



Boron removal from industrial wastewaters by means of optimized sequential chemical precipitation and coagulation processes

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ABSTRACT

In this work, the removal results of the application of sequential chemical precipitation (CP) and coagulation (CC) over boron-containing industrial wastewater were presented. Effect of amount of $\text{Ca}(\text{OH})_2/\text{B}_2\text{O}_3$ concentration ratio, initial pH and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ concentration on B_2O_3 removal was investigated using Box–Behnken based custom experimental design. Response surface methodology (RSM) was used to evaluate the effect of process variables and their interactions on boron removal. Results show that selected operational parameters and obtained regression model were statistically significant. The coefficient of determination was found as 0.9846, indicating that the model has a good fit with experimental data. Water has been obtained in a dischargeable quality according to Water Pollution Control Regulation of Turkish Authorities with 95% B_2O_3 removal from an initial concentration of 13.23 g/L under optimum operating conditions of 2.01 g $\text{Ca}(\text{OH})_2/1$ g/L B_2O_3 ratio, pH 8.12 and 13.5 g/L $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

Keywords: Wastewater treatment; Boron removal; Precipitation; Coagulation; Optimization

1. Introduction

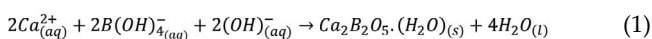
Boron is a non-metallic element widely distributed throughout the world [1]. Turkey is estimated to have 72% of the world's boron reserves [2]. Average boron ore production is 1.3 billion tons per year [3,4]. The boron contamination from anthropogenic sources in the environment is becoming a serious problem [5–7]. When discharged to soil, boron containing wastes are dissolved by rain water, and boron compounds pass into ground where they form some complexes with heavy metals [8,9]. Thus, the potential toxicity of heavy metals increases and when complexes enter the groundwater they cause serious health and environmental problems [2,5,10]. Boron is an indispensable element for plants in narrow concentration limits and therefore needs to be present

at a concentration range of 0.5–4 mg/L in irrigation water for some metabolic activities [11]. Low boron uptake (<0.5 mg/L) in plants may result in reduced growth, loss of yield and even death due to the severity of the deficiency [5]. If the boron concentration in the irrigation water is only slightly higher than the minimum value, plant growth is adversely affected and causes signs of boron toxicity [5]. The tendency of boron to accumulate in vegetable tissues constitutes a potential danger to the health of consumers and chronic exposure at low doses leads to reduced survival, and developmental and reproductive toxicity in animals [5,6,12]. The amount of boron in various water sources must be controlled in order to avoid possible adverse effects that the presence of boron can give to the environment, and therefore boron remediation

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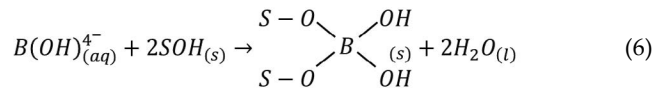
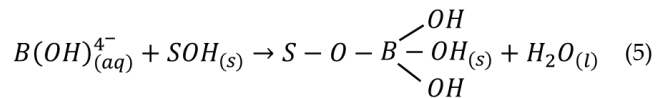
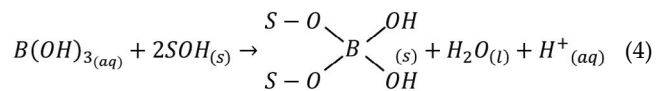
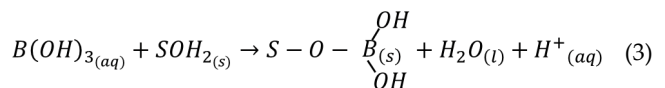
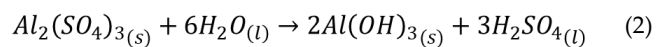
from water has become an important research topic nowadays [13]. Various regulations and communiqués have been prepared and published for the control of water pollution in order to protect underground and surface water resources. According to Water Pollution Control Regulation of Turkish Authorities, boron content of fresh water springs should be less than 1 mg/L, and the amount of boron in the water to be discharged to the sea should not exceed 500 ppm [13]. Various treatment processes have been developed for boron removal from water, including adsorption [14], ion exchange [15], reverse osmosis [16], electrodialysis [17], electrodeionization [18], electrocoagulation (EC) [4,19], sorption-membrane filtration [20] and precipitation [2,13]. Conventional biological treatment methods cannot be used for removal of boron from wastewater since boron compounds have antiseptic properties [2,4,20]. In the ion exchange studies, boron removal efficiencies were obtained in the range of 90%–98%, but in this method, regeneration cost is generally an important problem [21]. The removal efficiency was found to be 99% in the studies conducted with reverse osmosis at alkali pH [16]. In reverse osmosis method, the stability of the membrane, its cost, and clogging of the membrane with CaCO_3 are the main drawbacks of the method [13]. In addition, a more polluted waste stream is generated in this method, which must be disposed. On the other hand, chemical or electrochemical precipitation methods are characterized by simplicity, easy installation, wide application area, and the availability of boron-containing solid waste as a raw material in cement and ceramics industries [9,11,13]. Successful removal results of boron (>90%) have been reported by means of ion exchange, reverse osmosis, electrodeionization, electrocoagulation, sorption-membrane filtration, and precipitation [2] with the use of synthetic low amount of boron containing ($\leq 1,000$ ppm B content) solutions. Since the amount of boron in the wastewater generated by boron industry is very high, these treatment methods do not find a wide area of use for themselves.

Few studies on boron removal from industrial wastewaters with high B concentration ($\geq 1,000$ ppm B content) have been reported in the literature. Yilmaz et al. [2] reported 96% B removal by means of CP with high amount of $\text{Ca}(\text{OH})_2$ use at elevated temperatures. Bilen et al. [13] removed 93% of B from a highly saline industrial wastewater by using excessive amount of $\text{Ca}(\text{OH})_2$ at elevated temperatures with 3 h long treatment time. Use of $\text{Ca}(\text{OH})_2$ for CP increases pH value of the wastewater above 11 and boron found in the wastewater is in the structure of monoborate $\text{B}(\text{OH})_4^-$. Boron removal mechanism by means of CP was proposed by Bilen et al. [13] and is given below in Eq. (1). CP method requires a high amount of energy and chemicals to obtain water at dischargeable quality.



Coagulation is generally carried out with inorganic metal salts, for example, aluminum and iron sulphates and chlorides. Depending on coagulant dosage and pH, coagulation mechanism is generally explained in terms of two steps: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate [9]. The dissolved metal ions, at an appropriate pH, can form wide ranges of

coagulated species and metal hydroxides that destabilize and aggregate suspended particles or precipitate and adsorb dissolved contaminants [22]. When pH is between 4 and 9, the Al^{3+} and OH^- ions react to form various monomeric species such as $\text{Al}(\text{OH})^{+2}$, $\text{Al}(\text{OH})_2^{+}$, and polymeric species such as $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$ that finally transform into insoluble amorphous $\text{Al}(\text{OH})_{3(s)}$ through complex precipitation kinetics [23]. When pH is higher than 10, the monomeric $\text{Al}(\text{OH})_4^-$ anion concentration increases [24]. Yilmaz et al. [9] compared CC and EC for boron removal and achieved 24% and 94% removal efficiency, respectively, with the use of excessive amount of coagulants. Sayiner et al. [3] achieved 90% B removal by means of EC at high current density. Boron removal mechanism by means of CC was proposed by Su and Suarez [25] and given below in Eqs. (2)–(6).



Here, S symbolizes the metal cation (Al). A simple strength and weakness analysis of CP and CC processes are illustrated in Fig. 1.

Aim of this work was to reduce the consumption of chemicals and energy via RSM optimization for efficient boron removal from boron-containing industrial wastewater with the unique application of a Box-Behnken based custom experimental design for sequential CP and CC in order to obtain an effluent with a dischargeable quality according to Water Pollution Control Regulation of Turkish Authorities.

2. Materials and methods

2.1. Wastewater characteristics and analytical method

The wastewater samples used in the study were obtained from a boric acid production plant located in Turkey. Samples were stored in containers and kept at room temperature. The characterization of boron-containing industrial wastewater is given in Table 1.

B_2O_3 analyses of the liquid samples collected in the experiments were performed potentiometrically by mannitol, which forms a complex compound with boric acid according to ASTM D-3082-79 [5,12,13,26]. For this purpose, samples were filtered with 0.45 μm pore sized PVDF filter, then the solution pH was adjusted to 7.60 with 0.5 N HCl and 0.5 N KOH. Afterwards, 5 g of mannitol was added to

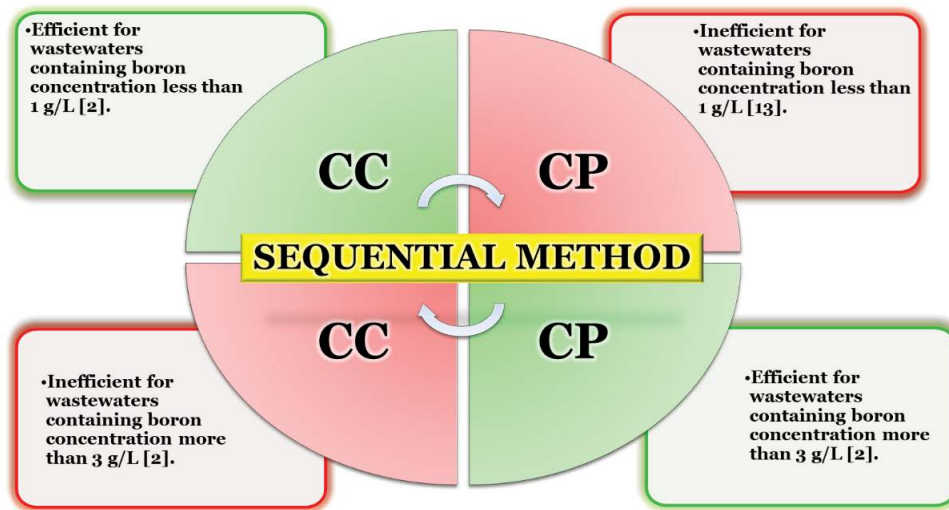


Fig. 1. Strength and weakness analysis on sequential use of chemical coagulation and chemical precipitation methods.

Table 1
Characterization of boron-containing industrial wastewater

Parameter	Unit	Value
pH	–	9.46
Electrical conductivity	mS/cm	12.55
B ₂ O ₃	g/L	13.23
Na ⁺	mg/L	5,320
Ca ²⁺	mg/L	2.43
SO ₄ ²⁻	mg/L	691
CO ₃ ²⁻	mg/L	331.84
Al ³⁺	mg/L	7.16
Mg ²⁺	mg/L	43.66

the solution and the solution was titrated with 0.5 N KOH until pH reaches 7.60. The amount of B₂O₃ was calculated from the consumption of KOH. Equivalence of 1 mL 0.5 N KOH consumption is 17.41 mg B₂O₃ [5,13]. B content of the samples were calculated by multiplying the values obtained from the analysis by 21.622/69.618 (2 moles of elemental mass B/1 mole of B₂O₃ mass) [5,13].

A pH meter, a conductivity meter and a thermocouple (Hanna HI9829, UK) were immersed into the wastewater for on-line pH, conductivity and temperature monitoring during treatment.

2.2. Experimental design

Box–Behnken design is often used in water and wastewater treatment studies since it contains fewer experiments compared with the full factorial design, and does not include any experimental points at the vertices of the cubic region, which is advantageous if the experiments at these points are expensive or not applicable [27]. In this study, Box–Behnken based custom experimental design was applied to investigate the main variables affecting sequential CP and CC, as well as their interactions and 16 experiments were performed. MINITAB

Table 2
Coded and real values of independent variables for sequential CP and CC treatment of boron-containing industrial wastewater

Level	Factors		
	x ₁	x ₂	x ₃
	Ca(OH) ₂ /B ₂ O ₃ (g/g L ⁻¹)	pH ₀	Al ₂ (SO ₄) ₃ ·18H ₂ O concentration (g/L)
–1	1	5	4.14
0	1.75	7	7.25
+1	2.5	9	10.36

17 software was employed for experimental design, modeling and data analysis. Amount of Ca(OH)₂/B₂O₃ concentration ratio, initial pH (pH₀) and Al₂(SO₄)₃·18H₂O concentration were chosen as factors whereas B₂O₃ removal was considered as response. In order to test the excess Al₂(SO₄)₃·18H₂O concentration effect on B₂O₃ removal, a custom experiment (16th experiment) was added to the design matrix. The 16th experiment was inspired by the +α experiment of the central composite design when determining the conditions. Each of the factors was coded at three levels (–1, 0 +1) and coded values along with the real values are given in Table 2 where the maximum and minimum values of parameters were chosen by considering boron-containing industrial wastewater characteristics and previously published studies by Bilen et al. [13] and Yılmaz et al. [2]. In this study, the pH₀ was used for all pH adjustment steps of the experimental procedure. Thus, initial pH adjustment of wastewater before CP, initial and final pH adjustments of CC were made to the same value specified in the experimental design matrix.

Experimental results were fitted to quadratic response surface models that are generally shown as in Eq. (7) [28].

$$y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \epsilon \quad (7)$$

Predictive ability of the model was verified by evaluating coefficient of determination (R^2) value between experimental and predicted results. For a model with good prediction efficiency, the value of R^2 should be close to 1.0 [27]. Since coefficient of determination increases with the increase in the number of terms in the model, R^2 was compared with R^2_{adjusted} and $R^2_{\text{predicted}}$.

The significance of each factor and interactions between each other were checked with the help of Fisher test. To indicate if the F value is large enough to imply the statistical significance, p -value related to the F value was used [28]. Visualization of the regression model was obtained by response surface plots which were constructed as a function of two independent variables varying within the experimental range and the other variables were kept constant at central level. Response surfaces were analyzed to obtain the maximum B_2O_3 removal response and the corresponding optimum conditions.

2.3. Experimental setup and procedure

Experiments were carried out in a batch 1-L glass reactor. In each run, 1 L of boron-containing industrial wastewater was fed to the reactor. Uniform concentration dispersion in the reactor was maintained by a magnetic stirrer (MTOPS MS300HS) operating at a prespecified speed.

All experiments were carried out at room temperature. In each experimental run, initial pH value of the wastewater was adjusted to the value specified in the experimental design matrix (pH_0) using 10% H_2SO_4 solution (w/w). In order to perform CP, specified amount of $Ca(OH)_2$ was added to the reactor and the reactor content was stirred at 1,200 rpm for 1 h. At the end of the run, sedimentation was performed for 1 h. Afterwards, supernatant was vacuum filtered with 2 μm blue ribbon ashless filter paper. 500 mL of filtrate was fed to CC reactor and secondary pH adjustment was performed using 10% H_2SO_4 solution to the value specified in the experimental design matrix (pH_0). Then, specified amount of $Al_2(SO_4)_3 \cdot 18H_2O$ was added to the reactor and final pH adjustment was performed with 1 M $Ca(OH)_2$ to the value specified in the experimental design matrix (pH_0). Reactor content was stirred vigorously at 1,200 rpm for 30 min. 5 mL of a commercial anionic polyelectrolyte solution at 1 ppm concentration (Flochem 3016, Turkey) was added to the reactor and vigorous stirring was performed for another 10 min. Stirring speed is then reduced to 200 rpm for a further 20 min for flocculation. At the end of CC, sedimentation was performed for 1 h. Samples were taken from supernatant for analyses. Experimental procedure of sequential CP and CC is presented in Fig. 2.

3. Results and discussion

Experimental design matrix showing combinations of three independent variables at various levels along with obtained and predicted responses are represented in Table 3. Experimental results were fitted to a statistically significant quadratic model to indicate the main and interaction effects of the factors on response. The effect of each variable on the predicted response was visualized on the basis of the model equation by response surface plots.

Regression model that describes the variations in B_2O_3 removal with operational parameters in terms of uncoded factors was developed and shown in Eq. (8). Multiple regression analysis was used to estimate the coefficients of the model.

$$B_2O_{3, \text{removed}} (\%) = 11.8 + 56.66x_1 + 8.34x_2 - 4.79x_3 - 9.69x_1^2 - 0.563x_2^2 - 2.067x_1x_2 + 0.783x_2x_3 \quad (8)$$

B_2O_3 removal model was statistically analyzed by applying Fisher test to verify the significance of the model and its terms individually. F value of the model and factors should be higher than that of the F distribution table value provided that the best fit of the experimental data with the model is desired [27,28]. Analysis of variance (ANOVA) results are given in Table 4. According to the results, F value of 48.50 revealed the statistical significance of B_2O_3 removal model compared with tabulated F value ($F_{0.05(7,9)} = 3.29$). The large F -values showed that the developed regression model can explain most of the variation in the output. The p -values of reduced quadratic model and terms are <0.001 which clearly confirm good fit of experimental data. If p -values are below 0.05 at 95% confidence level, then the model is significant at 95% confidence interval [28]. Statistically insignificant parameters were omitted from the model. ANOVA results showed that x_1 , x_2 , x_3 , x_1^2 , x_2^2 , x_1x_2 and x_2x_3 were significant terms for B_2O_3 removal of boron-containing industrial wastewater treated by sequential CP and CC methods.

R^2 was found as 0.9742 indicating that experimental results are in good fit with predicted data and only 2.58% of the total variation could not be explained by the developed model [29]. R^2 value should be compared with R^2_{adjusted} which reflects the number of factors in the experiment. When R^2 and R^2_{adjusted} values are close, there is a good chance that non-significant terms have not been included in the model [27,28]. R^2_{adjusted} value was found very close to R^2 , which is another good indicator for the statistical significance of the terms included in the model. $R^2_{\text{predicted}}$ which describes the prediction capability of the model for new responses, should not have difference of more than 0.2 with R^2 [27]. The difference between R^2 and $R^2_{\text{predicted}}$ value was found small enough to maintain predictive capability of the model. Comparison of actual and predicted B_2O_3 removal values was visualized in Fig. 3.

Fig. 4 shows the normal probability plots of the studentized residuals for B_2O_3 removal efficiency. A normal probability plot indicates if the residuals follow a normal distribution, in which case the points will follow a straight line [30]. Since some scattering is expected even with the normal data, as shown in Fig. 4, it was assumed that the data are normally distributed.

Fig. 5 shows the distribution of residuals for B_2O_3 removal efficiency. It is expected that the residuals occur near the center line in a random manner with no clustering or trending [31]. The fluctuations of the residuals are relatively small and regular, which is a clear indication that RSM model shows small deviation.

In the present study, effect of three parameters, $Ca(OH)_2/B_2O_3$ concentration ratio, pH_0 and $Al_2(SO_4)_3 \cdot 18H_2O$ was studied using RSM. Response surface plots of B_2O_3 removal were shown in Fig. 6. It is essential to determine the optimum

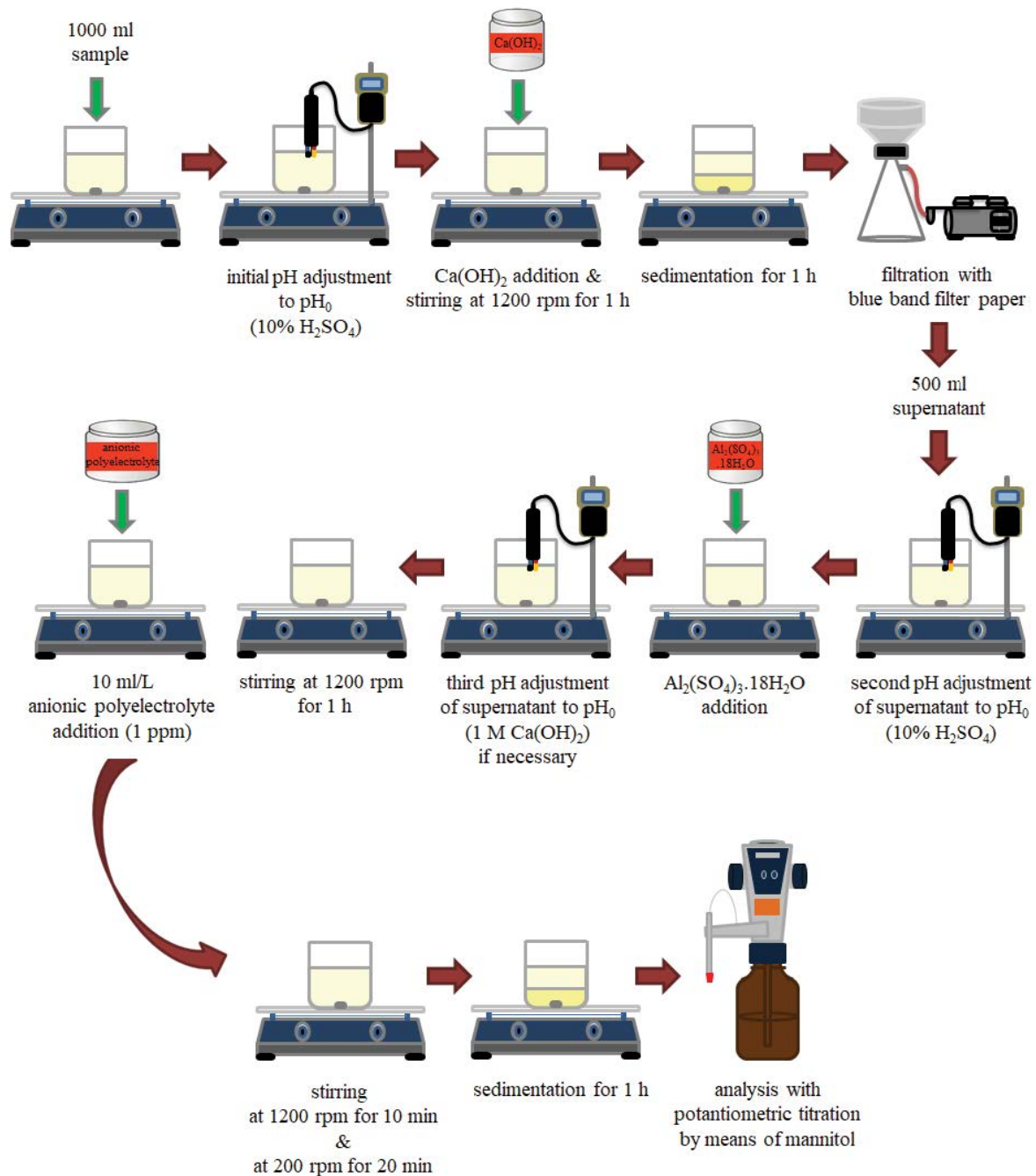


Fig. 2. Experimental procedure of sequential CP and CC.

$\text{Ca}(\text{OH})_2/\text{B}_2\text{O}_3$ ratio in order to avoid an excessive consumption of $\text{Ca}(\text{OH})_2$, which makes the process more expensive without achieving a significant increase in the removal yield. Also, it determines the precipitation efficiency. From Fig. 6 it can be seen that highest boron removal was obtained at higher $\text{Ca}(\text{OH})_2$ doses. It was also observed that the $\text{Ca}(\text{OH})_2/\text{B}_2\text{O}_3$ ratio, beyond which the increase in removal yield was not significant, was about 2 [32]. With the addition of $\text{Ca}(\text{OH})_2$ the final pH value of the CP process exceeds 11 [2,13]. Boric acid dissolves in water to form various borate ions. Their compositions change as a function of solution

pH and begins to dissociate into monoborate ions at $\text{pH} > 10$ [33]. At this point, there are two main mechanisms for boron removal; $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ evolution and adsorption [13]. Trend of the curve on $\text{Ca}(\text{OH})_2/\text{B}_2\text{O}_3$ concentration ratio implies that redissolution of $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ did not occur during CP process [34].

Optimizing the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ dosage is important because it determines not only the adsorption capacity for boron removal but also the cost of the treatment [29]. Hydroxides form the nuclei of the colloidal particles, and the adsorption layer of cations and anions is being formed

Table 3
Experimental design matrix and responses for sequential CP and CC treatment of boron-containing industrial wastewater

Run	Factors			Response	
	x_1	x_2	x_3	y_1	
	Ca(OH) ₂ /B ₂ O ₃ (g/g L ⁻¹)	pH ₀	Al ₂ (SO ₄) ₃ ·18H ₂ O concentration (g/L)	B ₂ O ₃ removal (%)	
				Experimental	Predicted
1	1 (-1)	7 (0)	4.14 (-1)	75.5668	76.4680
2	2.5 (1)	9 (1)	7.25 (0)	85.0394	83.9250
3	2.5 (1)	5 (-1)	7.25 (0)	89.9029	91.4170
4	1.75 (0)	5 (-1)	4.14 (-1)	89.8929	88.9400
5	1 (-1)	5 (-1)	7.25 (0)	71.7503	72.8300
6	1.75 (0)	7 (0)	7.25 (0)	89.4957	89.1830
7	1.75 (0)	5 (-1)	10.36 (1)	87.8517	86.2110
8	1 (-1)	9 (1)	7.25 (0)	79.2908	77.7420
9	1.75 (0)	7 (0)	7.25 (0)	89.6684	89.1830
10	1.75 (0)	9 (1)	10.36 (1)	88.8018	89.7900
11	1.75 (0)	9 (1)	4.14 (-1)	81.1066	82.7820
12	2.5 (1)	7 (0)	10.36 (1)	91.4269	90.9920
13	1.75 (0)	7 (0)	7.25 (0)	89.3229	89.1830
14	2.5 (1)	7 (0)	4.14 (-1)	88.8175	88.8530
15	1 (-1)	7 (0)	10.36 (1)	79.0385	78.6070
16	1.75 (0)	7 (0)	18.64 (1.7)	92.6667	93.1010

Table 4
ANOVA results of B₂O₃ removal for sequential CP and CC treatment of boron-containing industrial wastewater

Source	df	SS _{adj}	MS _{adj}	F	p	Remark
Model	7	618.511	88.359	48.50	0.000	S+
x_1	1	306.780	306.780	168.38	0.000	S+
x_2	1	11.859	11.859	6.51	0.031	S+
x_3	1	30.156	30.156	16.55	0.003	S+
x_1^2	1	114.621	114.621	62.91	0.000	S+
x_2^2	1	19.550	19.550	10.73	0.010	S+
x_1x_2	1	38.465	38.465	21.11	0.001	S+
x_2x_3	1	23.699	23.699	13.01	0.006	S+
Error	9	16.338	1.822			
Total	16	634.908				
R^2	0.9742	$R^2_{adjusted}$	0.9541	$R^2_{predicted}$	0.8016	

around the nuclei. So, the nucleus and adsorption layer form the positively charged colloidal granule. Diffusion layer then occurs around the granule and the particle becomes neutral. The metal hydroxides that are formed in the CC process have a high adsorption capacity. Coagulated particles attract and absorb micro-colloidal particles and ions from the wastewater. Reports in the literature indicate that boron species in water forms insoluble species with aluminium, and thus it is possible that isomorphic precipitation could provide a route for the transfer of soluble boron to the solid phase [33]. As can be seen from Fig. 6, higher boron adsorption with increase in Al₂(SO₄)₃·18H₂O dosage could be due to the increased availability of sorbent surface and sorption sites

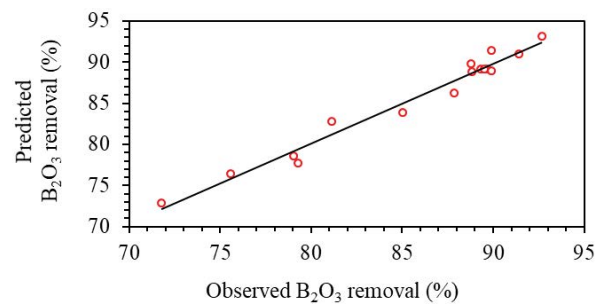


Fig. 3. Observed vs. predicted plot of B₂O₃ removal.

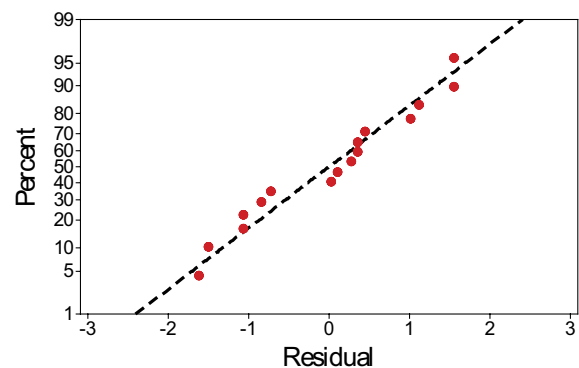


Fig. 4. Normal probability plot of B₂O₃ removal.

[29]. Although response surface plot indicated a raise in B₂O₃ removal at elevated Al₂(SO₄)₃·18H₂O concentration, result of run 16 showed that increasing Al₂(SO₄)₃·18H₂O concentration from 7.25 to 18.64 g/L yielded only 3% increase in B₂O₃

removal in comparison with run 9, which is a clear indication that B saturation on $\text{Al}(\text{OH})_3$ had not been attained [35].

pH of the process is among the most important parameters which affect the precipitation and adsorption efficiencies [29]. In Fig. 6 two areas can be clearly distinguished for CC process: around pH 8, a maximum in the curve's development appears and for a pH > 9.0 the yield decreases. The concentration of insoluble $\text{Al}(\text{OH})_3$ in solution is low for pH above 9 [36]. This encourages low boron removal in the form of borate, since the active surface for adsorption decreases [33]. According to this data and taking the previous considerations into account, it can be suggested that a complexation reaction of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ species occur with the OH-groups on the reagent surface [32]. At low pH values, the predominating species is orthoboric acid and, owing to its low electrical activity, the adsorbed quantity was lesser. This species presents a low affinity. As expected, when the pH was

increased, to a certain point, the adsorption process was more effective. It reached a maximum, the borate ion concentration rose quickly and the adsorbed boron concentration increased to a maximum of pH 8. Later, the pH increase raised the concentration of OH^- in relation to the concentration of borate ions and, owing to the competitiveness of these two species for adsorption sites, the adsorbed amount of boron decreased [32]. For CP process, the deterioration of the removal rate of boron from wastewater at lower pH values could be explained by the formation of CaSO_4 . This means that the probability of collision between boron and $\text{Ca}(\text{OH})_2$ decreased by the consumption of $\text{Ca}(\text{OH})_2$ before the treatment [34]. During process, second and third pH adjustments were essential for high CC removal yield since use of $\text{Ca}(\text{OH})_2$ for CP increased the wastewater pH drastically which may lead to formation of soluble $\text{Al}(\text{OH})_4^-$ anion during CC [23].

In order to achieve the highest treatment performance, the desired goal was maximization of B_2O_3 removal. According to single-objective optimization through desirability function, optimum values were obtained as 2.01 g $\text{Ca}(\text{OH})_2$ /1 g/L B_2O_3 ratio, pH 8.12 and 13.5 g/L $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. Optimized sequential CP and CC treatment study yielded 94.88% B_2O_3 removal. The results imply that maximum removal could be accomplished under operating conditions near center points, which showed that levels of factors for experimental design were well chosen. The validity of the predicted response value at optimum operating conditions was controlled by performing an experiment. Under optimized conditions, deviation between model estimation and experimentally observed value of B_2O_3 removal was found as 0.87%. It can be noted that estimated result at optimized conditions for sequential CP and CC treatment of boron-containing wastewater was successfully confirmed by experimental observation.

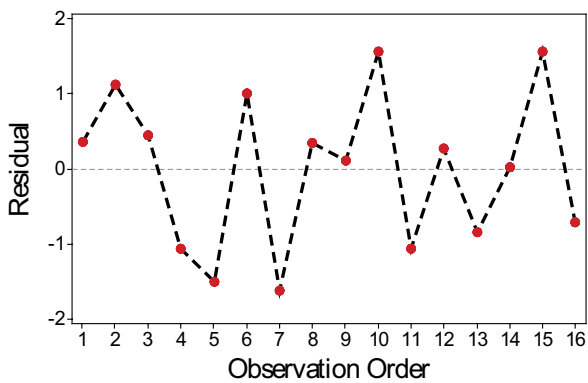


Fig. 5. Distribution of residuals of B_2O_3 removal.

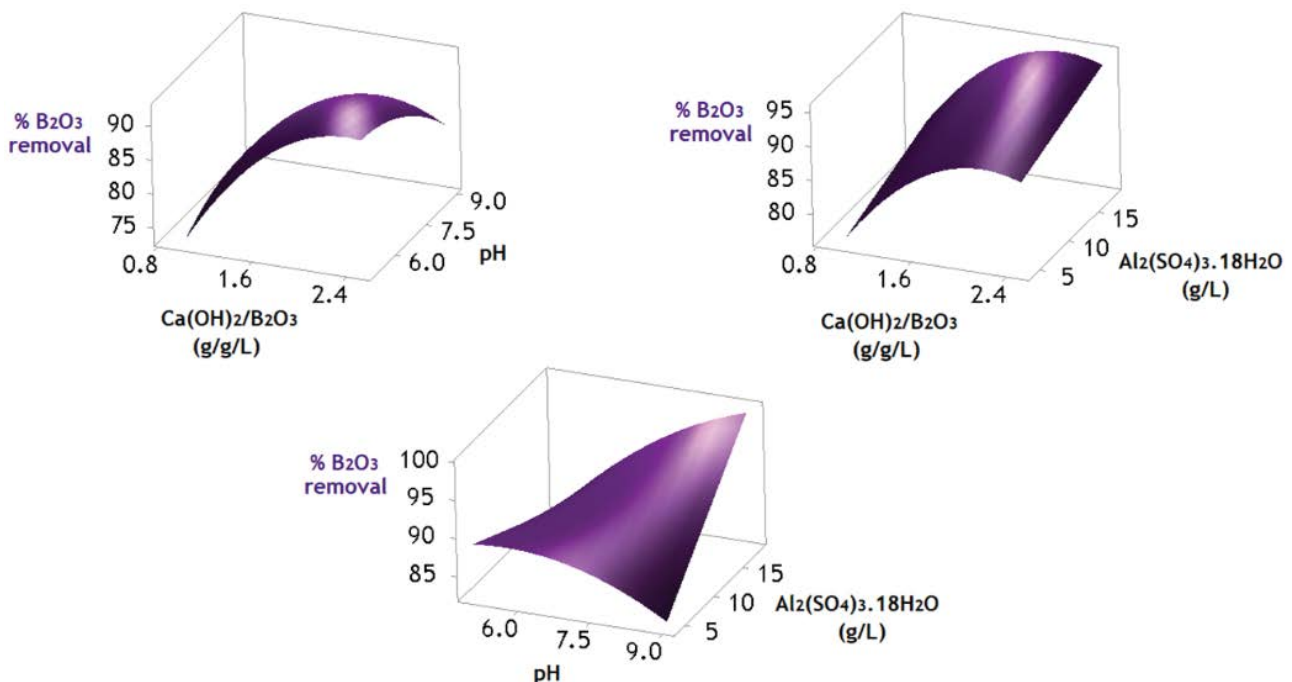


Fig. 6. Effect of variables on B_2O_3 removal for sequential CP and CC treatment of boron-containing industrial wastewater.

Table 5
Comparison of various treatment methods for boron containing wastewater

Reference	Concentration (ppm B)	Method	Parameters	Optimum conditions	B removal (%)	Final Concentration (ppm B)
[9]	1,000	CC	Coagulant dosage (g AlCl ₃ /L)	36.79	24%	760
			Initial pH	8		
		EC	Temperature (°C)	80	94%	60
			Current intensity (A)	5		
[3]	2,650	EC	Electrolysis time (h)	3	90%	265
			Initial pH	8		
			Temperature (°C)	40		
			Current density (mA/cm ²)	30		
[2]	2,500	CP	Electrode material	Al	96%	100
			Electrolysis time (min)	60		
			Initial pH	1		
			Stirring speed (rpm)	150		
[13]	7,006	CP	Ca(OH) ₂ concentration (g/L)	20	93%	490
			Treatment time (min)	25		
			Temperature (°C)	80		
			Initial pH	5.74		
Present study	4,109	CP + CC	Ca(OH) ₂ /B ₂ O ₃ (g/g/L)	5	95%	210.37
			Treatment time (min)	180		
			Temperature (°C)	76.5		
			pH	8.12		
			Ca(OH) ₂ /B ₂ O ₃ (g/g/L)	2.01		
			Coagulant dosage (g Al ₂ (SO ₄) ₃ ·18H ₂ O/L)	13.5		

4. Conclusion

This research noted unique and successful application of optimized sequential CP and CC techniques to the treatment of boron-containing industrial wastewater using Ca(OH)₂ for CP and Al₂(SO₄)₃·18H₂O for CC, respectively. The efficiency of the sequential method was assessed by B₂O₃ removal. Results showed that under 2.01 g Ca(OH)₂/1 g L⁻¹ B₂O₃ ratio, pH 8.12 and 13.5 g/L Al₂(SO₄)₃·18H₂O and room temperature conditions, 94.88% B₂O₃ removal was achieved. Settled sludge volume and final boron content of the treated wastewater were obtained as 200.1 mL/L and 201.37 ppm, respectively. Boron content of treated wastewater was below the discharge limit 500 ppm of Water Pollution Control Regulation of Turkish Authorities. CP has the ability to remove a large amount of boron from highly saline wastewater to a certain extent above discharge limit in the range of 600–1,000 ppm B depending on Ca(OH)₂ amount added. CC is able to reduce boron concentration below discharge limit from less boron containing wastewaters (≤1,000 ppm B content). Optimized sequential application combined the best abilities of CP and CC processes with less consumption of chemicals and energy compared with previously published studies.

Various treatment results of boron-containing wastewaters obtained from different sources in the previously published studies were compared with the present study in Table 5. Yilmaz et al. [9] reported that boron removal of CC was 24% under 36.73 g/L AlCl₃ coagulant concentration,

80°C temperature and pH 8 conditions, whereas EC treatment for 5 h yielded 94% boron removal under 5 A current intensity, 80°C temperature and pH 8 conditions. Sayiner et al. [3] obtained 90% boron removal using EC treatment under 50 mA/cm² current density and 1 h electrolysis time conditions. CP of boron containing wastewater was performed by Yilmaz et al. [2] and 96% boron removal with the Ca(OH)₂ consumption of 20 g/L under extreme conditions of 80°C temperature and pH 1 was obtained. Bilen et al. [13] reported 93% boron removal efficiency for CP with an excessive 5 g Ca(OH)₂/1 g L⁻¹ B₂O₃ ratio, under 76.5°C and pH 5.74 conditions.

It was observed that the operational ranges were well suited with the ones in literature. Ca(OH)₂ consumption of 2.01 g per 1 g L⁻¹ B₂O₃ and 13.5 g Al₂(SO₄)₃·18H₂O per 1 L wastewater under pH 8.12 and room temperature were considered to be highly competitive when compared with those reported in the literature. To conclude, an effluent with a dischargeable quality according to Water Pollution Control Regulation of Turkish Authorities was obtained with less consumption of chemicals and energy by the successful application of optimized sequential CP and CC techniques.

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Symbols

ANOVA	— Analysis of variance
β_0	— Constant coefficient
β_i	— Coefficient of linear effect
β_{ij}	— Coefficient of quadratic effect
β_{ij}	— Coefficient of interaction effect
CC	— Chemical coagulation
CP	— Chemical precipitation
df	— Degree of freedom
k	— Number of independent variables
MS_{adj}	— Adjusted mean squares
pH_0	— Initial pH
RSM	— Response surface methodology
R^2	— Coefficient of determination
$R^2_{adjusted}$	— Adjusted coefficient of determination
$R^2_{predicted}$	— Predicted coefficient of determination
S	— Metal cations
S+	— Significant
SS_{adj}	— Adjusted sum of squares
x	— Factor
y	— Response

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