data availability statement

Data and materials are available upon reasonable request.

Consent for publication

Authors of the present paper agree to transfer the article copyright to the Publisher.

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