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Boron Removal from Colemanite Mine Wastewater by Coagulation using Zinc Hydroxide—A Factorial Optimization Study

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Abstract

In this study, boron removal from synthetic solutions and colemanite mine wastewater by coagulation method using in-situ generated zinc hydroxide from zinc chloride salt was investigated. The parameters for Jar test experiments were solution pH (8-12), concentration (50-750 mg/L), temperature (12-40^{o}C), and zinc chloride dosage (1.0204-10.204 g). The saturation pH of zinc hydroxide is 8.93. The boron adsorption capacity reached to maximum value at pH value of 9 and this pH was selected as optimum value. Boron adsorption capacity increased with increasing concentration due to increasing driving force of concentration. High dosages increased the removal percentage. The adsorption of boron to zinc hydroxide had exothermic nature. The optimum conditions obtained from synthetic solutions were applied to the colemanite mine wastewater by 2^2 factorial designs. The maximum boron adsorption capacity of zinc hydroxide from colemanite mine wastewater was calculated as 43.57 mg/g. The used material and process was promising for boron mine wastewater. The end product of removal from mine wastewater may be used in zinc borate production by solid-state reactions by calcinations.

Keywords: Boron removal, coagulation, colemanite mine wastewater, factorial design, zinc hydroxide.

1. Introduction

Turkey has 61% of the world borate amount and its underground boron richness forms from colemanite, ulexide, pandermite, tincal and kernite minerals [1]. Boron has an average 5-50 ppm concentration in the earth crust [2]. The two of boron chemicals used as boron source in the industrial applications are boric acid and borax. While colemanite deposites of Turkey are located in Bigadiç, Mustafa Kemal Paşa and Kırka regions, the borax deposites are located in Eskişehir region [3]. The excavated colemanite minerals in Bigadiç region are waited in water for swelling of attached soils from the surface of colemanite mineral and these washing waters contain about 382 mg/L boron [4]. The general wastewater of Bigadiç colemanite mine is stored in Çamköy dam and has 627.36 mg/L boron concentration. The boric acid is produced from the reaction of colemanite ore ($Ca_2B_6O_{11}.5H_2O$) with sulphuric acid and gypsum is produced as solid waste from this reaction [5]. The boric acid production plant located in Bandırma District in Turkey discharges 2,750-3,500 mg/L boron containing wastewater [6].

Borax production in Bandırma plant is formed from the reaction of colemanite mineral with Na_2CO_3 and $NaHCO_3$ salts. The solid form of $CaCO_3$ is filtered from mother solution and borax is crystallized [7]. The removal of boron from the wastewater of Bandırma boric acid plant and Bigadiç colemanite mine (Çamköy dam) is necessary because boron is toxic at higher concentrations than needed for humans, animal and plants. For humans, daily intake of boron by drinking water and diet is expected in the range of 0.2–0.6 and 1.2 mg/day, respectively [8].The tolerable limit value of boron in the irrigation water has been reported as maximum 4 mg/L for asparagus, palm, sugarbeet, clover, onion and etc. [9].

Boron removal from wastewaters is possible by physico-chemical methods. The most investigated methods for boron removal are reverse osmosis, electrocoagulation, ion exchange, coagulation, electrodialysis, solvent extraction and adsorption. These mentioned processes are not capable of production economically valuable end product such as zinc borate except electrocoagulation in which zinc electrodes are

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used. Therefore, coagulation with zinc chloride is advantageous for production of zinc borate [10]. Kluckzka and coworkers studied the comparision of activated carbon, zirconium oxide and aluminum oxide and the boron adsorption capacities of the adsorbents were about 0.8, 0.4, 0.4 mg/g for aluminum oxide, activated carbon and zirconium oxide, respectively [11]. In an ion exchange study, Öztürk and coworker reported the optimum pH value as 9 for boron ion exchange reaction with the Dowex 2×8 resin [12]. Lee et al. has reported that the fraction of polyborate ions in solution is higher at 10 ^oC than 60 ^oC temperature for boron concentration of 1,000 mg/L [13]. Sayiner and coworkers have reported that the metal hydroxide forming in the electrocoagulation process was of a high adsorption capacity for anion and cations [14]. In another electrocoagulation study reported by Yılmaz and coworkers, the optimum conditions for boron removal from geothermal water were determined as pH (8), 6.0 mA/cm^2 current density and 333 (Kelvin) temperature [9]. Vasudevan and coworkers reported that the equilibrium data between boron and zinc hydroxide flocs from electrocoagulation process fitted to the Langmuir isotherm suggesting monolayer coverage of boric acid molecules [15]. The boron removal performance of CPA2 reverse osmosis membrane at pH 9 was reported as 61% and 45% at 500 mg/L and 15,000 mg/L NaCl concentrations [16]. Hu et al. reported the performance of a new prepared reverse osmosis membrane for boron removal from waters [17]. Yazicigil and coworker determined that the current density was an important operation parameter in electrodialysis process because it transports the ions from one cell to the other through the membrane via driving force of current density and the best removal efficiency was obtained at high current density [18]. The solvent extraction can be applied with organics containing diols.

In the literature, a few studies intending boron removal by chemical coagulation have been reported. In the reported studies, the performance of polyaliminum chloride (PAC) [19], alum [20], aluminum chloride [21] and ferric chloride [22] were tested; however, zinc hydroxide has not been reported in the literature for boron removal from wastewater by coagulation method The colemanite mine wastewater (The wastewater of Çamköy dam) had about 627.36 mg/L boron. As the zinc chloride addition to boron solution after pH adjustment will cause to residual zinc cation, the pH adjustment after zinc chloride addition is advantageous due to zero zinc concentration at pHs above 8.93. This process enables to production of zinc borate.

2. Materials and Methods

The process was coagulation as the formation of zinc hydroxide and binding of boron on it were occured simultaneously, but as a result there was a binding process and therefore it can be mentioned for adsorption process. The pure zinc cations did not remove boron and only in-situ formed zinc hydroxide adsorbed boron. Therefore, boron adsorption capacities of the zinc hydroxides could be calculated. A coagulation-flocculation process was conducted for boron removal from synthetic solutions and colemanite mine wastewater using in-situ generated zinc hydroxide from zinc chloride. The experiments were carried out by applying Jar Test experiments. The zinc chloride (Carlo Erba product) had≥98% purity and this purity percentage was taken into consideration when the zinc chloride amounts (1, 2.5, 5, 7.5, 10 g) were being calculated. The working boron solutions were prepared using solid boric acid (Merck Product). The boron solutions were prepared at 50-750 mg/L concentrations and solid zinc chloride salt was added and mixed for dissolution and then pHs of the solutions were adjusted on a magnetic stirrer. Thus, zinc hydroxide flocs became formed in the boric acid solutions. The temperature of the solutions was controlled by a temperature-controlled water circulator. The solution containing both of boron and zinc hydroxide in batch jacketed reactors were placed to the Jar Test apparatus and 2.5-5 min rapid mixed for coagulation at 120 rpm and 27.5-30 min slow mixed for flocculation at 30 rpm. At the end of the reaction, the formed flocs were allowed for settling during one hour and 10 mL boron solution was taken from clear portion of the solutions and boron analysis was done by potentiometric method. Boron analysis procedure was as follows [23]: A volume of 5 mL of solution was pipetted into 100 mL beaker and a volume of 50 mL of pure water was added and pH of the solution was adjusted to 7.6 and mannitol was added to the solution up to pH of the solution became stable. Then, the solution was titrated with 0.02 N KOH solution up to the solution pH became again 7.6. 1 mL 0.02 N KOH solution is equal to 0.6964 mg B_2O_3. The spended base volumes in the titration were recorded for boron concentration calculation and also the standardization factors for base solution were measured against 500 mg/L boron solution daily. The obtained optimum conditions from the synthetically prepared solutions were applied to the colemanite mine wastewater as a function of dilution (1 and 20-fold) and coagulant dosage (7.5 and 12.5 g). The characterization of colemanite mine wastewater was as follows: 713 mg/L sulphate, 627.36 mg/L boron, pH (8.50), conductivity 2,137 (μS/cm), total hardness 658.8 (mg $CaCO_3$/L) and suspended solids (9 mg/L). The used base and acid solutions had 4 M concentration for KOH and 20% (v/v) for concentrated HCl. Throughout the whole experiments the pure water had 22.5 ^oC temperature. The experimental setup is given in Figure 1. The results of time dependent experiments are given in Figure 2 and optimum time was determined as 32.5 min. The flocculation time was determined as 30 min because the classical flocculation process requires 20-30 minutes to maturate the flocs for healthy settling [24]. The boron removal was depended on flocculation. The

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approximate base volumes requiring for pH adjustment in synthetic solutions were (10.9-17.3 mL for pH range of 8-12), (10.35-17.5 mL for concentration interval of 50-750 mg/L), (12.3-13 mL for 12-40 ^oC) and (7.2-40.6 mL for 1.0204-10.2040 g coagulant dosage). The raw solutions throughout the experiments had 500 mL volume. The spended base volumes (10 M KOH) for colemanite mine wastewater in pH adjustment to 9 were around 15 mL for 7.5 g zinc chloride and 25 mL for 12.5 g zinc chloride at 12 ^oC. Boron adsorption capacities were calculated by the following equation:

$$Qe(mg/g) = \frac{((C_0 \times V_1/1000) - (C \times V_2/1000))}{M} \quad \textbf{(1)}$$

$Qe(mg/g)$, Boron adsorption capacity, C_0 is initial boron concentration (mg/L), V_1 is the solution volume before base addition (mL), C is the boron concentration at the end of the reaction (mg/L), and V_2 is the solution volume at the end of base addition (mL). M is the mass of zinc hydroxide (g) The saturation pH value for completely precipitation of zinc cations in the reactors was 8.93 and to avoid residual zinc cation after precipitation of zinc hydroxide, the minimum operation pH was selected as 9. The residual zinc concentrations for 2.5510 g zinc chloride at pH values of 9,10,11 and 12 and at pH 10 for 10.2040 g zinc chloride were zero. Residual zinc concentration at pH 8 was 224.7 mg/L. Therefore, after the pH 8 study, the taken solution pH was raised to 9-10 and the solution refiltered and then boron analyzed. For this operation the floc amount is very low.

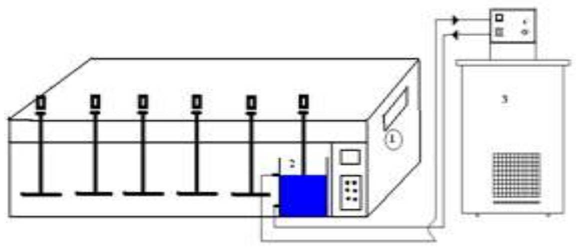

Figure 1. 1-) Jar test apparatus, 2-) Jacketed batch reactor, 3-) Temperature controlled water circulator.

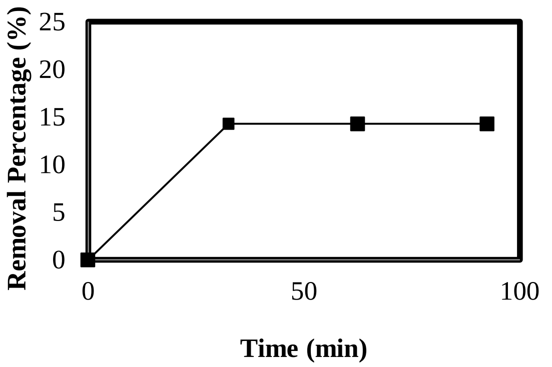

Figure 2. Time effect on removal of boron (pH=10, 22.5 ^oC, zinc chloride:2.5510g, 250 B-mg/L).

3. Results and Discussion

3.1. pH Effect on Boron Removal

The initial solution pH limits the performance of technologies such as adsorption, reverse osmosis, electrodialysis, electro-coagulation and etc. Solution pH affects the formation of metal hydroxides in the solution phase when chemical coagulation process is applied. For instance, the aluminum hydroxide is dominate at pH range of 5.5-10 based on aluminum concentration and aluminum hydroxide plays main role in electro-coagulation of boron [21]. Boron removal by zinc hydroxide was studied at pH range of 8-12. The results are given in Figure 3. The experimental parameters were as follows: Temperature (22.5 ^oC), boron concentration (250 mg/L), zinc chloride amount (2.551 g). The adsorption capacity of zinc hydroxide reached to maximum value at pH 9. The boric acid starts to convert to monoborate anion at pHs above 7 and turns completely to monoborate at pHs above 11 for boron concentration below 270 mg/L [13].

The adsorption capacities belonging to pH effect were 12.38, 20.78, 9.75, 8.59, 5.88 mg/g for 8,9,10,11,12 pHs. The removal percentages were 18.87, 31.80, 16.28, 14.76, 11.63% for 8,9,10,11,12 pHs, respectively. In this study, the dominate form of boron was boric acid and monoborate anion at pH value of 9 [13]. Boron ions adsorbed onto $Zn(OH)_2$ flocs during the removal. The zinc cations were existing at pH below 8.93 and are toxic. For instance, the residual zinc concentration was 224.7 mg/L for pH 8. Adsorption capacity of fresh zinc hydroxide flocs increased at pH 9 due to presence of boric acid molecules and monoborate anions against competitive hydroxyl ions. Boron removal for in-situ formed iron hydroxide was reported as pH (7) and for in-situ formed aluminum hydroxide was reported to reach to maximum value at pH (8) [25,26].

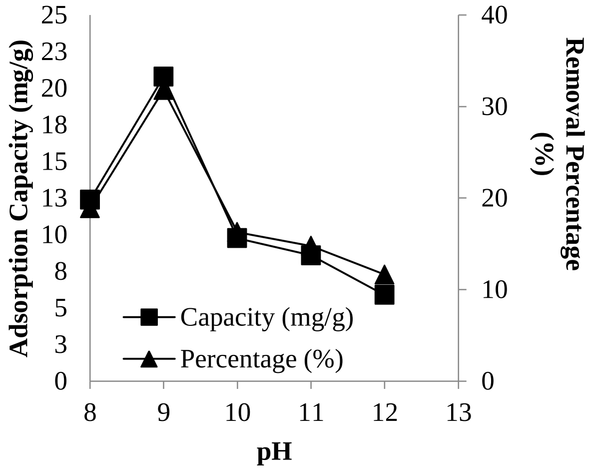

Figure 3. pH effect on removal of boron (250 mg-B/L, 22.5 ^oC, zinc chloride:2.5510g).

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3.2. Concentration Effect on Boron Removal

The polyborates are not present at concentrations below 270 mg/L boron; however, the molar fraction of polyborates rises by concentration increase above 270 mg/L boron [13]. The studied experimental parameters were as follows: Temperature (22.5 ^oC), pH (10), and zinc chloride amount (2.551 g). The results are given in Figure 4. Boron adsorption capacity change was studied at concentration range of 50-750 mg/L and the capacity increased with increasing concentration. Boron reacts as mainly monoborate anion and boric acid with $Zn(OH)_2$ at pH 10 for boron concentration below 250 mg/L and polyborates were adsorbed on zinc hydroxide flocs at 500-750 mg/L [13].The adsorption capacities were 5.03, 5.70, 9.75, 26.54 and 42.60 mg/g for 50, 100, 250, 500 and 750 mg/L concentrations, respectively. The removal percentages were 38, 22.49, 16.28, 21.71, 20.71 for concentrations of 50, 100, 250, 500 and 750 mg/L. The high percentage of 750 mg/L than 250 mg/L can be attributed to polyborate formation. The reason of increase of adsorption capacity at high boron concentrations was the low zinc hydroxide-to-boron ratio or high driving force of concentration [4]. Boron adsorption capacity of in-situ formed iron hydroxide was increased with concentration increase [25].

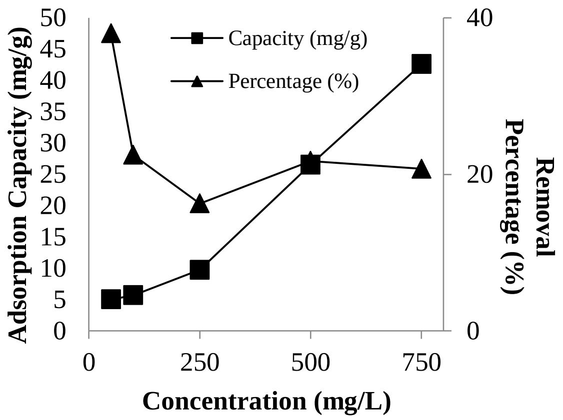

Figure 4. Concentration effect on removal of boron (pH 10, 22.5 ^oC, zinc chloride:2.5510g).

3.3. Dosage Effect on Boron Removal

The coagulant dosage is important parameter to obtain the maximum removal yield and it should be determined before operation of coagulation-flocculation process. The zinc chloride dosages between 1.0204 and 10.204 g were applied for boron removal from synthetic solutions. The experimental parameters were as follows: Temperature (22.5 ^oC), pH (10), concentration (250 mg/L). The results are given in Figure 5. Boron adsorption capacities were 9.95, 9.75, 13.76, 12.25 and 9.05 mg/g for 1.0204, 2.551, 5.102, 7.653, and 10.204 g coagulant dosages. Thus, optimum dosage was determined as 5.102 g. The differences in these results can be attributed to the effective ion-to-adsorbent ratio. The removal percentages were 7.14, 16.28, 42.06, 56.35, 56.35% for 1.0204, 2.551, 5.102, 7.653, and 10.204 g coagulant dosages. The increase of removal percentages with dosage increase was the result of adsorbent active surface increase [1]. Boron adsorption capacity of in-situ iron hydroxide increased with dosage decrease [25].

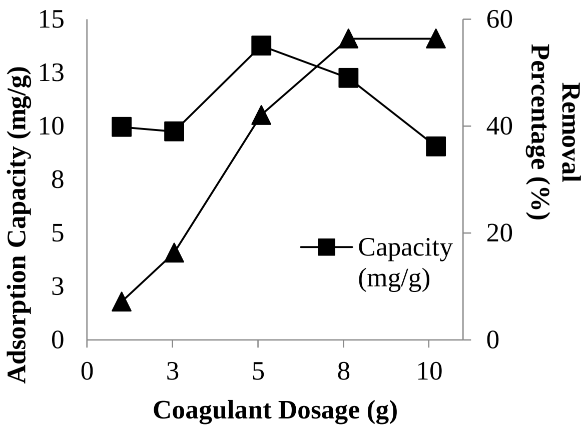

Figure 5. Dosage effect on removal of boron (250 B-mg/L, 22.5 ^oC, pH 10).

3.4. Temperature Effect on Boron Removal

Polyborate molar fraction increases by decreasing temperature for boron concentration above 270 mg/L [13]. The experimental parameters were as follows: Zinc chloride dosage (2.551 g), pH (10), concentration (250 mg/L). The results are given in Figure 6. Boron adsorption capacities were 12.38, 9.75, 2.99 and 0 mg/g for 12, 22.5, 30, 40 ^oC temperatures. Boron reacted with $Zn(OH)_2$ species as monoborate anion and boric acid for all the temperatures. The coagulation was exothermic process suggesting the increasing trend of removal yield with decreasing temperature. The removal percentage values for 12, 22.5, 30, 40 ^oC temperatures were 18.87, 16.28, 6.78 and 0%. Similarly, boron removal by in-situ formed iron hydroxide was reported as exotermic process [25].

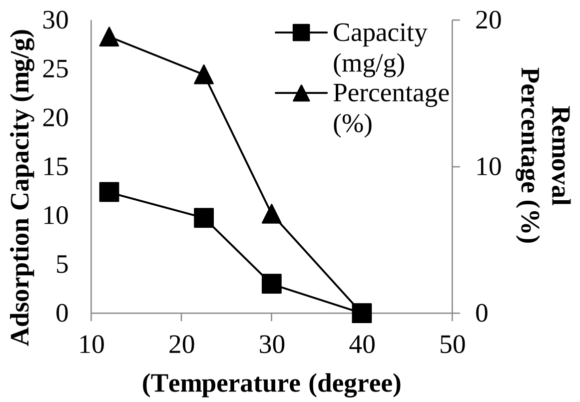

Figure 6. Temperature effect on removal of boron (250 mg-B/L, zinc chloride2.5510 g, pH 10)

3.5. 2^2 Factorial Design of Experiments

A factorial experimental design was applied to colemanite mine wastewater with 627.36 mg/L concentration. The design of experiments is a well-known approach for optimization of independent factors. The factorial design of experiments analyzes the responses for changing parameters from low value to the high value. If the limits of parameter levels have been determined before; for example, by traditional classical experiments, the analysis of data set by factorial design will be helpful for establishment of interaction effects belonging to experimental factors. To determine the main (i.e pH or coagulant dosasge) and interaction effect (i.e., pH*coagulant dosage) of parameters for boron removal by zinc hydroxide, the four factorial experiments (2^2) were carried out. For the present study, the effect of parameters such as dilution factor (1and 20-fold) and coagulant dosage (7.5 and 12.5 g) were optimized by 2^2 factorial design using Minitab 16.0 programme. The response used in the statistical analysis was the adsorption capacity (mg/g) of the zinc hydroxide. The number of experiments in the experimental matrix was calculated by the equation of $a^{k1}\times b^{k2} = 2^1\times 2^1=4$ where a and b are the number of levels and $k_1$and k_2 are the number of factors [4, 27]. The P values (confidence constants) were used as control parameter to check the reliability of the developed statistical model, individual and interaction effects of the parameters. In general, the larger the magnitude of t (Student t-test) and the smaller the value of p, the more significant is the corresponding coefficient term [4, 27]. The general regression model equation is given as follows.

$$Zn(OH)_2 \text{ (Capacity mg/g)} = b+b_1X_1+b_2X_2+b_3X_1X_2 \quad \textbf{(2)}$$

Here; b, b_1, b_2, b_3 are model constants and X_1, X_2 and X_1X_2 are coded factors representing coagulant dosage, dilution factor and dosage-dilution interaction, respectively.

The low and high levels of parameters are given in Table 1. The low and high levels of coagulant dosage (zinc chloride) were 7.5 and 12.5 g while the low and high levels of dilution factor were 1 and 20-fold. The factors and their levels were determined according to preliminary experiments conducted on synthetic solutions. The optimum results (T=12^{o}C, pH=9) determined by synthetic solution experiments were applied to colemanite mine wastewater with 627.36 mg/L concentration. The factorial matrix of experimental design is given in Table 2. The ANOVA analysis (student-t test and confidence levels, p) was performed and is given in Table 3. The confidence limit value (p) for main and interaction effects of parameters was selected as 88% ($p<0.12$). The optimized factors were abbreviated to be dilution factor (D) and coagulant dosage (CD).The regression model for boron removal from colemanite mine wastewater by coagulation method was obtained as follows:

$$\text{Capacity (mg/g)} = 52.8534-1.4040CD -1.8384D \quad \textbf{(3)}$$

The regression model was developed according to uncoded factors. The results of ANOVA analysis are given in Table 3. According to analysis of ANOVA, only model constant and dilution were found as important parameter and the coagulant dosage was above confidence level ($p<0.12$). The importance sequence of the parameters and interactions were as follows: dilution and dosage factor. R-Sq, R-Sq(adjusted) values were calculated as 97.09 and 91.26% respectively by Minitap 16.0 programme. The Pareto chart is given in Figure 7. The limit value of the Pareto chart for confidence level was calculated as 5.242 by the programme and the statistically insignificant parameter was dosage. The dilution-dosage interaction factor distorted the fitness of the regression model to the data; therefore, this term was omitted in the analysis in the programme. The maximum boron adsorption capacity of zinc hydroxide from colemanite mine wastewater was calculated as 43.57 mg/g and 92.48% removal was obtained at 20-fold dilution and 12.5 g zinc chloride dosage. Although the boron concentration of colemanite mine wastewater was high from 250 mg/l, the removal percentage of 7.5 g dosage for mine water (627.36 mg/L, initial pH=9, 12 ^{o}C) was found as high from synthetic solution (7.6530 g dosage, pH=10 and 250 mg/L concentration, 22.5 ^{o}C, Figure 4). This result can be attributed to the formation of polyborates at high concentration and initial pHs and temperatures differences for mine water and synthetic solutions. The removal percentage of 750 mg/L is high than 250 mg/L for synthetic solution (Figure 4) and this result can be related with the polyborate formation. Also, the content of mine water may cause to these results. The residual boron concentrations from colemanite mine wastewater at 7.5-12.5 g dosages and 20 fold dilutions were 4.72-2.36 mg/L, respectively and these values are suitable for usage as irrigation water of mine water.

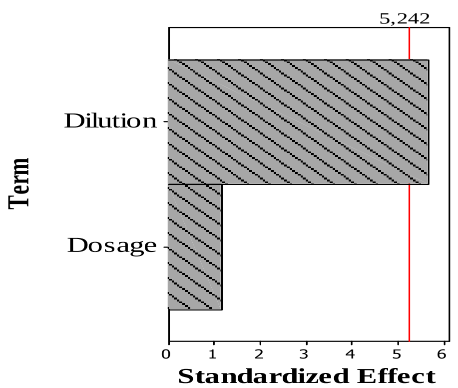

Figure 7. Paretographic of analysis

Table 1. Low and high levels of parameters for optimization

Parameters	Abbreviation	Low Level	High Level
Zinc Chloride			
Coagulant Dosage (g)	CD	7.5	12.5
Dilution (Fold)	D	1	20

Table 2. Experimental matrix for optimization and responses (pH:9, temperature:12 ^oC, concentration: 627.36 mgB L^{-1})

Experimental Parameters			Adsorption capacity (mg/g)	Removal Percentage (%)
Run	**Dosage (g) $ZnCl_2$**	**Dilution (Fold)**	**Analyzed data by Minitab***	**Unanalyzed data by Minitab****
1	7.5	1	43.57*	75.19**
2	7.5	20	2.47*	84.96**
3	12.5	1	30.38*	87.22**
4	12.5	20	1.62*	92.48**

1 fold dilution: (627.36 mg/L/1) and 20 fold dilution: (627.36 mg/L/20)

Table 3. Factorial fitness to boron removal from colemanite mine wastewater (pH:9, temperature:12 ^oC, concentration: 627.36 mgB L^{-1})

Term	Effect	Model Coefficients (Uncoded Units)	T	p
Constant		52.8534	6.32	0.100
CD	-7.02	-1.4040	-1.1	0.459
D	-34.93	-1.8384	-5.6	0.111

T:Student T-test, p-value: Statistically confidence value

3.6 Economical Evaluation of Treatment and Comparison with Conventional Coagulants

The kilogram price of commercial zinc chloride, iron chloride and aluminum chloride are \$1, \$0.5, \$0.22. In the study, the zinc chloride was used as raw material for preparation of zinc hydroxide in reactor body and for this purpose 10 M KOH was used. The prices of metal chlorides are very low and their boron removal performances close to each other. In our previous studies, the boron removal performances of iron and aluminum chlorides were studied [25,26]. For instance, boron removal was 44.7 % at 250 mg/L boron solution for 2.5 g/515 mL aluminum chloride at pH=8 and boron removal was 29.71% at 250 mg/L boron solution for 2.5 g/520 mL iron chloride at pH=7 [25,26]. In this study, boron removal was 50.4% at 250 mg/L boron solution for 2.551/510 mL zinc chloride at pH=10. The removal performances of coagulants in the basis of (price)/ (% removal × gram total coagulant amount) was in the sequence of 0.00506, 0.00123, 0.00421 (\$)/(% removal×gram coagulant) for zinc, aluminum, iron chlorides. Therefore, the advantage sequence of the coagulants was aluminum, iron and zinc chlorides. The treated colemanite mine wastewater is a big problem in Bigadiç boron mine in Balıkesir city and region underground water quality. Also, the solid waste of treatment may be used in zinc borate production by calcination or solid-state reactions [10]. Therefore, this produced zinc borate will contribute an economical value to Turkey and this treatment will solve the environmental problem of the wastewater

4. Conclusion

Boron removal by coagulation from synthetically prepared solutions and colemanite mine wastewater was studied using in-situ generated zinc hydroxide from zinc chloride salt. The results of the study were summarized as follows. The optimum initial solution pH was determined as 9 and the coagulation process had exothermic nature. Boron adsorption capacity increased with increasing concentration and maximum capacity was obtained at 5.1020 g zinc chloride dosage for synthetic solutions. The results obtained from the synthetically prepared solutions were applied to colemanite mine wastewater supplied from the Bigadiç colemanite mine in Balıkesir city of Turkey. The maximum adsorption capacity for optimum conditions in mine wastewater (7.5 g zinc chloride dosage and 1-fold dilution) was obtained as 43.57 mg/g at pH of 9 and 12^oC temperature. The experimental factors were optimized by factorial design approach and while dilution factor was statistically important, coagulant dosage was statistically unimportant for boron removal. And also, the treated water can be reused in mine field due to low boron content.

Author's Contributions

Mustafa Korkmaz: Performed the experiment, result analysis and manuscript preparation.
Cengiz Özmetin, Elif Özmetin, Elif Çalgan, Öznur Ziyanak: Helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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