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Full factorial design of experiments for boron removal by iron hydroxide from colemanite mine wastewater

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Abstract

In this study, iron hydroxide was in-situ generated from iron chloride in the jar test reactors and used for boron removal from both synthetic solutions and colemanite mine wastewater. A time span of 32.5 minutes was enough for equilibrium between boron and iron hydroxide. In the synthetic boron solutions, the variations of boron adsorption capacity of iron hydroxide were investigated by the experimental parameters chosen as pH (7-10), concentration (50-250 mg/L), iron chloride amount (2.5-10 g) and temperature (22.5-40 ^oC). The optimum pH value for boron removal was determined as 7. Because the higher boron concentrations supported to the boron uptake of iron hydroxide, the optimum boron concentration was 250 mg/L. The boron uptake capacity of iron hydroxide increased with decreasing iron chloride dosage. The boron adsorption onto the iron hydroxide was an exothermic process. The optimum conditions obtained from the synthetic solution experiments were applied to the colemanite mine wastewater by 2^2 full factorial experimental design of factors which were dilution (1 and 10 fold) and iron chloride amount (5 and 10 g). The optimization of boron removal by iron hydroxide was realized by analyzing Pareto chart. Maximum capacity was calculated as 23.80 mg/g.

Keywords: *Boron removal, colemanite mine wastewater, full factorial design, iron hydroxide.*

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Demir hidroksitle kolemanit madeni atıksuyundan bor gideriminin full faktöriyel deney tasarımı

Özet

Bu çalışmada, jar testi reaktörlerinde demir klorür kullanılarak demir hidroksit üretildi ve bor içeren sentetik çözeltiler ile Kolemanit madeni atık suyundan bor gideriminde kullanıldı. Bor ve demir hidroksit arasındaki denge süresi 32.5 dakika olarak belirlendi. Sentetik çözeltilerde demir hidroksitin bor adsorpsiyon kapasitesindeki değişim; pH (7-10), konsantrasyon (50-250 mg/L), demir klorür miktarı (2.5-10 g) ve sıcaklık (22.5-40 ^{o}C) olarak belirlenen parametre aralıklarında araştırıldı. Bor giderimi için optimum pH 7 olarak elde edildi. Bor konsantrasyonundaki artış bor adsorpsiyonunu artırdığından, optimum bor konsantrasyonu 250 mg/L olarak elde edildi. Demir hidroksitin bor adsorpsiyon kapasitesi azalan demir hidroksit dozajı ile arttı. Demir hidroksit üzerine bor adsorpsiyonunun ekzotermik olduğu belirlendi. Sentetik çözeltilerden elde edilen veriler 2^2 full faktöriyel deney tasarımı kullanılarak kolemanit madeni atık suyuna uygulandı ve faktörler seyreltme (1 ve 10 kat) ve dozaj (5 ve 10 g) olarak alındı. Demir hidroksit ile bor gideriminin optimizasyonu Pareto kartı ile yapıldı. Maksimum kapasite 23.80 mg/g olarak hesaplandı.

Anahtar kelimeler: *Bor giderimi, kolemanit madeni atıksuyu, full faktöriyel tasarım, demir hidroksit.*

1. Introduction

Today, the usage field of boron is increasing in parallel with the industrial development due to the unique properties of boron such as hardening, neutron capture, semi-conductive and anti microbial [1]. The healthy growing of animals, plants, and humans needs to intake boron at a useful concentration interval. Boron is a component of sedimentary rocks, coal, shale, and some soils, and enters into the environment by the weathering of boron containing rocks, the rising of boron from oceans by aerosols to the atmosphere, distribution of volcanic eruptions and discharge of boron to the receiving environment by wastewaters [2]. Boron is a required microelements for plants. When boron deficiency is encountered in the plant at a serious degree, the growth of plant reduces, losses of yield occur and even the plant dies [3]. In humans, the boron takes part a role in calcium utilization and metabolic activity in addition to its role in the development of brain function; however, its adverse effects at high amounts are nausea, vomiting, diarrhoea, dermatitis, and lethargy [4]. The permissible boron concentration in drinking waters has been reported as 2.4 mg/L and therefore the boron containing wastewaters should be treated with appropriate method [5]. Boron is used in a variety of industrial applications such as in the manufacture of glass and porcelain, the production of leather, carpets, cosmetics and photographic chemicals, fireproofing fabrics, weather proofing wood, certain fertilizers, bactericide and fungicide, disinfectant, food preservative, weed control on railways, in timber yards, welding and brazing of metals, hand cleansing, high-energy fuels and catalysts [6].

Turkey is one of the biggest boron exporting countries and its boron mines are located in Kırka, Bigadiç and Kestelek regions. In the colemanite open pit plant located in Bigadiç region in Turkey, the excavated colemanite minerals contain clays and soils as gangue minerals, so the colemanite mineral is washed. Boron content of the washing waters and the floor waters originated from the mine is between 50-562 mg/L [7]. The mine water also contains about 250-1178 mg/L total hardness [7]. The washing waters of the colemanite mine are stored in the clay based dams and they may cause to underground water pollution. The effective methods for boron removal are adsorption, coagulation, reverse osmosis, electrocoagulation, electrodialysis and solvent extraction [8]. The calcium, magnesium, iron, aluminum, zinc, and etc. metal hydroxides can be used for boron removal from the wastewater, and for this purpose a simple coagulation-flocculation process can be applied. The in-situ formation of the metal hydroxide is one of the coagulation processes because the biggest surface area of the metal hydroxide can be provided in this process due to a chain like a combination of iron hydroxide flocs. In this study, the iron hydroxide in-situ generated from iron chloride was used as coagulant, and the full factorial experimental design was applied. For this purpose, in this current investigation, the iron hydroxide was in situ-generated in jar test reactors using iron chloride and boron removal from synthetic solutions and colemanite mine wastewaters was investigated by selection appropriate parameters to applied method.

2. Material and methods

2.1 Equipments and the used chemicals

A Jar test equipment was used for coagulation-flocculation experiments (VELP JLT6 Jar Test). The six glass jacketed reactors were used for the experiments and the temperatures of the solutions was kept constant with a temperature controlled water circulator. A glass automatic burette and a magnetic stirrer were used for boron titration. A pH meter was used for boron analysis and pH adjustment of solutions. Boron solutions were prepared by using solid boric acid (Merck Grade). The pH of solutions was adjusted using 20% HCl (V/V) and 2.5 M NaOH. NaOH and HCl solutions with 0.1 M concentration were used for pH adjustment of boron solutions that would be analyzed, and D-Mannitol (Merck Grade) was used in boron analysis.

2.2 Synthetic solution experiments

The results of the time experiments are given in Figure 1. Boron removal was realized in a jar test equipment connected with a temperature controlled water circulator and six glass jacketed reactors were used for boron removal experiments. Boron solutions with concentration interval of 50-250 mg/L were prepared from stock boron solutions with 1000 mg/L concentration. A volume of 500 mL solution was used through the experiments and 500 mL solutions were put into reactors. The reactor content was heated to the desired temperature and the desired amount of iron chloride was added, stirred and pH of the solutions was adjusted to a constant value. Thus, the flocs of the in-situ generated iron hydroxide were formed in boron solutions. Boron analyses were done in boron solution taken from the settled boron solution during one hour. The procedure of the boron analysis was as follows: A volume of 5 mL supernatant boron solution was poured in 100 mL beaker and 50 mL pure water was added and pH of the solution was adjusted to 7.6. Then mannitol was added up to constant pH value and pH of the solution was titrated again to 7.6 [9]. In boron analysis, 0.02 N KOH was used and 1 mL 0.02 N KOH solution is equal to 0.6964 mg B_2O_3. Boron adsorption capacity of the iron hydroxide was calculated by the following equation.

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

$Qe(mg/g)$, 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, V_2 is the solution volume at the end of base addition. M is the mass of iron hydroxide (g). The used pure water throughout the experiments had 22.5±2.7 ^{o}C temperature.

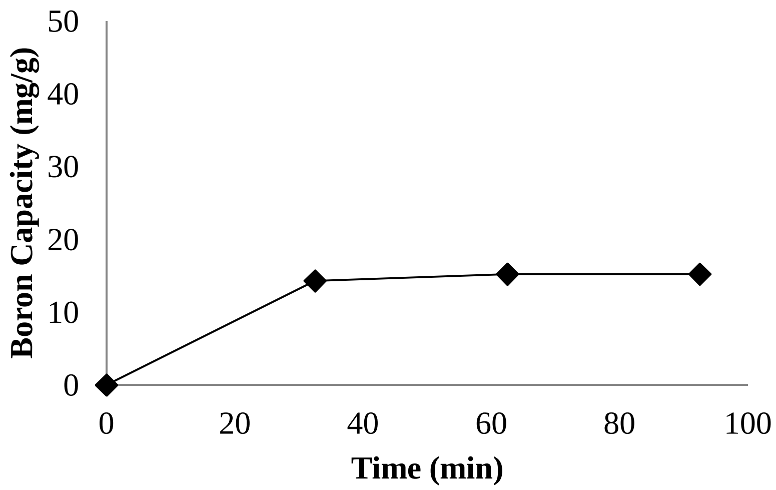

Figure 1. Time effect on the boron removal.

2.3 Full factorial experiments

The colemanite mine wastewater with 356.06 mg/L boron concentration was poured to the six jar test reactors at appropriate dilutions (1and 10 fold). The iron chloride was added to the boron solutions and then the solutions pHs were adjusted to the appropriate value to form iron hydroxide flocs. The boron removal experiments were optimized by 2^2 full factorial design experiments and the factors in the experimental design were dilution (1 and 10 fold) and coagulant dosage (5 and 10 g).

3. Results and discussion

3.1 pH effect

The solution pH is one of the significant operation parameters for the coagulation processes because the ionization of the ions and the state of the coagulating salts are based on the solution pH. The experiments were carried out at pH range of 7-10 and the other parameters were concentration (250 mg/L), iron chloride dosage (2.5 g) and temperature (22.5 ^{o}C). The boron exists as boric acid below pH 7 and monoborate starts to form above pH 7 at concentration below 0.025 M and what ever the pH is, the polyborates presents at unsignificant amount for concentration below 0.025 M. The results are given in Figure 2. The adsorption capacities of iron hydroxide were calculated as 21.34, 17.96, 17.70, 14.25 mg/g for 7, 8, 9, 10 pH values. The reason of high capacity of pH 7 than other pHs was explained with the competition of boron and hydroxyl adsorption on the surface. The removal percentage of pH 6 is 0%.

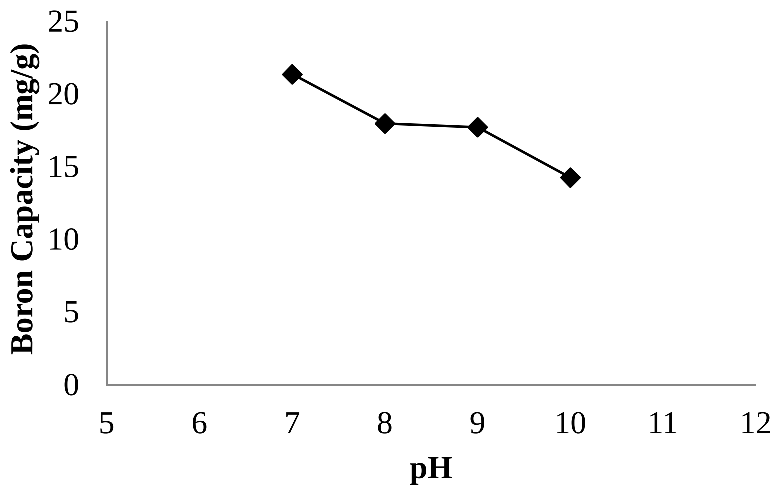

Figure 2. pH effect on the boron removal.

3.2 Concentration effect

The fraction of boric acid, monoborate and polyborates is dependent on boron concentration and this generally affects the boron adsorption due to both driving force of concentration increase and polymerized boron ions with more negative sites at high concentrations. The triborates start to form above 0.025 M boron and the molar fraction of high boron atom containing polyborates increases at above 0.1 M boron [10]. The effect of concentration was studied at 50-250 ppm concentration interval and the other parameters were pH (10), iron chloride amount (2.5 g) and temperature (22.5 ^{o}C). The results are given in Figure 3. The capacity values were 4.2, 5.59, 14.25 mg/g for 50, 100, 250 mg/L concentration. The capacity increase by increasing concentration was attributed to the high driving force of the boron ions. Only boric acid and monoborate ions exist at boron concentration 250 mg/L for pH 10 [10].

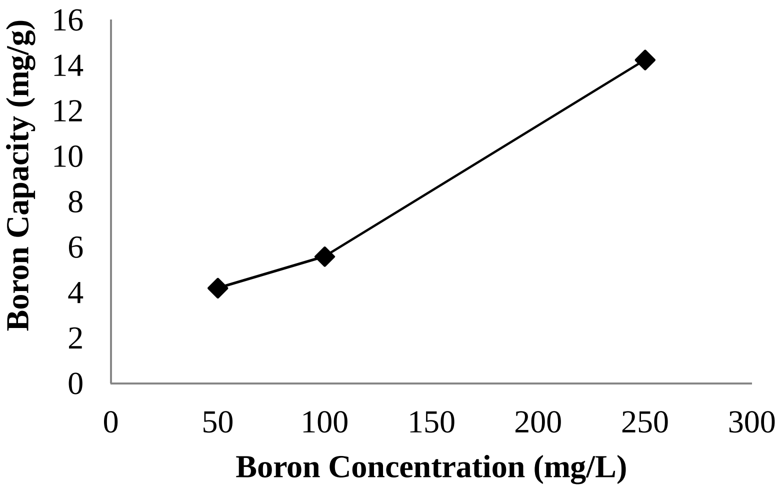

Figure 3. Concentration effect on the boron removal.

3.3 Dosage effect

The optimization of coagulant dosage for pollutant removal is important for optimum removal yield and cost-effectiveness of the coagulation-flocculation process. The experiments were carried out at the iron chloride dosage range of 2.5 and 10 g. The other parameters were concentration (250 mg/L), pH (10) and temperature (22.5 ^oC). The results are given in Figure 4. The adsorption capacities of the iron hydroxide for 2.5, 5, 7.5 and 10 g dosage were calculated as 14.25, 8.08, 7.99 and 5.95 mg/g. The high value of capacity for 2.5 g dosage than 10 g was considered to be due to the ion equilibrium between solid and liquid phase for the solutions with approximately equal initial boron concentration.

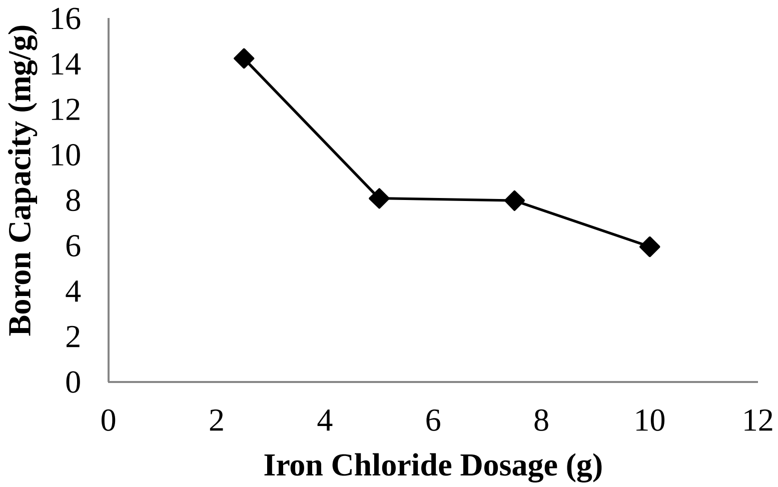

Figure 4. Dosage effect on the boron removal

3.4 Temperature effect

The polymerization of borate ions is an exothermic process and in the aqueous solutions, the molar fraction of polyborates increases with temperature decrease and concentration increase [10]. The temperature dependent experiments were carried out at the temperature range of 22.5 to 40 ^oC and the other parameters were concentration (250 mg/L), pH (10), iron chloride dosage (2.5 g). The results are given in Figure 5. The adsorption capacity values of iron hydroxide were 14.25, 11.62, 1.98 mg/g for 22.5, 30 and 40 ^oC. The decrease of capacity by increasing temperature showed the exothermic nature of the adsorption.

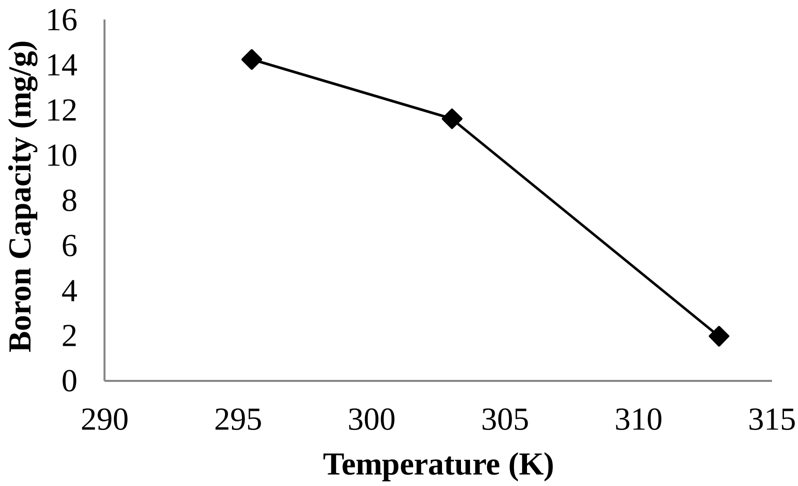

Figure 5. Temperature effect on removal.

3.5 Thermodynamic of the adsorption

The thermodynamics of adsorption data show the adsorption nature i.e. chemical or physical and whether the adsorption is spontaneous or not. The Gibbs free energy change is a function of the equilibrium constant, enthalpy and entropy as follows.

$$\Delta G = -RT(\ln K) \tag{2}$$
$$\ln K = (\Delta S/R) - (\Delta H/RT) \tag{3}$$
$$K = Qe/Ce \tag{4}$$

where ΔG is the free energy change (J/mol). ΔH is the enthalpy change (J/mol). ΔS is the entropy change (J/mol K). $K=(Qe/Ce)$ is the equilibrium constant (L/g). T is absolute temperature (K) and R is the universal gas constant (8.314 J/mol K). Thus ΔH and ΔS can be determined from the slope and intercept of the linear Eq. (3), respectively.

The enthalpy and entropy of the process were calculated as -90.81 (kj/mol) and 327 (j/mol K), respectively. The Gibbs free energy change of the adsorption process was calculated as 0.073, 0.079 and 0.123 j/mol for 295.7, 303.2 and 313.2 Kelvin temperatures. The positive values of Gibbs free energy change with increasing temperature indicated the unspontaneous nature of the adsorption. The negative value of enthalpy indicates the exothermic nature of adsorption and the positive value of entropy showed the increasing adsorption-desorption rate at the solid-solution interface by increasing temperature.

3.6 Design of experiments

The experimental designs are generally applied to factors at situations in which the effects of factors are unknown on the response at the start of the study. The responses are obtained from the experiments done according to experimental matrix determined by an appropriate computer programme. In this study, the Minitab 16.0 programme was used for design and optimization of factors. The full factorial design contains limitations like untaken into consideration the parabolic terms and provides an analysis in the experimental factor space [11]. But the full factorial experimental design is useful in the analysis of data of which limits are known and the method is cheap and the cost-effective.

The experimental design is used for seeing the single effects of more than one factor, analyzing the interaction effects of factors, determination of the factors affecting the statistical confidence, to gain more information on the factors, development of a model that helps the process to improve product yield [12].

The full factorial design is a practical approach for only three or four factors because the high number of factors may require too more time and cost. The number of experiments is calculated by 2^k formula. At the calculation algorithm, the low and high limits of factors are determined by -1 and +1 codes. A model is developed which reflects the individual effects of parameters and their interactions. The response change by factor values from low to a high value can be shown by surface plots for two-factor models; however, for three-factor models, the surface plots can be offered by keeping the one factor constant and thus the other two factor can be offered in the surface plot [13].

In this study, the 2^2 full factorial experimental design for boron removal from the colemanite mine wastewater was studied by the coagulation method using in-situ formed iron hydroxide. The low and high level of parameters are given in Table 1. The factors in design are dilution (1and 10 fold) and iron chloride dosage (5 and 10 g). The response used in the statistical analysis was the adsorption capacity (mg/g) of the iron hydroxide. 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. In general, the larger the magnitude of t and the smaller the value of P, the more significant is the corresponding coefficient term [14,15]. It is useful to consider the factor and response relationship in terms of a mathematical model such as the response function.

$$Fe(OH)_3 \text{ (Adsorption capacity, mg/g)} = b+b_1X_1+b_2X_2+b_3X_1X_2 \quad (5)$$

Here; b, b_1, b_2, b_3 are model constants and X1, X2 and X_1X_2 are coded factors representing coagulant dosage and dilution factor, respectively.
Experimental matrix and responses are given in Table 2. The parameters determined from the synthetically prepared solutions were applied to colemanite mine wastewater with 356.06 mg/L boron concentration. The ANOVA analysis of the data is given in Table 3. According to Anova analysis table, the confidence level (p) for dilution factor is below 0.11(89% confidence level) and the dilution factor term should be added to the statistical model but iron chloride dosage is above the confidence level ($p=0.11$), therefore it cannot be added to the model. On the other hand, the interaction effect of dilution and coagulant dosage gave an error for full factorial design analysis and its confidence factor (p) is not shown in Table 3. The confidence level for the analyzed factors were 89% ($p<0.11$). Therefore, an useful model could not be developed from the statistical analysis. The R-Sq and R-Sq(adj) values were calculated from the Minitab programme as 97.22% and 91.66 %, respectively. The Pareto chart of the responses is given in Figure 6. As can be seen in the Pareto chart the statistically important factor was only dilution.

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

Parameters	Abbreviation	Low Level	High Level
Iron 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 ^{o}C, concentration:356.06 mg L^{-1}).

Experimental Parameters			**Boron Removal Percentage**
Run	**D**	**CD**	**Adsorption Capacity, mg/g**
1	1	5	23.80
2	10	5	3.55
3	1	10	16.80
4	10	10	2.54

Table 3. Factorial fitness to boron removal from colemanite mine wastewater (pH:8, temperature:22.5±2.7 ^oC, concentration:356.06 mg L^{-1}).

Source	Seq SS	Adj SS	Adj MS	F	P
Dilution	297.735	297.735	297.735	33.19	0.109
Dosage	16.040	16.040	16.040	1.79	0.409
Error	8.970	8.970	8.970		
Total	322.745				

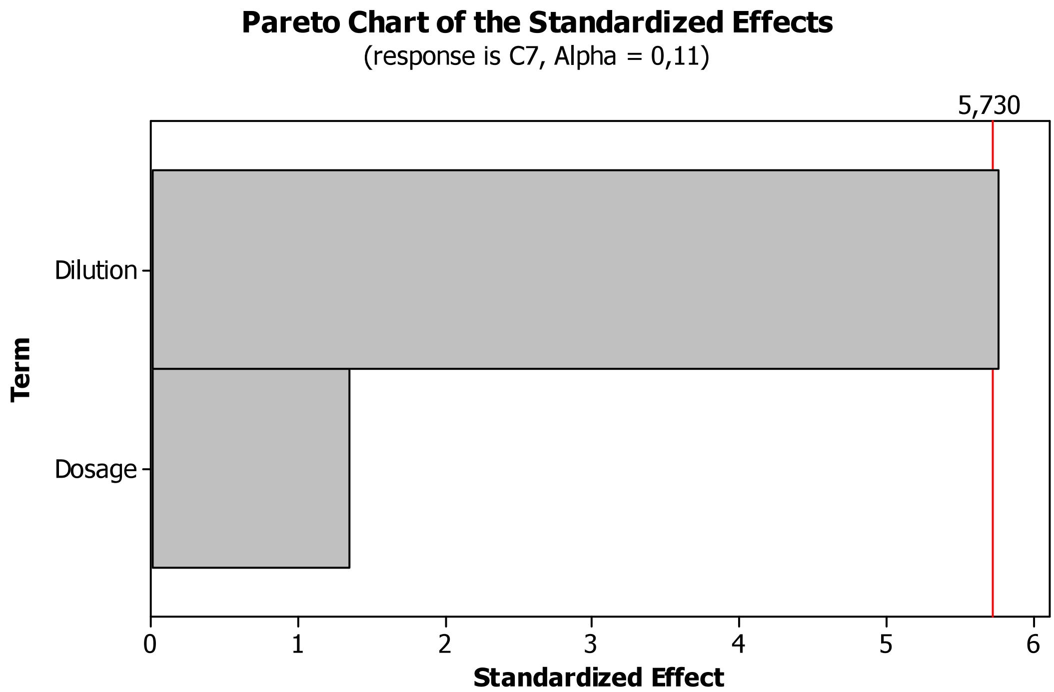

Figure 6. Pareto chart of factors.

4. Conclusion

Boron removal from synthetically prepared solutions and colemanite mine wastewater was studied at changing experimental conditions. The optimum pH was determined as 7 and high concentration increased the capacity. The boron adsorption capacity of the produced iron hydroxide increased at low coagulant amounts and the boron adsorption onto adsorbent was an exothermic process. The optimization of boron adsorption onto iron hydroxide from colemanite mine wastewater was analyzed by full factorial experimental design and the dilution factor was significant statistically but the coagulant dosage was insignificant. Therefore, the statistical model of the process could not be developed. The R-Sq and R-Sq(adj) values were calculated from the Minitab programme as 97.22% and 91.66 %, respectively.

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