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Boron Removal by Aluminum Modified Pumice and Aluminum Hydroxide from Boron Mine Wastewater-Full Factorial Experimental Design

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Abstract

Boron removal by raw and aluminum modified pumice from Bigadiç colemanite mine wastewaters in Turkey were investigated. At Bigadiç mine, the colemanite ore is waited in water pools for swelling of attached clays (382 mg Boron/L) and then washed. The general wastewater of mine is stored in Çam Köy dam (608.1 mg Boron/L). The influence of pH (3-9), dilution ratio (1-10) and adsorbent dosage (1-05 g/50 mL) was studied for waiting pool wastewater. The maximum adsorption capacities of modified and raw pumice were calculated as 1.06 mg/g and 0.607 mg/g for waiting pool wastewater. In the experimental design for waiting pool wastewater, low and high parameter levels were pH (3 and 7), dilution fold (1 and 10) and adsorbent dosage (1 and 5 g/50 mL). According to confidence level ($p<0.1$) (2^3 factorial design), the statistically important sequence of factors for modified pumice were model constant, adsorbent amount, dilution, adsorbent amount-dilution ratio, pH-dilution ratio, pH, pH-adsorbent amount. The pseudo second order kinetic model described the boron adsorption. The isotherm data of study fitted to the Langmuir isotherm than Freundlich isotherm. As the adsorption capacity of aluminum modified pumice was not so high, the in-situ formed aluminum hydroxide was tested and provided about %75.35 boron removal from Çam Köy dam wastewater (608.1 mg Boron/L).

Keywords: Aluminum hydroxide, aluminum modified pumice, boron mine wastewater, factorial experimental design, pumice

Bor Madeni Atık Suyundan Alüminyum Hidroksit ve Alüminyum Modifiye Edilmiş Ponza ile Bor Giderimi-Tam Faktöriyel Deneysel Tasarım

Öz

Türkiyedeki Bigadiç kolemanit madeni atıksuyundan bor giderimi ham ve alüminyumla modifiye edilmiş ponza minerali ile araştırılmıştır. Bigadiç madeninde kolemanit minerali yapışmış olan killerin şişmesi için havuzlarda bekletilmekte (382 mg Boron/L) ve yıkanmaktadır. Madenin genel atıksuyu Çam Köy barajında depolanmaktadır (608.1 mg Boron/L). pH (3-9), seyreltme oranı (1-10) ve adsorbent dozajı (1-5 g/ 50 mL) etkisi bekletme havuzu atıksuyu için çalışılmıştır. Bekletme havuzu atıksuyu için maksimum adsorpsiyon kapasiteleri modifiye edilmiş ve saf ponzalar için 1.06 mg/g and 0.607 mg/g olarak hesaplanmıştır. Deneysel tasarımda parametreler pH (3 ve 7), seyreltme oranı (1ve 10) and adsorbent dosajı (1ve 5 g/ 50 mL). Güvenilebilirlik katsayısına göre ($p<0.1$) (2^3 faktöriyel tasarım), istatistiksel olarak modifiye ponza için parameter sırası, model sabiti, adsorbent miktarı, seyreltme, adsorbent miktarı-seyreltme oranı, pH-seyreltme oranı, pH, pH-adsorbent miktarı olarak bulunmuştur. Yalancı ikinci mertebe reaksiyon modeli bor adsorpsiyonunu açıklamıştır. İzoterm verileri Freundlich izoterminden daha çok Langmuir izotermine uymuştur. Aluminyum ponzanın

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kapasitesi çok fazla yüksek olmadığı için, yerinde üretilmiş aluminyum hidroksit test edilmiştir ve %75.35 oranında Çam Köy barajı atıksuyunda bor giderimi sağlamıştır (608.1 mg Boron/L).

Anahtar Kelimeler: Aluminyum hidroksit, alüminyum modifiye ponza, bor madeni atıksuyu, faktöriyel deneysel tasarım, ponza

1. Introduction

In the nature, boron originates from boron ores, geothermal springs, volcanoes and ocean waters [1]. Volcanoes are the main sources of formation of borate deposits. The pure boron element is a brown powder [2]. Boron only exists as metal-oxide compounds in the nature such as colemanite, ulexide, tincal, pandermite and kernite [3]. The biggest borate processing industries of the world are belonging to USA and Turkey. The industrially important boron chemicals are boric acid and borax. In Turkey and Europe, the boric acid is produced by the reaction of colemanite with sulphuric acid [4]. The colemanite deposits of Turkey are located in Bigadiç, Kırka, Kestelek and Emet regions [3]. In the Bigadiç mine and enrichment plant, the raw colemanite ore is excavated from open pits and refined from impurities like soil and clay by waiting in water and washing of ore. The wastewater from ore waiting pools contains about 382 mg/L boron [3]. The mixture of wastewaters from mine floor, mine waiting pools and ore washing is sent to Çam Köy wastewater dam (608.1 mg/L). The wastewater stored in Çam Köy wastewater dam threats the underground water and surface water quality because acute toxicity of boron may cause various illnesses in human [1]. Cheap boron removal technologies should be developed for boron removal from industrial wastewaters. The methods such as adsorption, ion exchange, reverse osmosis, electrocoagulation, electrodialysis, solvent extraction are applied for boron removal from waters [4,5].

The pKa of boric acid is 9.22 and boron has complex solution chemistry. Borate ion types in the aqueous solutions have been identified as boric acid, monoborate, diborate, triborate, tetraborate and pentaborate ions at boric acid concentration of 0.4 M. The presence of polyborates in solutions increases above 0.025 M boron concentration and is related with concentration, pH and temperature [6]. The main boron types in colemanite waiting pool wastewater (382 mg/L and pH=8) and Çam Köy dam wastewater (pH=8.5 and 608.1 mg/L) are boric acid, monoborate and triborate [6].

The surface of pumice mineral is very suitable for modification and in the literature NaOH and HCl [7], iron nano particles [8], magnesium chloride ($MgCl_2$) and hydrogen peroxide (H_2O_2) [9] were reported for pumice modification.Rao and coworkers studied the TiO_2 coated pumice as carrying media for removal of acid orange-7 and 3-NBSA dyes [10]. Mahvi and coworkers studied the fluoride uptake by pumice and the capacity was found to be 13.51 mg/g [11]. Helard and coworkers studied the nitrate adsorption on pumice in batch system from which the capacity was reported as 164.37 mg/g of nitrate uptake [12]. Öztürk and coworkers studied the cadmium adsorption by pumice and the optimum conditions were 7.01, 107.14 mg/L and 32.48°C for pH, concentration and temperature [13]. Turan and coworkers studied the arsenate adsorption by chitosan modified pumice and raw pumice displays arsenate adsorption below 20%, whereas chitosan modified pumice gives approximately 90% sorption [14]. Asgari and coworkers studied to evaluation of humic acid adsorption from solution by pumice modified with cationic surfactant [15]. Shokoohi and coworkers studied the phenol adsorption onto iron coated pumice giving optimum results as increasing the contact time, adsorbent dosage and decreasing pH and initial concentration [16].But the raw and aluminum modified pumice mineral have not been used as adsorbent material for boron removal from solutions. Pumice had been formed after volcanic eruptions, and has low density and porous structure of which pores are not connected with each other. The experiments conducted between 0.125- and 8-mm pumice particle sizes gave up to the 0-1.2 mL/g pore volumes for 100-0.001 µm pore diameters [17]. The pumice is used as abrasive material in cleaning and polishing and as light construction material [18]. The total amount of world pumice deposits is sixteen billion tons and the reserves are hosting in ABD, Turkey, Italy, Greece, Spain, France, Yugoslavia and Germany [19].

The full factorial design of experiments can especially be applied when the values of parameters are determined before analysis because its experimental runs are limited for wide investigation. Therefore, in this study, the limit values of parameters were determined before full factorial analysis. The 2^3full factorial design of experiments analyses data in a cube block and its estimation the response is limited in that cube block, that is, anyone can not estimated the any analysis result out of cube block. The response term is obtained experimental data.On the other hand, 2^3 full factorial desing of experiments provides low time consumption, effort and cost. By this method, the main and interaction effects of parameters on the response can be seen and evaluated. In this method, there is only one analysis which is the Anova analysis and this Anova analysis shows the regression model parameters and statistically confidence level of parameters. The regression model is formed from constant values belonging to saparetely each parameter and these model constant values are obtained after Anova analysis by Minitab 16.0 programme.

The aim of the study is to determine the feasibility of raw pumice and aluminum modified pumice for boron removal from colemanite mine wastewater and its ballast coagulation effect with aluminum hydroxide for removal of boron from mine wastewater. Ballast coagulation is the supported coagulation by a solid matter like a clay.In this study, the influence of parameters such as pH, dilution ratio and adsorbent dosage on boron removal from colemanite mine pool wastewater by modified pumice and raw pumice was examined. The optimization of boron removal data for modified pumice was carried out by using 2^3 factorial design. Adsorption kinetics and diffusion models were tested for the use of modified pumice in boron removal from Çam Köy dam wastewater. The wastewater in the dam may permeate to ground and surface waters. The treatment of this wastewater is therefore necessary. The feasibility of application of pumice or modified pumice is a new approach for boron removal but in-situ formed aluminum hydroxide instead of pumice or aluminum modified pumice was found as more effective.

2. Material and methods

2.1. Raw and modified pumice adsorption experiments

In this study, two type wastewaters were used as colemanite waiting pool wastewater (382 mg/L boron) and Çam Köy dam wastewater (608.1 mg/L boron). The used pumice mineral was supplied from Nevşehir city in Turkey. The general characteristic XRF analysis results of Nevşehir pumice are given in Table 1 [20]. The pumice powder was grinded and sieved to 0-1.44 mm particle size fraction. Aluminum chloride dosage experiments for modification of pumice were carried out by applying 0.25, 0.5, 1, 2, 4 g/10 g pumice/50 mL pure water volume for 25 mg/L boron and the other parameters were pH=3, 30 ºC, 150 rpm, 24 hours, 1 g modified pumice, 50 mL solution volume.The 1g $AlCl_3$/10 g pumice/50 mL solution was determined as ideal value and it was used in further experiments. The modified pumice was produced as follows: An amount of 100 g pumice powder with 0-1.44 mm fraction was treated with 10 g AlCl3 in 500 mL distilled water during 24 hours at 200 rpm and room temperature. After treatment, modified pumice was filtered and dried at 103 ºC during 24 hours. The pumice had about 0.0098 meq/g cation exchange capacity [21]. The pH of wastewater samples was adjusted to the desired values by diluted acid and base solutions and predetermined amount of raw pumice or modified pumice was added to wastewater samples. The prepared samples were treated by modified pumice or raw pumice for 24 hours in an incubator shaker at 150 rpm of agitation speed and 30 ºC of temperature.

In the experiments on adsorption kinetics, the wastewater sample from Çam Köy wastewater dam which collects the all wastewaters of mine was used and had 608.1 mg/L of boron concentration. The kinetic studies were carried out at 500 mL of wastewater volume, 30 ºC of temperature, 400 rpm stirring speed and 8.64 of pH value. The modified pumice is used as adsorbent and contact time was selected as 10, 20, 30 and 40 minutes. The equilibrium time was determined as 10 min for adsorption kinetic studies. The process was very rapid.

The treated samples were filtered or centrifuged at 5,000 rpm. Boron analysis in treated samples was done according to potentiometric method and procedure was as follows: A volume of 5 mL treated sample was transferred to 100 mL baker and 50 mL pure water was added and pH of the mixture was fixed to 7.6 and D-mannitol was added up to constant pH value and the mixture was titrated again to pH 7.6 with 0.02 N KOH. In titration, a glass burette was used.Boron concentration was calculated from base consumption. 1 mL 0.02 N KOH solution is equal to 0.6964 mg B_2O_3. The base solution needs to standardization before analysis daily. Boron concentration was calculated using following equation (Eq.1).

$$Boron(mg / L) = ((V_1 - V_2) \times 0.21627 \times 1000 \times SF) / V_3 \quad (1)$$

Where, V_1 is the volume of consumed base (mL), SF is standardization factor, V2 is base consumption for pure water (about 0.2 mL), and V3 is the volume of boron solution (mL). Boron adsorption capacity was calculated by using the following equation (Eq.2).

$$Qe(mg / g) = ((C_0 \times V / 1000) - (C_e \times V / 1000)) / M \quad (2)$$

Where, Qe is the adsorption capacity (mg/g), C0 is initial concentration (mg/L), Ce is the equilibrium concentration (mg/L), m is the adsorbent amount (g) and V is the volume of boron solution (L). Adsorption capacity is the amount of binded boron quantity on pumice mineral and its high values are wanted.

To determine the effect of in-situ formed aluminum hydroxide and pumice-aluminum hydroxide binary system, the following experiments were applied. For this purpose, the conditions for single pumice:(10 g raw pumice, 617.4 mg/L Çam Köy dam wastewater, pH=8.64, 21 ºC, 60 rpm, 250 mL wastewater volume), for pumice-aluminum hydroxide binary system:(10 g raw pumice, 617.4 mg/L Çam Köy dam wastewater, pH=8, 21 oC, 60 rpm, 250 mL wastewater volume, 5 g $Al(Cl)_3$), for single aluminum hydroxide system:(617.4 mg/L Çam Köy dam wastewater, pH=8, 21 oC, 60 rpm, 250 mL wastewater volume, 5 g $Al(Cl)_3$). The aluminum chloride was added to the wastewater and then the pHs of the wastewaters were adjusted to desired value to produce the aluminum hydroxide flocs. The experiments were carried out in a Jar test device.

Table 1. The general characteristic XRF analysis results of Nevşehir pumice [20]

Element	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Others
Percentage (%)	72.0	12.75	1.30	0.2	0.70	3.90	4.30	4.28

2.2 Why 2^3 full factorial design

By Minitab 16.0 programme, there are response surface method, factorial design method and taguchi method which can be applied for data analysis. The response surface method has both cube block and axial data for analsis but its parameter points as well should be known before analysis, that is both cube corner parameters and parameters out of cube surface should be known. The taguchi method does not give numerical optimization opportunity and give estimation of positive or negative effect of parameter values. Therefore, if the limits of parameters were determined and there is no necessitate for wide space analysis, the 2^3 full factorial design is the most effective approach. The intervals of the factors used in optimization is given in Table 2.

Table 2. The intervals of the factors used in optimization

Parameter	**Abbreviation**	**Low Level (1)**	**High Level (2)**
pH	pH	3	7
Solid (g/50mL)	AD	1	5
Dilution (Fold)	DR	1	10

3. Results and discussion

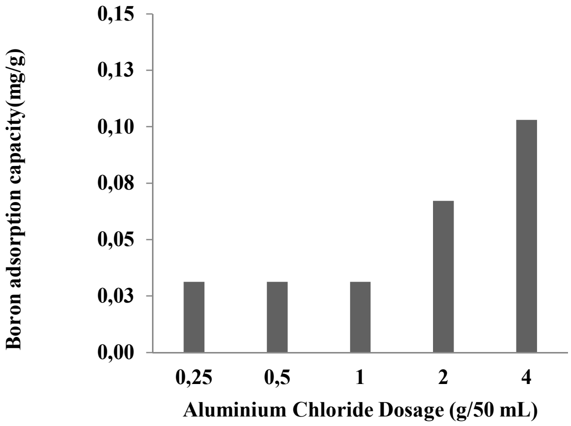
3.1 The effect of aluminum loading for synthetic solution

The boron removal experiments from borated pure water were carried out for 25 mg/L concentration. For this purpose, the effect of aluminum chloride dosage on raw pumice was studied for modification conditions of 0.25, 0.5, 1, 2, 4 g/10 g pumice/50 mL solution. The experimental conditions for boron adsorption were 25 mg/L boron, pH=3, 30 ºC, 150 rpm, 24 hours, 1 g modified pumice and 50 mL boron solution volume. The results showed that boron removal was almost the same for increasing aluminum chloride on the raw pumice while a bit increase for increasing loading was observed. The results are given in Fig. 1A. The reason of this trend can be related with surface saturation of pumice for aluminum cations because pumice has low cation exchange capacity. The applied aluminum loading is highly above the cation exchange capacity of Nevşehir pumice. A bit increase in capacity for increasing aluminum loading on pumice showes the pores and surface of pumice mineral were saturated with aluminum.

3.2. The effect of pH for mine pool wastewater

Because of the effect of pH on boron ion type in solutions, the determination of optimum pH is necessary. Therefore, boron removal from colemanite mine pool wastewater by raw pumice and modified pumice was studied at pH range of 3 and 9. The experimental parameters were 30 ºC of temperature, 150 rpm of speed, 1 g of modified pumice or raw pumice, 50 mL solution, 24 hours, 100 g pumice/10 g $AlCl_3$ in 500 mL. Optimum pH value for modified pumice was determined as 3. This tendency was thought to be related with the hydrogen ions acquired by the modified pumice surface. The boron type adsorbed onto the protonated modified pumice surface was boric acid due to pH value of below 7 at 382 mg/L concentration. The optimum pH of raw pumice was determined as 5. The results are given in Fig 1B. The decrease of adsorption capacity at high pHs for modified pumice and raw pumice was considered to be occurred due to competition of hydroxyl ions for boron adsorption. Boron adsorption yield of flay ash increased with decrease of solution pH to 2, probably due to increasing hydrogen bond of boric acid with flay ash surface [22]. The hydrogen accumulation on raw pumice did not strongly increased the boron adsorption (optimum pH=5), this result shows the binary effect of adsorbed aluminum cation and hydrogen ions on modified pumice.Therefore, it was considered that hydrated aluminum cation hydrogen interaction increased the adsorptive sites on pumice mineral and boron adsorption onto modified pumice increased.

(A)



(B)

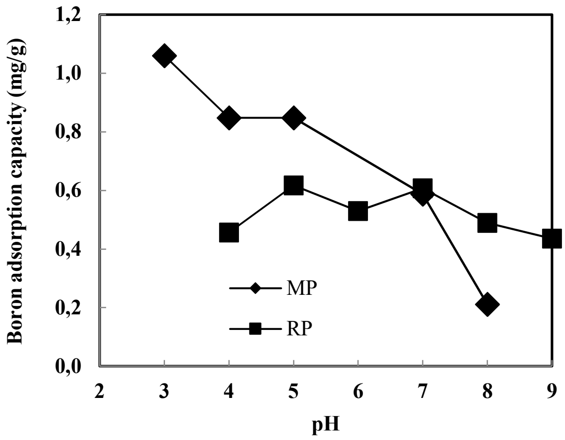
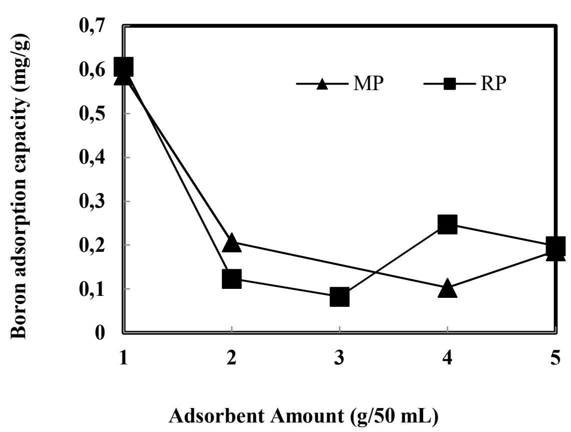


Fig. 1 A-B. A (Aluminum dosage effect, pH=3, 25 ppm boron, 30 ºC, 150 rpm, 24 hours, 1 g modified pumice, 50 mL solution volume), **B** (pH effect for colemanite mine waiting pool wastewater, MP:Modified pumice, RP:Raw pumice, 30 ºC of temperature, 150 rpm of agitation speed, 1 g of modified pumice or raw pumice, 50 mL solution, 24 hours, modification condition 100 g pumice/10 g $AlCl_3$ in 500 mL.).

3.3 The effect of adsorbent dosage for mine pool wastewater

Boron removal from colemanite mine pool wastewater was studied by modified pumice and raw pumice as a function of adsorbent dosage in the range of 1 and 5 g/50 mL. The experimental parameters were 7 of pH, 30 ºC temperature and 150 rpm agitation speed, 50 mL solution, 24 hours, 100 g pumice/10 g $AlCl_3$ in 500 ml. The optimum dosage which gave the maximum boron adsorption capacity from colemanite mine pool wastewater was determined as 1 g/50 mL for both of modified pumice and raw pumice. It was due to the high concentration gradient on the less amount of pumice. The results are given in Fig 2A. Similarlay, it was reported that low red mud amount increased the boron adsorption capacity [23]. Also, high boron concentration forced to boron molecules to entrance to porces of the pumice and modified pumice.

(A) (B)



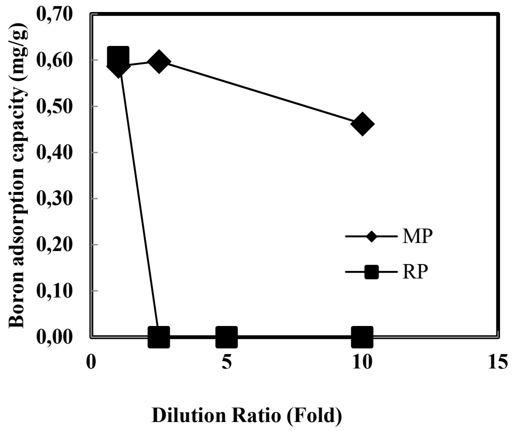


Fig. 2. A (Dosage effect for colemanite mine waiting pool wastewater (MP:Modified pumice, RP:Raw pumice, 7 of pH, 30 ºC temperature and 150 rpm agitation speed, 50 mL solution, 24 hours, modification condition 100 g pumice/10 g $AlCl_3$ in 500 mL.), **B** (Dilution effect for colemanite mine waiting pool wastewater, MP:Modified pumice, RP:Raw pumice, 30 ºC temperature, 150 rpm agitation speed, 382 mg/Linitial boron concentration and pH 7, 1 g modified pumice or raw pumice, 50 mL solution, 24 hours, modification condition 100 g pumice/10 g $AlCl_3$ in 500 mL)

3.4 The effect of dilution ratio for mine pool wastewater

Boron removal from colemanite mine pool wastewater was studied at 0, 2.5, 5 and 10-fold dilution ratios. The experimental parameter values were 30 ºC temperature, 150 rpm agitation speed, 382 mg/Linitial boron concentration and pH 7, 50 mL solution, 24 hours, 100 g pumice/10 g $AlCl_3$ in 500 mL. Boron adsorption capacity of modified pumice decreased with increasing dilution ratio. This was due to the decreasing driving force of the boric acid molecules between solution and surface. The boron adsorption capacity of raw pumice was zero above 2.5 fold for dilution ratio and this result was considered as to be related with decreasing driving force of concentration. The results are given in Fig 2B. Also, for raw pumice the triborate molecules may play role in binding because the triborate fractions in 382 mg/L concentration was about 5%.

3.5 Factorial design of experiments for mine pool wastewater by modified pumice

If the limits of the experimental design matrix are known, the experimental design reduces the number of experimental run and by this meanwhile the experimental cost reduces. In this study, modified pumice was used as adsorbent and the experimental parameters (pH, adsorbent dosage and dilution ratio) were designed by 2^3 factorial design using Minitab 16.0 programme. The factor intervals were 3-7 for pH, 1-5 g/50 mL for adsorbent dosage and 1-10 fold for dilution ratio, 24 hours interaction, 50 mL wastewater volume. The modification was 100 g pumice/10 g $AlCl_3$ in 500 mL pure water. Adsorption capacity was selected as response for the experimental design. The number of runs in the matrix was 8. The ANOVA analysis for investigation of importance of main and interaction effects of factors is done by taking into consideration of confidence levels (p). The confidence level is the indication of the significance of model constants. In general, the high value of t and small value of p show the statistically importance of model constant [3,24]. The developed statistical model was as follows (Eq. 3).

$$\text{Capacity (mg/g)} = 1.36152 - 0.0136816pH - 0.202974AD - 0.103993DR - 0.00030111pHAD + 0.00254231pHDR + 0.0142100ADDR \quad (3)$$

Here, solution pH, adsorbent dosage and dilution ratio are abbreviated as pH, (AD) and (DR), respectively. The model constants were obtained according to the uncoded factors.In calculation of adsorption capacities the coded values should accepted i.e. pH must be 3 or 7, dilution 1 or 10, dosage 1 or 5.

The regression model given above is used to understand of change of responses under various experimental conditions.Experimental matrix for boron removal from colemanite mine waiting pool wastewater is given in Table 3 and the analysis of ANOVA is given at Table 4. The confidence level for ANOVA analysis was assumed as 90%. According to confidence level, the statistically important sequence of factors for modified pumice were model constant>AD>DR>AD-DR>pH-DR>pH>pH-AD. The cube plot was given in Fig 3A. The cube graph showed that the boron adsorption capacity from mine pool wastewater increased by decreasing pH, AD and DR. Contour plots for capacity are given in Fig 3B. Pareto chard for capacity is given in Fig 3C and the statistically important factors are only AD, DR.

The corner of the cube plots showes the adsorption capacities of pumice for boron and the parameter levels of full factorial analysis are given in cube plot. For instance, when pH changed from 3 to 7, the boron adsorption capacity of pumive was changed from 1.05973 to 0.96339 mg/g. The axis of counter plots showes the parameters i.e. dilution*pH showes the dilution ratio at y axsis and pH at x axsis, respectively. The color of counter graph showes the boron adsorption capacities of pumice at different conditions. The pareto chart of statistically analysis indicates to statistically important factors which pass to right side of vertical line. The standardized effects are t-statistics that test the null hypothesis that effect is 0. A null hypothesis is a type of conjecture used in statistics that proposes that there is no difference between certain characteristics of data generating process. That is, the left side of vertical line shows statistically unimportant parameters, the right side of vertical line shows statistically important parameters.

Table 3. Experimental matrix for boron removal from colemanite mine waiting pool wastewater

Trial	pH	Solid (AD)	Dilution (DR)	Capacity (mg/g)
1	3	1	1	1.05973
2	3	1	10	0.26975
3	3	5	1	0.25048
4	3	5	10	0.07322
5	7	1	1	0.96339
6	7	1	10	0.36609
7	7	5	10	0.06358
8	7	5	1	0.25048

1 Fold dilution:(382 mg/L)/1; 10 Fold dilution: (382 mg/L)/10

Table 4. Analysis of ANOVA is given at Table 4.

Term	Coefficient for coded parameters	T-value	p
Constant	0.4121	16.30	0.039
pH	-0.0012	-0.05	0.970
Solid (AD)	-0.2526	-9.99	0.064
Dilution (DR)	-0.2189	-8.66	0.073
pH-Solid (AD)	-0.0012	-0.05	0.970
pH-Dilution (DR)	0.0229	0.90	0.532
Solid (AD)-Dilution (DR)	0.1279	5.06	0.124

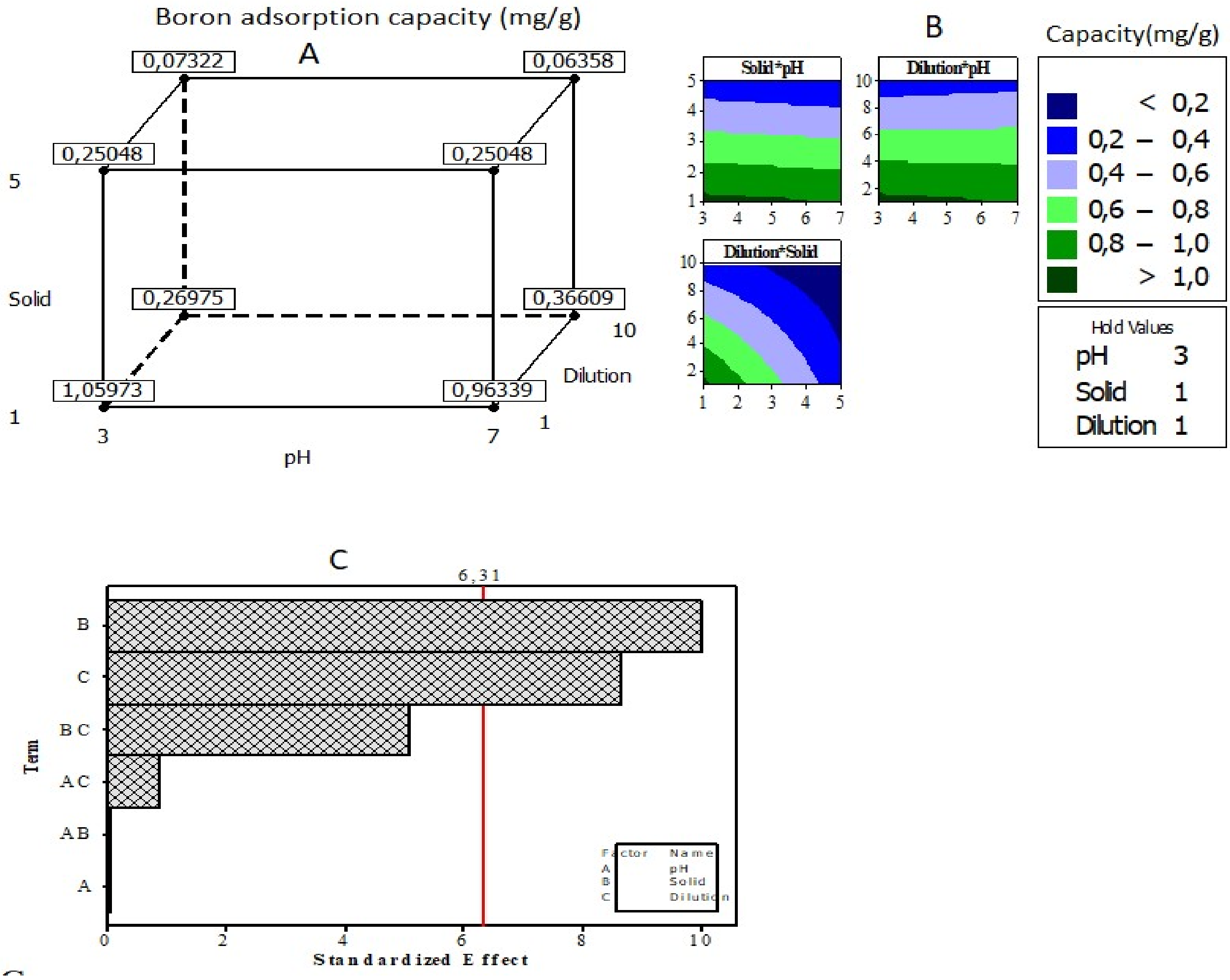


Fig. 3. **A**(Cube plot), **B**(Contour plots), **C** (Pareto chard).

3.6. Kinetic analysis for Çam Köy Dam wastewater

The kinetic models are generally used for design and appropriate operation of batch reactors. The kinetic and diffusion models give also information about removal mechanism such as rate controlling step (film layer diffusion, pore diffusion or ash layer diffusion). In this study, the pseudo-first order and pseudo-second order kinetic models were applied to adsorption data and are given as follows.

Lagergren first order kinetic model is given as follow (Eq. 6) [25].

$$\ln(qe-qt) = \ln qe-k_1 t \tag{4}$$

The pseudo second order kinetic model is given as follow (Eq. 7) [26].

$$t/q_t = \left(1/k_2 q_e^2\right) + \left(t/q_e\right) \tag{5}$$

where k_1, pseudo first order model rate (1/min). k_2, pseudo second order model rate (g/mg min). qe is the adsorbed capacity at equilibrium (mg/g). qt is the adsorbed capacity at time t (mg/g). The coefficient of determination value near to 1 indicates the fitness.

The adsorption of boron on modified pumice including the diffusion of boron like liquid film, pore resistance and surface reactions, three limitations for removal can be suggested as follows [27].

A fractional approach to the equilibrium (Eq. 6):

$$F = [(Co - Ct)/(Co - Ce)] \quad (6)$$

If film-diffusion controlled process is dominant (Eq. 7):

$$\ln(1 - F) = -k_f t \quad (7)$$

If particle-diffusion controlled process is dominant (Eq. 8):

$$\ln(1 - F^2) = -k_p t \quad (8)$$

If moving boundary process (ash layer diffusion model) is dominant (Eq. 9):

$$3 - 3(1 - F)^{2/3} - 2F = k_m t \quad (9)$$

Where, F is the fractional approach to the equilibrium. kf is the film diffusion rate constant. kp is the particle diffusion rate constant. km is the moving boundary process rate constant.

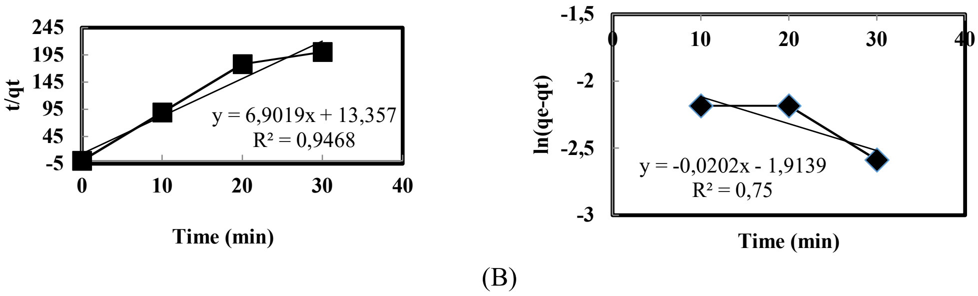


Fig. 4 A-B: **A** (Pseudo second order kinetic plot) **B** (Pseudo-first order model) (500 mL of Çam Köy Dam wastewater volume, 30 ºC of temperature, 400 rpm stirring speed and 8.64 of pH value, 60.18 gram modified pumice, 10, 20, 30 and 40 minutes)

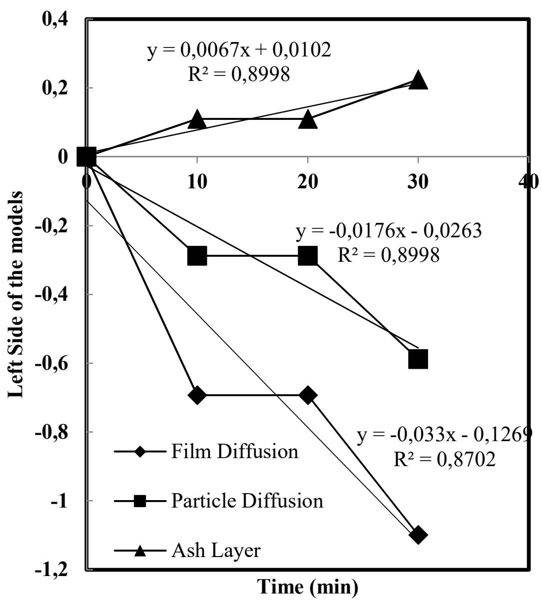


Fig. 5 (Diffusion models 500 mL of Çam Köy Dam wastewater volume, 30 ºC of temperature, 400 rpm stirring speed and 8.64 of pH value, 60.18-gram modified pumice, 10, 20, 30 and 40 minutes)

Only modified pumice was used for kinetic analysis. The kinetic analysis results are given in Figure 4A-B and the data could be described by pseudo second order kinetic model (R^2=0.946) and pseudo first order model had R^2=0.75 value. Also, the more resistant mechanisms are pore diffusion and ash layer models. Diffusion mechanism analysis for boron adsorption is given in Figure 5. The fitness of boron adsorption data to the pseudo second order model indicated to concentration controlled process. The pseudo second order moder is very usefull model for description of adsorption data.

The rate constants of pseudo first order model and pseudo second order model are calculated as 0.0202 min^{-1} and 25.85 g/mg min. The pseudo first order kinetic model plots are generally show digit lines and indicates different adsorption rate constants. In the analysis of pseudo first order model, whereas, an avarage rate constant is calculated. However, the pseudo second order kinetic model plots show a straight line for analysis and is therefore more suitable for analysis. As described above, the rate controlling mechanism in boron adsorption onto pumice was pore diffusion and ash layer model. This shows that the pores of pumice bloked by aluminum cation and boron molecules.

3.7 Isotherm analysis

The isotherm models are useful equations that used for gaining information about the surface of adsorbent and mechanism of adsorption. Also, adsorption isotherms are used to design of batch adsorption data. The widely used isotherm models are Langmuir and Freundlich models. The Langmuir isotherm is generally characterized by monolayer adsorption of pollutants and it is given as fallows [3]:

$$Ce / qe = 1 / q_m k_L + Ce / q_m \tag{10}$$

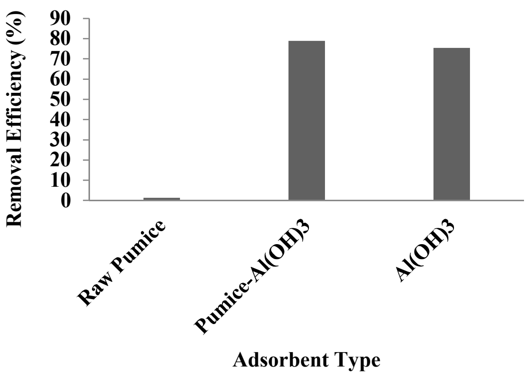
Where, Ce is the equilibrium concentration in liquid phase (mg/L). qe is the maximum amount of the boron adsorbed (mg/g). qm is qe for a complete monolayer (mg/g). ka is a sorption equilibrium constant (L/mg). The Freundlich isotherm generally describes the multilayer adsorption and it generally describes the physical adsorption and the model is as follows [3]:

$$\ln qe = \ln k_F + (1/n) \ln Ce \tag{11}$$

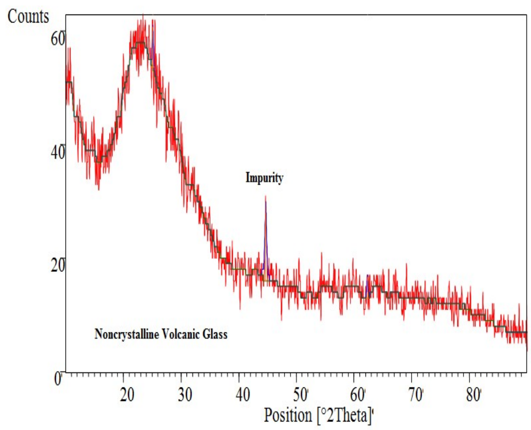
Where, Ce is the equilibrium concentration in liquid phase (mg/L). qe is the maximum amount of boron adsorbed (mg/g). k_F is the Freundlich adsorption capacity. 1/n is sorption equilibrium constant. The isotherm analsis showed that Langmuir isotherm fitted well to data than Freundlich model and this indicated to the chemical binding of boron. Also, surface energy distribution on the surface was homogeneous. The coefficient of determination values of analysis are R^2=0.999 for Langmuir and R^2=0.841 for Freundlich. Isotherm data belongs to Fig. 2B for modified pumice.

3.8 Boron adsorption from Çam Köy Dam wastewater onto pumice and Al(OH)3

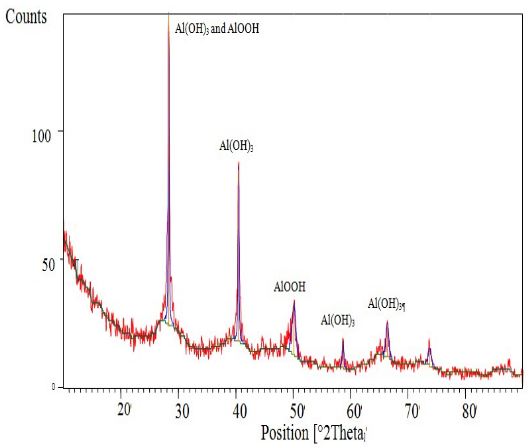
The results are given in Fig 6A. Although the raw or modified pumice powder do not have high capacity for completely boron removal from boron mine wastewaters, the usage of aluminum chloride for generation of aluminum hydroxide in reactor as adsorbent provided best result for boron removal from dam wastewater. The removal percentage was about 75.35% for aluminum hydroxide single system in treatment of dam wastewater. As a result, boron removal from colemanite mine wastewaters by pumice or modified pumice is not effective, the application of aluminum hydroxide with pumice or without pumice is very feasible. The XRD pattern of raw pumice, boron adsorbed aluminum hydroxide are given in Fig 6B-C and only Al(OH)3 and AlOOH formed as crystal structure and aluminum boron was not detected [28].



(A)



(B)



(C)

Fig. 6A (The effect of adsorbent type), B (XRD pattern of Nevşehir pumice), C(XRD pattern of boron adsorbed aluminum hydroxide, Initial temperature from 38 to 26.5 °C, 10 g $AlCl_3$, 500 mL Çam Köy Dam wastewater, 1-hour interaction, 24 hours drying at 105 °C, pH=9) (The water temperature increased from room temperature to 38 °C by aluminum chloride addition.

4. Conclusion

Boron removal from colemanite waiting pool wastewater by modified pumice and raw pumice was studied. Boron adsorption capacity onto modified pumice increased with decreasing pH, increasing concentration and decreasing dosage. Optimum parameters of modified pumice for pH, concentration and adsorbent dosage were determined as 3, 382 mg/L and 1 g/50 mL. Boron adsorption onto raw pumice from colemanite waiting pool wastewater increased at pH 5, adsorbent dosage 1 g/ 50 mL and concentration 382 mg/L. The importance sequence of parameters for modified pumice was as follows: AD, DR, pH-DR, pH, pH-AD, AD-DR. The maximum boron adsorption capacities of the modified pumice and raw pumice were calculated as 1.06 and 0.607 mg/g for colemanite mine waiting pool wastewater (382 mg/L). Kinetic data could be described with pseudo-second order model for Çam Köy dam wastewater. The ash layer and pore diffusion limitations controlled the boron adsorption. The application of pumice-$Al(OH)_3$ binary process or single $Al(OH)_3$ process is more effective than raw pumice or modified pumice.As a result, we aimed the determine the feasibility of raw and aluminum modified pumice for boron removal from mine wastewaters and also a ballast coagulation using modified pumice by aluminum hydroxide was tested, the polymerization effect of pumice for aluminum hydroxide is low or not and ineffective.

5. Acknowledgement

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6. References

[1] Korkmaz M., Özmetin C., and Fil B.A., "Modelling of boron removal from solutions using Purolite S 108 in a batch reactor", ***Clean Soil Air Water***,44, 949–958, (2016).

[2] Bayar D.,"Boron removal from aqueous solutions by adsorption and experimental design", Osmangazi University, Institute Science and Technology, Master Thesis, 135 pp.,Eskişehir, Turkey, (2001).

[3] Korkmaz M., Fil B.A., Özmetin C., Yaşar, Y.,"Full factorial design of experiments for boron removal from Colemanite mine wastewater using Purolite S 108 resin", ***Bulgarian Chemical Communucation***, 46, 594–601, (2014).

[4] Özmetin C., Aydın Ö., Kocakerim M.M., Korkmaz M., Özmetin E., "An empirical kinetic model for calcium removal from calcium impurity-containing saturated boric acid solution by ion exchange technology using Amberlite IR–120 resin", ***Chemical Engineering Journal***, 148, 420–424, (2009).

[5] Duman M.V., and Özmetin E., "Boron removal from wastewater originating in the open pit mines of Bigadic Boron Work by means of reverse osmosis", ***International Journal of Global Warming***, 6, 252-269, (2014).

[6] Na J.W., Lee K.J., "Characteristics of boron adsorption on strong-base anion-exchange resin", ***Annals of Nuclear Energy***, 20, 455–462, (1993).

[7] Yousefi M.,Arami S.M., Takallo H.,Hosseini M., Radfard M., Soleimani H.,Mohammadi, A.A.,"Modification of pumice with HCl and NaOH enhancing its fluoride adsorption capacity: Kinetic and isotherm studies", ***Human and Ecological Risk Assesment***, 25, 1508–1520, (2019).

[8] Shokoohi R., Zolghadrnasab H., Azarian G., Mehdipous M., "Cadmium removal by using pumice modified with iron nanoparticles", ***Global NEST Journal***, 18, 426-436, (2016).

[9] Sepehr M.N., Sivasankar V., Zarrabi M., Kumar M.S., "Surface modification of pumice enhancing its fluoride adsorption capacity: An insight into kinetic and thermodynamic studies",***Chemical Engineering Journal***, 228, 192-204, (2013).

[10] Rao K.V.S., Rachel A., Subrahmanyam M., Boule P., "Immobilization of TiO2 on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants", ***Applied Catalysis B: Environmental***,46, 77–85, (2003).

[11] Mahvi A.H., Heibati B., Mesdaghinia A.L., and Yari A.R., "Fluoride adsorption by pumice from aqueous solutions", ***E-Journal of Chemistry***, 9, 1843-1853, (2012).

[12] Helard D., Indah S., Sari C.M., Mariesta H., "The adsorption and regeneration of natural pumice as low-cost adsorbent for nitrate removal from water", Journal of Geoscience, Engineering, ***Environment, and Technology***, 3, 86-93, (2018).

[13] Öztürk D., Şahan T., Dişli E., Aktaş N., "Optimization with response surface methodology (RSM) of adsorption conditions of Cd(II) ions from aqueous solutions by pumice", ***Hacettepe Journal of Biology and Chemistry***, 42, 183-192, (2014).

[14] Turan D., Kocahakimoğlu C., Boyacı E., Sofuoglu S.C., Eroğlu A.E., "Chitosan-immobilized pumice for the removal of As(V) from waters", ***Water Air Soil Pollution***,225, 1931-1942, (2014).

[15] Asgari G., Ebrahimi A., Mohammadi A.S., Ghanizadeh G., "The investigation of humic acid adsorption from aqueous solutions onto modified pumice with hexadecyl trimethyl ammonium bromide", ***International Journal of Environmental Health Engineering,*** 1, 1-7, (2012),.

[16] Shokoohi R., Torkshavand Z., Bajalan S., Zolghadnasab H., and Khodayari Z., "Efficient phenol removal from aqueous solution using iron-coated pumice and leca as an available adsorbents: evalution of kinetics and isotherm studies", ***Global NEST Journal***, 21, 91-97, (2019).

[17] Ersoy B., Sariisik A., Dikmen S., Sariisik G., "Characterization of acidic pumice and determination of its electrokinetic properties in water", ***Powder Technology***, 197, 129–135, (2010).

[18] Farizoğlu B., Nuhoğlu A., Yıldız E., Keskinler B., "The performance of pumice as a filter bed material under rapid filtration conditions", ***Filtration Separation***, 40, 41-47, (2003).

[19] Çiftçi E., Earth Sciences Technical Terms Dictionary, Hambe Offset, Niğde, Turkey, (2003).

[20] Sapcı N., Gündüz L., Ulusoy M., "Karaman and vicinity pumice formation of lightweight concrete aggregate sector role and importance", ***5th Symposium on Industrial Raw Materials***, Izmir, Turkey, 138-148, (2004).

[21] Tunç S., and Duman O., "Effects of electrolytes on the electrokinetic properties of pumice suspensions", ***Journal of Dispersion Science and Technology***, 30, 548–555, (2009).

[22] Öztürk N., and Kavak D., "Adsorption of boron from aqueous solutions using fly ash: Batch and column studies", ***Journal of Hazardous Materials***, 127, 81–88, (2005).

[23] Cengeloglu Y., Tor A., Arslan G., Ersoz M., Gezgin S., "Removal of boron from aqueous solution by using neutralized red mud", ***Journal of Hazardous Materials***,142, 412-417, (2007).

[24] Kavak D., "Removal of boron from aqueous solutions by batch adsorption on calcined alunite using experimental design", ***Journal of Hazardous Materials***, 163, 308-314, (2009).

[25] Lagergren S., "Zur theorie der sogenannten adsorption gelöster stoffe", ***Kungliga Svenska Vetenskapsakademiens Handlingar***, 24, 1-39, (1898).

[26] Ho Y.S., "Adsorption of heavy metals from waste streams by peat,"University of Birmingham, Ph.D. Thesis, 356 pp., Birmingham UK, (1995).

[27] Alguacil F.J., Alonso M., Lozano L.J., "Chromium (III) recovery from waste acid solution by ion exchange processing using Amberlite IR-120 resin: batch and continuous ion exchange modelling",***Chemosphere***, 57, 789-793, (2004).

[28] Kartikaningsih D., Shih Y.J., Huang Y.H., "Boron removal from boric acid wastewater by electrocoagulation using aluminum as sacrificial anode", ***Sustainable Environmental Research***,26, 150-155, (2016).