Boron removal by coagulation using Al(OH)₃ and factorial optimization of data for boron mine wastewater

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Abstract

In this study, boron removal from synthetic solutions and boron mine wastewater by coagulation method using in-situ formed Al(OH)₃ from AlCl₃ salt was investigated. The experimental parameter for synthetic solution was solution pH. The optimum condition for synthetic boron solutions was determined as pH (8). The ideal pH value obtained from the synthetic solutions was applied to the boron mine wastewater with concentration of 373.19 mg L^{-1} by $2^1 \times 2^1$ full factorial experimental design. The parameters in the design were dosage of aluminium chloride (5, 10 g) and dilution factor (1,10 fold). The aluminium hydroxide provided maximum 100% removal from mine wastewater at optimum conditions. Also, the data obtained were analyzed by means of Pareto chart and surface plot. P values for all the parameters were found as above 95% confidence limit value (p<0.05). These means that all the parameters are statistically important at 95% confidence level in the developed regression model.

Keywords: *Boron removal, mine wastewater, factorial design, aluminium hydroxide.*

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Koagülasyonla Al(OH)$_3$ kullanarak bor giderimi ve bor madeni atık suyu için verilerin faktoriyel optimizasyonu

Öz

Bu çalışmada, sentetik çözeltilerden ve bor madeni atık suyundan AlCl$_3$ ile yerinde üretilmiş Al(OH)$_3$ kullanarak bor giderimi araştırılmıştır. Sentetik çözeltiler için deneysel parametre çözelti pH idi. Optimum koşul sentetik çözeltiler için pH (8) olarak belirlenmiştir. Sentetik çözeltilerden elde edilmiş optimum pH değeri 373.19 mg/L konsantrasyona sahip kolemanit madeni atık suyuna $2^1 \times 2^1$ faktöriyel deneysel tasarımla uygulanmıştır. Deneysel tasarımdaki parametreler dozaj (5-10 g) ve seyreltme idi (1-10 kat). Aluminyum hidroksit kolemanit madeni atıksuyundan %100 oranında giderim sağlamıştır. Bunun yanı sıra elde edilen parametreler Pareto kart ve yüzey grafikleri ile optimize edilmiştir. P değerleri bütün deneysel parametreler için % 95 lik güven seviyesinin üzerinde bulunmuştur (p<0.05). Bu sonuç istatistiksel olarak bütün parametrelerin geliştirilen regrasyon modelinde % 95 güven oranında önemli olduğunu göstermiştir.

Anahtar kelimeler: Bor giderimi, maden atıksuyu, faktöriyel tasarım, aluminyum hidroksit.

1. Introduction

The element boron (B), existing at top of the third group of the periodic table, has two stable isotopes with mass numbers of 10 (18.83%) and 11 (81.17%) [1]. Whereas boron does not exist as pure element in nature, it presents as metal borates such as colemanite ($Ca_2B_6O_{11}.5H_2O$), ulexide ($NaCaB_5O_9.8H_2O$), tincal ($Na_2O.2B_2O_3.10H_2O$), and etc [2]. Boron constitutes 0.001% of the earth crush [3]. In Turkey and USA, the big borate deposites formed by the reaction of metal cations with the boron erupted from volcano via volcanic ashes in the lake medium [4]. It has been estimated that more than half of the World's borate amount are located in Turkey. The colemanite ($Ca_2B_6O_{11}.5H_2O$) deposites found in Turkey are located in Bigadiç, Kırka, Mustafa Kemal Paşa and Emet regions [5]. The excavated colemanite ore in Bigadiç deposite is subjected to waiting in water and washing for removal of attached impurities such as soil and clays. During the waiting operation in water, the colemanite ore is dissolved and the wastewater with concentration of about 382 mg L^{-1} boron is produced [6]. These wastewaters produced in the Bigadiç colemanite mine are stored in soil dams threatening underground water quality [6]. Therefore, the treatment of these wastewaters is necessary. On the other hand, the colemanite mine wastewaters are not suitable for irrigation due to high boron content. Maximum irrigation water boron concentration for agricultural crops has been reported as only several milligrams in per liter [7]. Boron limit value for drinking water is proposed as 2.4 mg L^{-1} by the World Health Organization (WHO) [8].

The most common forms of boron in waters are boric acid and monoborate anion. Also, boron exists as polyborate anions in waters [9]. The molar fraction of the monoborate and polyborate anions such as $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{-2}$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ vary in aqueous solutions based on concentration, pH, and temperature [9,10]. Molar fraction of polyborates increases with the temperature decrease and

concentration increase. In waters, boric acid dissociates reversibly to the monoborate anion according to the following reaction [10].

$$B(OH)_{3(aq)} + H_2O \leftrightarrow B(OH_4)_{(aq)}^- + H_{(aq)}^+ \qquad (Ka = 6 \times 10^{-10}, \, pKa \, 9.22) \qquad (1)$$

Boron is a problematic pollutant due to the difficulty of removing it from the waters. Based on the removal contiditons such as pH, concentration, temperature and etc., coagulation process can enable to complete boron removal. The application of chemical coagulation to the wastewaters contains rapid and slow mixing steps. The coagulant, aluminium chloride, was used to produce aluminium hydroxide for complexation of the negatively charged monoborate, polyborate and neutral boric acid molecules in the wastewater phase. The formed flocs in the coagulation step were combined to enlarge the microflocs under flocculation and these enlarged flocs were settled at end of the reaction. In the literature, several studies intending the boron removal by coagulation method are available. Karakaş and coworkers studied the boron removal from solutions using polyaluminium chloride (PAC) and optimum pH value varied at range of 9-11 based on coagulant dose [11]. Wided and coworkers reported the boron removal from solutions with 5 mg L^{-1} concentration by using alum as coagulant, magnesium chloride as coagulation adjuvant and an anionic flocculent [12]. In the reported study, the removal efficiency increased at high alum dosages and was not affected significantly from the presence of magnesium chloride and anionic flocculent [12]. In another study, boron removal (50 mg L^{-1}) by alum in the presence and absence of turmeric extract was studied and it was reported that optimum parameters were 7 for pH, 18,367 mg L^{-1} for alum dosage and 82 mg L^{-1} for turmeric extract dosage [13]. In a study of Golder and coworkers, only optimum pH value for 160 mg L^{-1} boron concentration was reported and its value was 9 for alum and ferric chloride, respectively [14]. The literature survey has showed that there is no any study intending the boron removal by in situ formed aluminium hydroxide from aluminium chloride salt as a function of various experimental conditions and the optimization of boron removal from colemanite mine wastewater by this hydroxide. Among the optimization procedures, the taguchi, response surface and factorial experimental design approaches are the widely applied for statistical analysises of the experimental data. When compared the statistic methods, the factorial experimental design method requires less time and is cost-effective [6]. Therefore, for the present study, optimum parameter value in pH for boron removal from synthetic boron solutions were determined by the traditional one-factor-at-a-time experiments. Then, the obtained ideal condition were applied to colemanite mine wastewater for optimization of experimental parameters using the factorial experimental design method.

2. Material and method

2.1 Time experiments
To determine the effect of time on boron removal by the aluminium hydroxide produced from aluminium chloride in the solution phase, the experiments were carried out at pH 10, concentration 250 mg L^{-1}, temperature 22.5±2.7 ^{o}C, coagulant dosage 2.5 g. The boron solution was transferred to the jacketed reactor and heated to desire temperature by a temperature controlled water circulator and solid aluminium chloride was added. The temperature increase was two degree when the 2.5 g aluminium chloride was added. Then, pH of the solution was adjusted to pH 10. During the time experiments,

four times 40 mL solution was taken from the reactor to be settled during one hour in the four different beakers at 32.5, 62.5, 92.5 and 122.5 minutes time intervals and 4 mL clear solutions were taken from the upper side of the bakers. Boron content of the clear solutions was analyzed by titrimetric method [15]. The results of time experiments are given in Figure 1. Throughout the whole experiments the temperature of the pure water was 22.5±2.7 °C. The solution had 500 mL volume before pH adjustment.
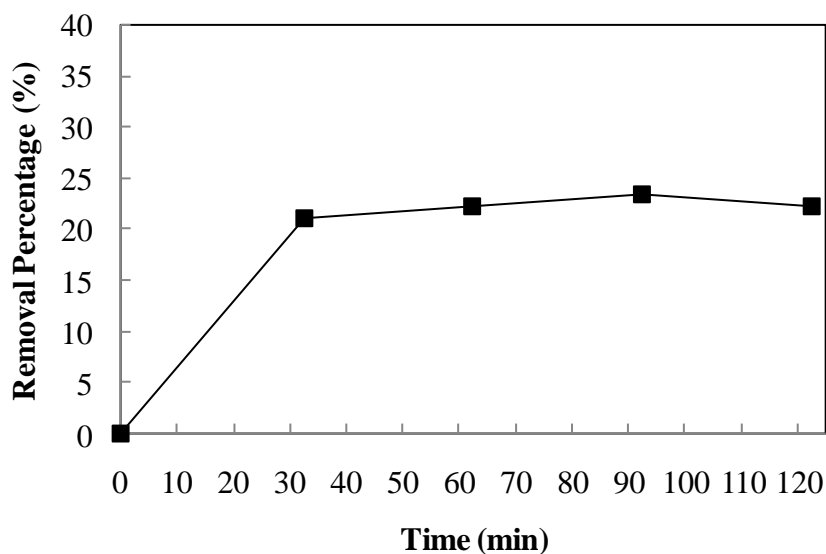

Figure 1. Time effect on removal (pH 10, concentration 250 mg L^{-1}, temperature 22.5±2.7 °C, coagulant dosage 2.5 g).

2.2 Coagulation experiments with synthetic solutions

The experimental setup is given in Figure 2. Boron removal experiments from synthetically prepared solutions were conducted using in situ formed aluminium hydroxide. Boron removal experiments were carried out by a Jar test device. For pH adjustment, 4 M KOH and 20% HCl (v/v) solutions were used. The dilution of the solutions by pH adjustment was assumed as a part of the removal and approximate base volumes for pH adjustment were in the range of (~14-15.5 mL for pH range of 6-9), respectively. Boron solutions were prepared by dissolving the appropriate amount of boric acid (H_3BO_3, Merck Product, assay 99.5-100.5%) in the pure water. On the contrary to the time experiments, the aluminium chloride was added to the boron solutions in the liquid form to obtain total 500 mL solution. Prepared boric acid solutions which were in the mixed form with aluminium chloride solutions were transferred to the jacketed glass reactors at 22.5±2.7 °C (four numbers). Thereafter, pH of the solutions was adjusted to the fixed value and metal hydroxides were formed. The assay of coagulant ($AlCl_3$, merck product) was ≥98%. In the Jar test, the solutions in which metal hydroxide was formed firstly mixed at speed of 120 rpm during 2.5-5 minutes and then mixed at speed of 30 rpm during 27.5-30 minutes. The flocs were allowed to settle at the end of the reaction during one hour and 10 mL solutions were taken for boron analysis from the clear portion of the solutions. Boron analyses were done by titrimetric method as follows: A 5 mL of boron solution was pipetted into 100 mL beaker and 50 mL pure water was added. Then solution pH was adjusted to 7.6 and mannitol was added to the solution up to solution pH became stable [15]. Thereafter the solution was titrated with 0.02 N KOH up to solution pH became again 7.6. 1 mL 0.02

N KOH solution is equal to 0.6964 mg B_2O_3 [10]. The KOH solution was standardized by 250 or 500 mg L^{-1} boron solution and standardization factors were calculated. The standardization factors were in the range of 0.837-0.98. The solutions had 500 mL before pH adjustment. Boron removal percentage was calculated by the following equation.

$$\eta(\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (2)$$

η is the boron removal percentage (%). C_0 is initial boron concentration (mg L^{-1}), C is the boron concentration at the end of the reaction (mg L^{-1}).
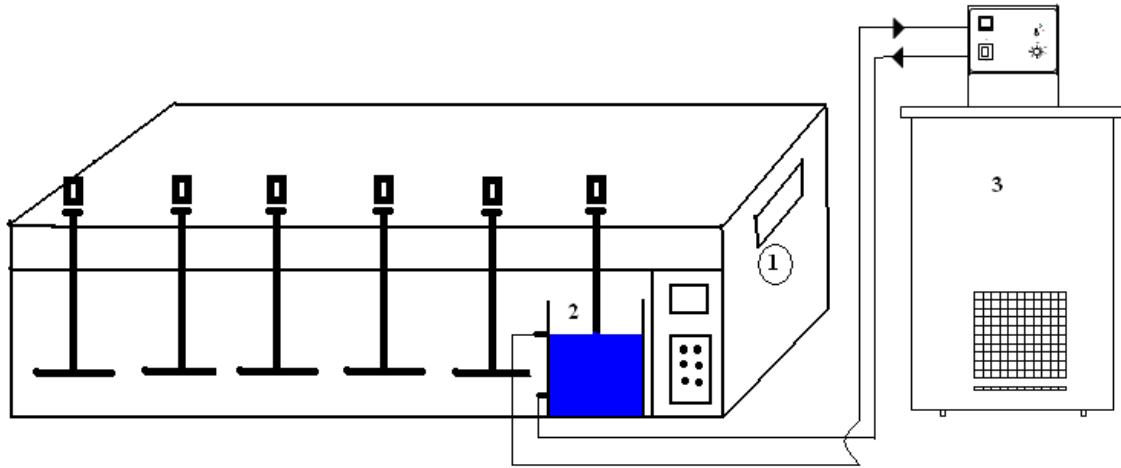

Figure 2. 1-) Jar test apparatus, 2-) Jacketed batch reactor, 3-) Temperature controlled water circulator.

2.3 Coagulation experiments with colemanite mine wastewaters

The optimum pH obtained from the synthetically prepared solutions was applied to the colemanite mine wastewater using the $2^1 \times 2^1$ factorial experimental design. Boron concentration in the colemanite mine wastewater was determined as 373.19 mg L^{-1}. The colemanite mine wastewaters with 500 mL volume were transferred to the glass jacketed reactors (four numbers). After the solutions were heated to 22.5 ± 2.7 °C by a temperature controlled water circulator, the solid form of $AlCl_3$ was added to the wastewater. The wastewaters were again cooled under unstirring situation because aluminium chloride heats the solution and then the pH of the wastewater was adjusted to 8 (obtained optimum value) and metal hydroxides became to be formed while stirring the solution. A 10 g amount of aluminium chloride heats the solution from 22.5 °C to 30 °C. The reason of addition of aluminium chloride as solid form was to prevent the dilution of raw colemanite mine wastewater. When the solid aluminium chloride was added to the colemanite mine wastewater before pH adjustment, the formed aluminium flocs were at unimportant amount. The solutions were fast mixed at 120 rpm during 2.5-5 minutes and slow mixed at 30 rpm during 27.5-30 minutes. After reaction, the flocs were settled during one hour and solutions were taken from the clear portion of the solution. Boron analysis was done by titrimetric method [15]. The pH of the pure water was around 6-7.

3. Results and Discussion

3.1 pH effect on boron removal

Boron removal from synthetically prepared solutions using in-situ formed aluminium hydroxide from $AlCl_3$ salt was studied as a function of solution pH (6-9). The other parameters were temperature (22.5±2.7 °C), concentration (250 mg L^{-1}), and coagulant dosage (2.5 g). Experimental results for pH effect on removal are given in Figure 3. Boron removal percentages for $AlCl_3$ were 27.61, 31.34, 46.27, 44.78% for pH values of 6, 7, 8, 9 respectively. Optimum pH value was found as 8 for $Al(OH)_3$. In general, only monoborate ion exists for boron concentration <0.025 M, triborate ion starts to form for boron concentration >0.025 M and several polyborate ions presents at 0.1 M concentration and polyborate ion molar fraction increases at above 0.1 M boron [9]. Monoborate ions starts to form at pH above 7 and the boron ions completely turn to monoborate at pH above 11 for concentration below 1,000 mg L^{-1} [9]. For the boron concentration range of 250 and 1 000 mg L^{-1}, the polyborates presents at pH range of 7-11 [9]. Activity–pH diagram for Al (III) species in equilibrium with $Al(OH)_3$ is given in Figure 4 [16]. As can be seen in Figure 4, the aluminium type in the solution phase at pH range of 4–11 is dominantly $Al(OH)_3(s)$ at 2.5 g aluminium chloride. The dominant boron ion type is boric acid for pH range of 1-9 and monoborate ions start to increase above pH 7 and monoborate anions are dominate for pH range of 9-11 at 250 mg L^{-1} concentration [9]. Therefore, the aluminium hydroxide flocs showed highest removal efficiency against boric acid molecule and monoborate anion at pH 8 as related with the equilibrium by OH ions. Because OH^- anions compete with the boron ions at high pHs above 9 and removal efficiency decreased above pH 9 [17].
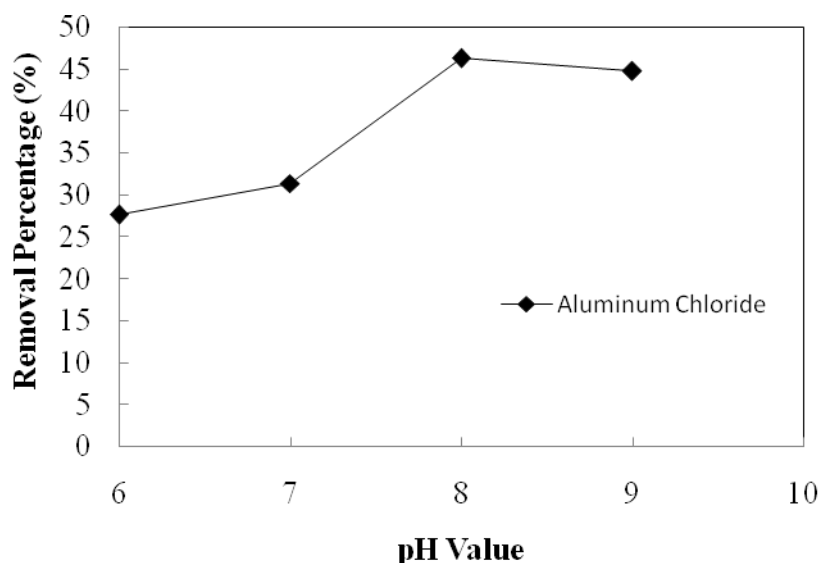

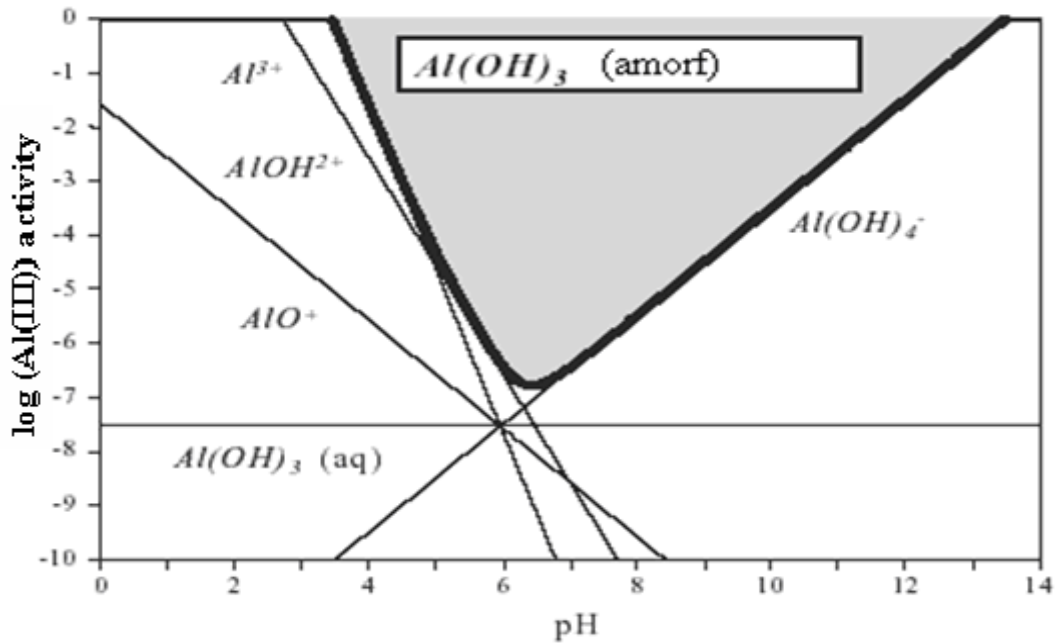Figure 3. pH effect on removal (concentration 250 mg L^{-1}, temperature 22.5±2.7 °C, coagulant dosage 2.5 g).

Figure 4. Activity–pH diagram for Al (III) species in equilibrium with Al(OH)$_3$ (amorphous) [16].

3.2 Full factorial design of experiments for mine wastewater

The general full factorial experimental design requires too few experimental runs when compared with the response surface and taguchi methods. Therefore, in this study, factorial design approach was used for statistical evaluation of data set. The low and high levels of parameters for boron removal from boron mine wastewater are given in Table 1. A $2^1 \times 2^1$ factorial experimental design was applied to the boron mine wastewater after determination of optimum pH in boron removal from synthetically prepared solutions. The optimized parameters in factorial design were dilution factor (1, 10 fold) and coagulant amount (5, 10 g/500 mL). Boron concentration in colemanite mine wastewater was measured as 373.19 mg/L. The optimization matrix is given in Table 2. The response for the statistical analysis is the boron removal percentage (%). The significance of the model coefficients was determined by the analysis of the Student's t test. The P values (probability constants) were used as control parameter to check the reliability of the developed statistical model, individual and interaction effects of the parameters [6,18]. In general, the larger the magnitude of t and the smaller the value of p, the more significant is the corresponding coefficient term [6,18]. Factorial fitness of parameters is given in Table 3. As can be seen in Table 3, based on the statistical analysis, p values for all the parameters were found as above 95% confidence limit value (p<0.05). These means that all the parameters are statistically important at 95% confidante level in the developed model. The developed regression model is below:

$$AlCl_3 \ (Boron \ removal \ \%) = 45.7339 + 3.1040 CD + 2.37111 D \qquad (3)$$

The model was developed according to uncoded factor approach. The greatest effect on boron removal by AlCl$_3$ is belonging to dilution factor (D), and is followed by coagulant dosage (CD). The general model term for aluminium chloride is within the confidence value described with p values given below 0.05. The model represented a square correlation coefficient R-Sq of 99.87% for aluminium chloride, fitting the statistical model is relatively high. The equation (3) generally enables to calculation of

responses (removal percentages) as a function of dilution factor and coagulant dosage, however, the prediction of the model responses by the equation will give the distorted responses when CDD is added to the analysis. The R-squared (adj) statistic indicated that the first-order model explained 99.60 % extent the response variability for aluminium chloride [19]. The relative importance of the main effects of parameters was also analyzed by the Pareto chart. A limit value for statistically comparison of importance of the factors was calculated by t-test as 12.71 for aluminium chloride [6]. As can be seen in Pareto chart (Figure 5), the all parameters (dilution factor and coagulant dosage) were statistically significant for aluminium chloride. The surface plot is given in Figure 6, respectively.
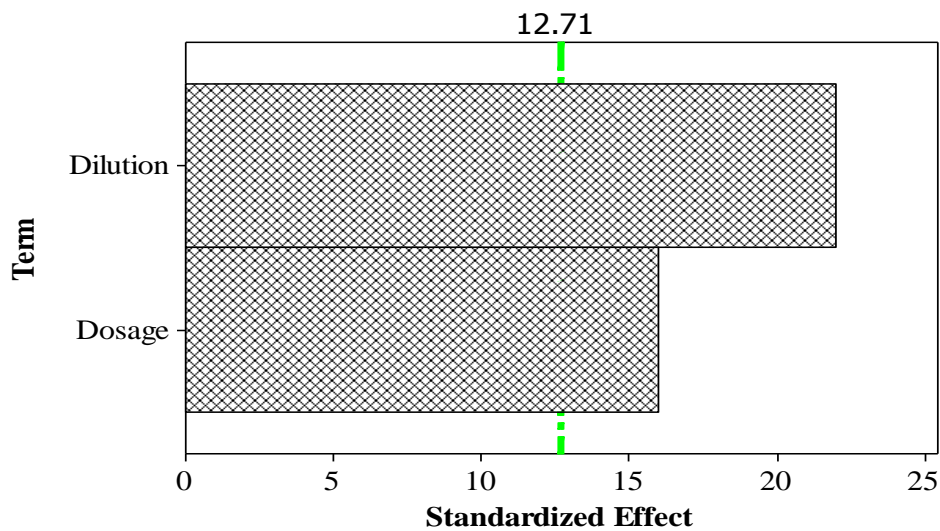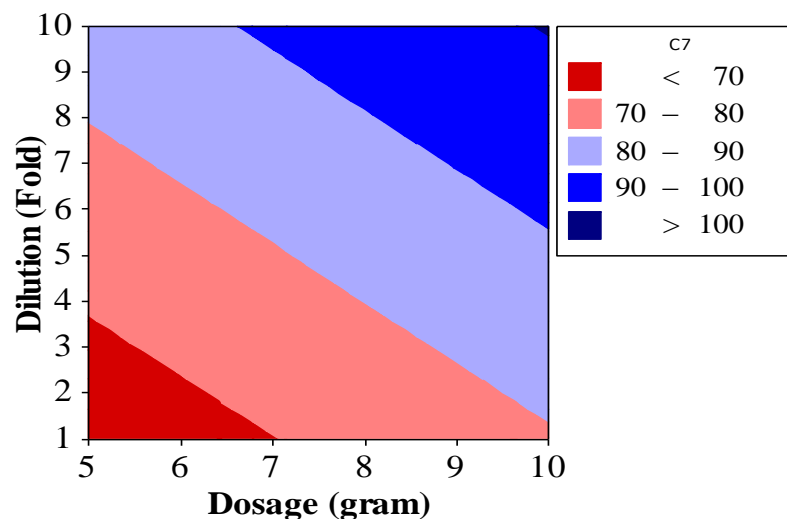
Figure 5. Pareto chart for optimization.

Figure 6. Surface plots for optimization

Table 1. Low and high levels of parameters for optimization.

Parameters	Abbreviation	Low Level	High Level
Aluminum Chloride Coagulant Dosage (g)	CD	5	10
Dilution (Fold)	D	1	10

Table 2. Experimental matrix for optimization and responses (pH:8, temperature:22.5±2.7 $^{\circ}$C, concentration:373.19 mgB L^{-1})

	Experimental Parameters		Boron Removal Percentage
Run	CD	D	AlCl$_3$ (%)
1	10	1	79.63
2	10	10	100
3	5	1	63.14
4	5	10	85.45

Table 3. Factorial fitness to boron removal from colemanite mine wastewater (pH:8, temperature:22.5±2.7 $^{\circ}$C, concentration:373.19 mg L^{-1})

Coagulant	Term	Effect	Constant (Uncoded)	t-value	p-value
AlCl$_3$	Constant	-	45.7339	169.19	0.004
	D	21.340	3.1040	22.00	0.029
	CD	15.520	2.3711	16.00	0.040

4. Conclusion

Boron removal from synthetically prepared solutions and boron mine wastewater by coagulation method was investigated in this study. Optimum pH for boron removal from synthetic solution was determined as 8 for AlCl$_3$ coagulant. Boron removal increased with increasing coagulant dosage and optimum value was 10 g for aluminium chloride. Optimum concentration for boron removal was determined as 37.32 mg L^{-1} (10 fold dilution). The obtained optimum condition from the synthetic solutions were applied to boron mine wastewater and $2^1 \times 2^1$ full factorial experimental design was applied to mine wastewater for response optimization. Maximum boron removal was obtained as 100% for mine wastewater for optimum conditions. The greatest effect on boron removal by AlCl$_3$ is belonging to dilution factor (D), and is followed by coagulant dosage (CD) and coagulant dosage-dilution factor interaction (CDD).

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