Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24829

172 (2019) 260–269
December

Boron removal from solutions by talc clay

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Received 18 March 2019; Accepted 25 August 2019

ABSTRACT

In this study, boron uptake from solutions by raw and modified talc clay was investigated. The raw talc mineral was modified in aluminum chloride solution. Firstly, the pH experiments were carried out by raw and modified talc. Due to the relatively low adsorption capacity of the raw talc, the modified talc was used in further experiments. Boron adsorption experiments for the modified talc were conducted by different initial pH of the solution, temperature, boron concentration and adsorbent amount. Optimum parameters for the modified talc were determined as pH (7), concentration (500 mg/L), temperature (25°C) and adsorbent dosage (0.8 g/50 ml). The optimum pH was determined as 9 for raw talc use. Maximum boron adsorption capacities for the modified talc and raw talc were calculated as 3.10 and 2.4 mg/g, respectively. The thermodynamic parameters such as enthalpy, entropy and Gibbs free energy change were calculated, and the boron adsorption had exothermic nature. The optimization of boron adsorption data for the modified talc was performed by applying 2^3 factorial experimental design. The isotherm analysis data best fitted to the Langmuir model than the Freundlich model. The kinetic data fitted to the pseudo-second-order model rather than the pseudo-first-order model. Boron adsorption onto modified talc was controlled relatively by particle diffusion. Attenuated total reflection fourier-transform infrared spectroscopy analyses were performed for modified talc and boron adsorbed modified talc samples.

Keywords: Aluminum talc clay; Boron removal; Factorial design; Isotherm; Kinetics

1. Introduction

Boron's presence in groundwater and surface water is caused by both natural and anthropogenic factors [1]. Boron use in the manufacturing of boron-doped products has increased due to its peerless properties such as hardening, neutron capture, fire-resistive, semi-conductive, heat resistant and anti-microbial [2]. Although boron does not present as a pure element in nature, it exists as metal-boron compounds such as colemanite, ulexite, tinkal, kernite and pandermite. Turkey possesses the biggest borate deposits of the world [3] and in the regions where boron mining and processing activities are being carried out, environmental problems are encountered. For instance, the borate mines and geothermal establishments in the West Anatolia Region pollute the environment around the Menderes River [4]. Treatment of boron-containing geothermal wastewater occurring from electrical production and building heating activities is also a necessity. The Bandırma boric acid plant in Turkey discharges annually 320,000 tonnes borogypsum together with the wastewater which contains about 3,000 mg/L boron [5]. The colemanite ore washing water arising from the Bigadiç colemanite mine in Turkey contains about 382 mg/L boron [3]. Boron has a narrow concentration interval for its useful and toxic effects on plants, humans and animals [6]. Therefore, boron-containing wastewaters should be treated

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by a proper technique because the boron discharge concentration is about 1 ppm in most countries [7].

So far, several physicochemical methods are widely reported for boron removal from wastewaters. These methods are adsorption, coagulation, electrocoagulation, electrodialysis, reverse osmosis, membrane filtration after complexation and solvent extraction [8]. Among these methods, adsorption is a cheap method and applicable easily. Once the use of the adsorption method is in question for boron removal, the clay minerals such as sepiolite [9], montmorillonite [10], kaolinite [11], illite [10] are considered as primary adsorbents. The clay minerals show different adsorption capacities. The clay type for boron removal from sea, geothermal or wastewaters is determined based on the maximum adsorption capacities of the clays. Couch and coworkers reported that the irreversible uptake of boron onto three different illite clays was increased by increasing boron concentration, salt concentration, temperature and time of the treatment and the mechanism of boron uptake was proposed as rapid chemical adsorption of $B(OH_4)^-$ onto fraged edges of the clays and slow diffusion into the lattice [12]. Mattigod et Al. [13] studied the boron adsorption on kaolinite in $Ca(ClO_4)_2$ and $KClO_4$ solutions and determined that the boron adsorption was higher in $Ca(ClO_4)_2$ solution at high pHs (9–10). Seyhan et al. [14] studied the boron adsorption onto bentonite clays and the optimum conditions for factorial experimental design approach were reported as pH (10), temperature (45°C), clay (0.25 g), and solution volume (20 mL) at 180 min treatment time. Karahan et al [4] reported the boron adsorption onto raw and modified with nonyl ammonium chloride illite, bentonite, and sepiolite. The boron adsorption increased with modification of illite and bentonite, and maximum boron adsorption was achieved by regulating pH value to the range of 8–10. Keren and Mezuman [11] reported that maximum boron adsorption capacities of Ca-kaolinite, Ca-montmorillonite and Ca-illite were 2.94, 11.8, and 15.1 μmol/g respectively. Öztürk and Kavak [9] studied the boron adsorption on raw and HCl activated sepiolite and found the Langmuir isotherm capacities as 96.15 and 178.57 mg/g, respectively.

The stability of colloids in a suspension is mainly dependent on electrostatic surface potential is known as zeta potential. Generally, the surface charge development in clays is related to the density of broken bonds like silicon and aluminum and the hydroxylation or protonation of the surface of clays. Talc is a layered hydrous magnesium silicate with the chemical formula of $Mg_3(Si_2O_5)_2(OH)_2$. Talc clay belongs to 2:1 group of clays (two tetrahedral and one octahedral layer) [15]. The world's total talc reserves have 2.4 billion tons capacity. The economically valuable talc deposits are ultramafic-related talc deposits and talc deposits within dolomites [15].

In this study, boron adsorption onto modified talc clay was optimized by applying 2^3 factorial experimental design. One of the optimization approaches is the use of an optimization program such as Minitab for applying factorial design, response surface and Taguchi methods to data. The optimization of parameters by the Minitab program is useful for operating the removal process such as adsorption, reverse osmosis, electrocoagulation, etc. But the parameter intervals to be analyzed should be determined correctly. Therefore, the theory and mechanism of the removal process are rather well be known or preliminary experiments should be done. When preliminary experiments are performed, the optimum conditions become already to be determined but parameter interactions cannot be known. For this purpose, in this study, the preliminary experiments were done to determine the parameter intervals and parameter interactions were evaluated by ANOVA analysis and graphical inferences using 2^3 factorial experimental design. The literature survey showed that the raw and aluminum loaded talc have not been used for boron removal from solutions. Therefore, the modified talc and raw talc were tested for boron adsorption. Attenuated total reflection fourier-transform infrared spectroscopy (ATR-FTIR) analyses for modified and boron adsorbed modified talc were performed.

2. Material and method

2.1. Batch adsorption experiments

The used talc clay was provided from the Emirdağ District of Afyon province in Turkey. The clay was ground before being modified. The modification procedure of the talc was as follows: An amount of 100 g natural talc clay was treated at 200 rpm speed and room temperature during 24 h with 10 g aluminum chloride dissolved in 500 mL pure water. Then, the talc suspension was filtered by filter paper and dried in an oven for 24 h at 103°C and sieved to 180–425 μm particle size. The modified talc was stored in a polyethylene bottle. This aluminum chloride amount was the optimum value. The X-ray powder diffraction pattern of the raw talc is given in Fig. 1. In the experiments, the effect of pH, concentration, solid-to-liquid ratio and temperature were tested. A time span of 45 min was found as enough for equilibrium between solution and raw and modified talc, the experiments were conducted during 24 h in an incubator shaker. pH values of the solutions were adjusted using 0.1 M HCl or NaOH solutions. Boron solutions were prepared using Merck grade (Germany) solid boric acid. The raw and modified talc samples were added to the boron solutions (50 mL) of which pH and concentrations were adjusted to the desired value and treated in the orbital incubator shaker for 24 h at 150 rpm agitation speed. The boron adsorbed talc particles were centrifugated at 5,000 rpm or filtered with Whatman filter paper when needed. Boron was measured by the titrimetric method. The procedure was as follows: 5 mL clear boron solution was transferred to 100 mL beaker and 50 mL pure water was added. The pH of the solution was adjusted to 7.6 and then D-mannitol was added up to pH decrease become stable. After D-mannitol additions, the solution was titrated using 0.02 N KOH solution up to pH became again 7.6. The base consumption was used in the calculation of boron concentration. The base solution was daily standardized with a 500 mg/L boron solution. 1 mL of 0.02 N KOH solution is equal to 0.6964 mg B_2O_3. The factorial experimental design experiments were carried out according to experimental matrix conditions. The boron adsorption capacity was calculated by using the following equation.

$$Q_e = \frac{\left(C_0 - C_e\right)}{m} \times V \quad (1)$$

Here Q_e is the adsorption capacity (mg/g), C_0 is initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), m is the adsorbent amount and V is the solution volume (L).

2.2. ATR-FTIR and kinetic experiments

The aluminum loaded talc clay was prepared by stirring 100 g talc with 10 g $AlCl_3$ in 500 mL solution at 200 rpm speed and dried at 103°C temperature. The particle size was 0–425 μm in ATR-FTIR analysis. The ATR-FTIR analysis of this material was measured as aluminum talc. The boron adsorbed aluminum talc clay was prepared by stirring 15 g aluminum loaded talc clay with 500 ppm boron solution at 500 mL, pH = 7, 1,000 rpm, 22.5°C, 45 min, 100–200 μm. The ATR-FTIR analysis of this material was measured as boron adsorbed aluminum talc. Boron removal kinetic experiments were carried out in a jacketed batch reactor with pH = 7, 500 mL, 25°C, 10 gram, 180–425 μm, 500 mg/L boron, and 500 rpm conditions.

3. Results and discussion

3.1. pH effect on boron adsorption

The industrial boron wastewaters have changing pH levels. In this study, boron adsorption onto raw and aluminum modified talc clay was studied at a pH range of 4–12. The experimental parameters were as follows: 0.8 g/50 mL solid-to-solution ratio, 25°C temperature, 500 mg/L boron concentration, 150 rpm agitation speed. The results are given in Fig. 2a. The highest boron adsorption capacity value of the modified talc clay was obtained at pH 7 as 3.1 mg/g. The reason for the maximum capacity at pH 7 was that the adsorbed aluminum on the modified talc was at positive aluminum cation and the aluminum hydroxide

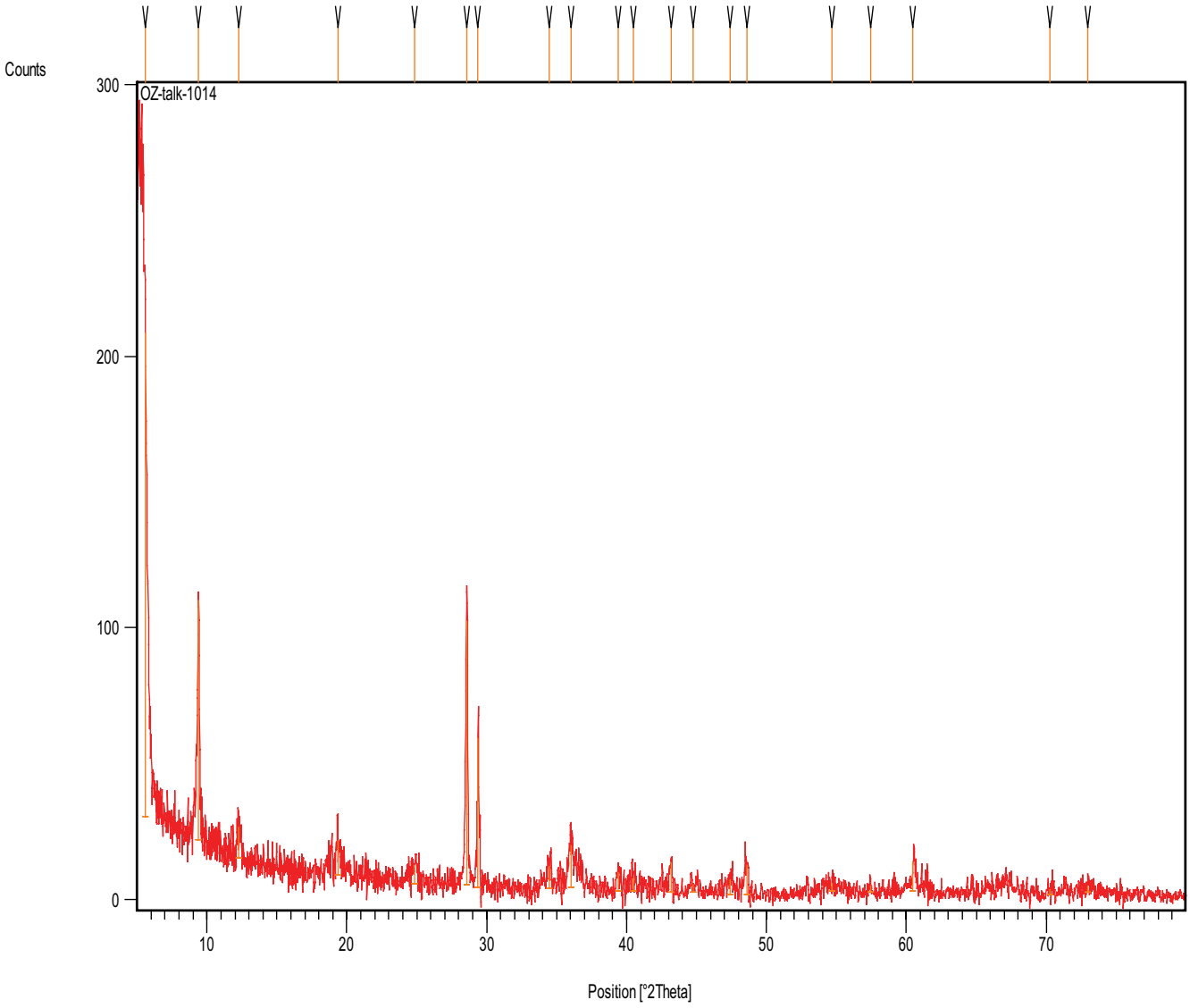

Fig. 1. XRD pattern of raw talc clay.

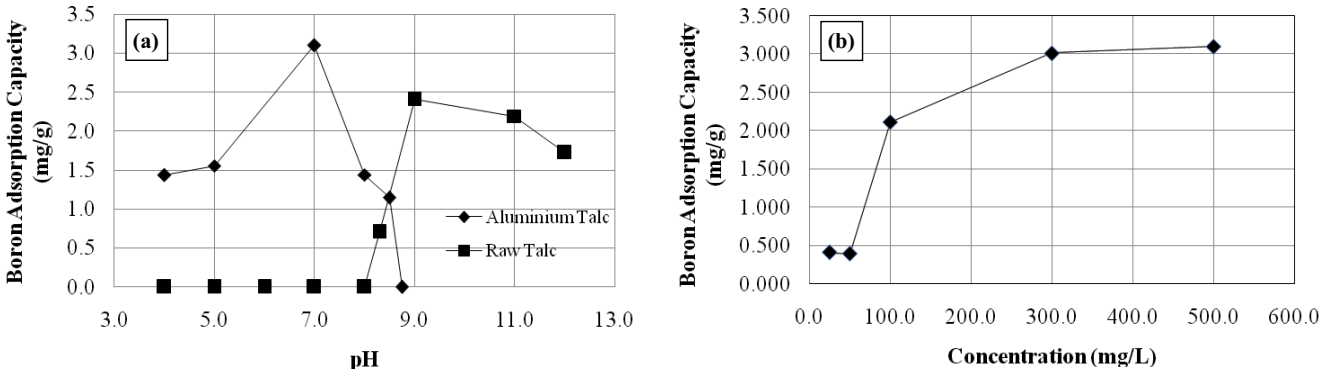

Fig. 2. (a) pH effect on boron adsorption of raw and modified talc and (b) Concentration effect on boron adsorption of modified talc.

forms. Also, at high pHs above pH 7, hydroxyl ions in solutions competed against to boron. The modified talc clay had high capacity than raw talc and modified talc was used in further experiments. The optimum pH value was determined as 9 for raw talc and this situation was due to the more affinity of the talc surface against $B(OH)_4^-$ (monoborate ions) under minimal competition state with hydroxyl anions. The capacity increase of raw talc after pH 8 is probably the affinity increase of structural magnesium hydroxide against monoborate and thus boron capacity of magnesium hydroxide increased to upper value at pH 9 [16]. The magnesium hydroxide has a high percent fraction as can be seen in the formula of talc clay ($Mg_3(Si_2O_5)_2(OH)_2$). The magnesium hydroxide shows a similar trend with raw talc at a pH range of 8–12 and as an example to this situation magnesium oxide is present as magnesium hydroxide above pH 8.5 and showed similar trend at a pH range of 8–12. The raw talc gained a more positive charge for boron adsorption after modification with aluminum and more boron adsorbed at pH = 7. Yılmaz et al. [17] reported to the coagulation property of aluminum hydroxide generated in an electrocoagulation process had high capacity at pH around 8 for boron removal. Xu et al. [18] reported that boron adsorption by am-$Al(OH)_3$ was high at pH range of 8–9. Maximum boron adsorption onto kaolinite clay was reported at a pH between 8 and 9, close to the pKa of boric acid [13].

3.2. Concentration effect on boron adsorption

The degree of boron removal is important to reduce the boron concentration to limit value which is 2.4 mg/L for drinking water and 1 mg/L for irrigation water use for sensitive plants and wastewater discharge. High boron discharge affects the health of living organisms in the ecosystem. Boron concentration effect on the removal capacity was studied at a range of 25–500 mg/L and other parameters were pH (7), temperature (25°C), solid-to-solution ratio (0.8 g/50 mL), 150 rpm agitation speed. The results are given in Fig. 2b and as can be seen in Fig. 2b, the boron adsorption capacity increased with increasing concentration. The optimum concentration was determined as 500 mg/L. The increasing effect of high boron concentration was due to the high driving force of elevated concentrations of boron. It was reported by Çengeloğlu et al [19] that the effect of decreasing red mud dosage-to-boron ratio increased the boron uptake capacity.

3.3. Solid-to-solution ratio effect on boron adsorption

The optimum adsorbent amount in the removal of pollutants like boron is a critical matter in the operation of the removal process and control of sludge production. Boron removal as a function of solid-to-solution ratio was carried out at a range of 0.8–3 g/50 mL and other parameters were pH (7), concentration (500 mg/L), temperature (25°C), 150 rpm agitation speed. The results are given in Fig. 3a. The optimum solid-to-solution ratio was determined as 0.8 g/50 mL and the low adsorbent amount caused to increase of capacity as a result of high concentration gradient on low adsorbent active site. It was reported by Çengeloğlu et al [19] that the effect of decreasing red mud dosage increased boron uptake capacity. In another study on boron removal, it was reported that the removal percentage of boron was increased with increasing calcined alunite dosage, which was due to the increase in surface area of the calcinated alunite [20].

3.4. Temperature effect on boron adsorption

There are two effects of temperature on boron adsorption onto adsorbents which are endothermic or exothermic processes. Boron adsorption onto modified talc clay was studied at a temperature range of 25°C–45°C and other parameters were concentration (500 mg/L), solid-to-solution ratio (0.8 g/50 mL), 150 rpm agitation speed, pH (7). The results are given in Fig. 3b. Boron adsorption onto modified talc was exothermic nature and the capacity increased at low temperatures. Similarly, the boron adsorption onto alunite was reported as an exothermic process for operation temperatures of 25°C, 35°C, and 45°C [20].

3.5. Solution volume effect on boron adsorption

The volume effect was studied for modified talc clay. The solution volume effect was studied at pH = 7, 25°C, 150 rpm, 1 g for 50 ppm boron and 0.4 g for 10 ppm at 10, 20, 30, and 40 mL synthetic borated solution volumes. The maximum boron removal percentages were 53.01% and 42.86% for 10 and 50 ppm boron solutions at 10 mL volume. For

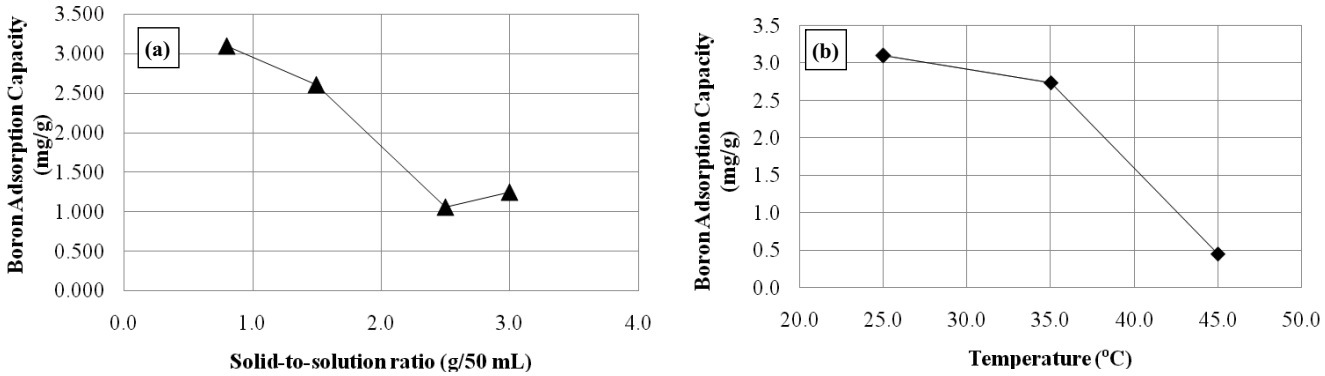

Fig. 3. (a) Solid amount effect on boron adsorption of modified talc and (b) Temperature effect on boron adsorption of modified talc.

the other solution volumes, the boron removal percentages were about constant and were 23.81%, 6.02% for 50 ppm and 10 ppm. The constant removal percentages of boron after 10 mL solution volume were considered to be related to the increase of boron adsorption driving force between solution and adsorbent surface because of the volume increase of the solution at the same boron concentration causes to the high driving force. On the other hand, it is expected that high volume results in a low removal percentage. The results are given in Fig. 4a.

3.6. Thermodynamic analysis

The thermodynamic analysis of adsorption data based on temperature provides to obtain information for the nature of the adsorption process (i.e. physical or chemical reaction or spontaneous or unspontaneous). The Gibbs free energy change is a function of the equilibrium constant, enthalpy and entropy as follows.

$$\Delta G = -RT\left(\ln K\right) \tag{2}$$

$$\ln K = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \tag{3}$$

$$K = \frac{Q_e}{C_e} \tag{4}$$

where ΔG is the free energy change (J/mol). ΔH is the enthalpy change (J/mol). ΔS is the entropy change (J/mol K). $K = (Q_e/C_e)$ 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 linear Eq. (3) respectively. The Gibbs free energy change of the process was calculated as 12.341, 13.101, and 18.49 kJ/mol for 25°C, 35°C, and 45°C temperatures. The enthalpy of the boron adsorption onto aluminum loaded talc clay was calculated as –78.545 kJ/mol and entropy of the process was calculated as 302.4 J/mol K.

The negative value of enthalpy indicated to the exothermic nature of the adsorption. The positive value of Gibbs free energy change indicates the unspontaneous nature of the adsorption. A positive value of entropy is the evidence of increasing the adsorption–desorption rate of boron [21]. The figure belonging to ln(K) vs. (1/T) is given in Fig. 4b.

3.7. Design of experiments for boron removal from solutions

When the statistical importance of factors and their interactions on the response is to be known, the statistical analysis methods such as response surface and factorial design are applied. In this study, the Minitab 16.0 program was used for the design and optimization of factors. The factorial design contains limitations like untaken into consideration the parabolic terms and like an analysis in the

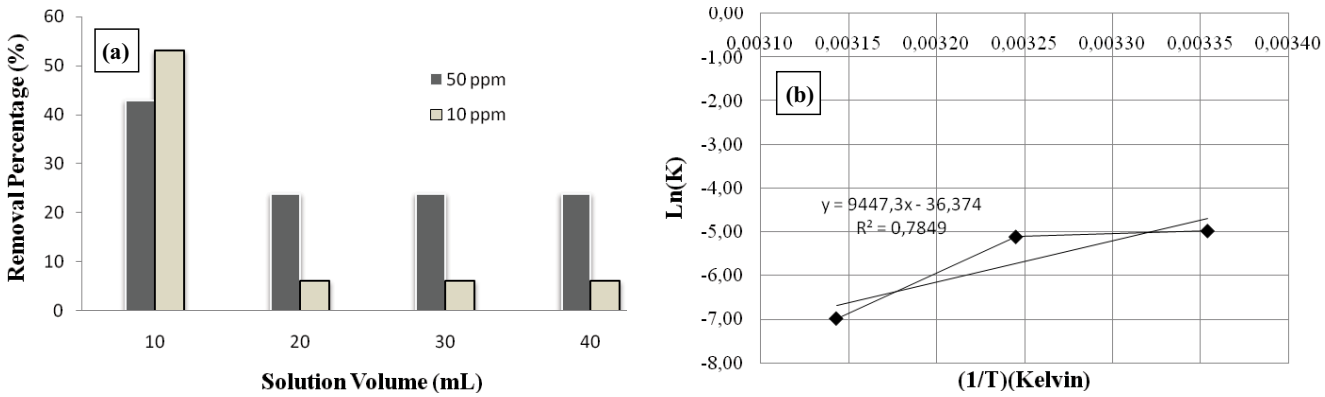

Fig. 4. (a) Effect of solution volume on boron removal and (b) Thermodynamic analysis of boron adsorption of modified talc.

experimental factor space [22]. The response for the statistical analysis was the boron adsorption capacity. 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 [3,20]. In general, the larger the magnitude of t and the smaller the value of p, the more significant is the corresponding coefficient term [3,20]. The general regression model is given as follows.

$$\text{Capacity (mg/g)} = b + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_2 + b_5X_1X_3 + b_6X_2X_3 + b_7X_1X_2X_3 \quad (5)$$

Here; b, b_1, b_2, b_3, b_4, b_5, b_6, b_7 are model constants and X_1, X_2 and X_3 are coded factors representing pH of the solution, solid amount and concentration, respectively.

The experimental matrix for boron removal from solutions is given in Table 1. As can be seen in Table 1, the matrix factors are solution pH, solid-to-solution ratio and concentration. The ANOVA analysis of boron removal by modified talc clay is given in Tables 2 and 3. The confidence level of analysis was assumed as 85% to determine a limit at which maximum factors are significant and also to obtain a regression model covering all parameters within statistical confidence. In the analysis, the pH-concentration-solid interaction effect was highly distorted the statistical analysis of parameters and therefore this factor was omitted from the regression model. The regression model was developed as follows.

$$\text{Capacity (mg/g)} = 1.1219 + 0.5276C + 0.1151\text{pH} - 0.3879S + 0.1594\text{CpH} - 0.2196\text{CS} - 0.0141\text{pHS} \quad (6)$$

The significance row of the factors and their interactions were obtained as follows: Model constant, concentration, solid amount, concentration-solid amount, concentration-pH, pH, pH-solid amount. The Pareto chart of the analysis is given in Fig. 5a. The concentration and solid amount were found as statistically important at 85% confidence level and it can be seen in Fig. 5a. The contour plots of the analysis are given in Fig. 5b. As can be seen in Fig. 5b, boron adsorption capacity of the modified talc increased with increasing pH-concentration, low solid-high concentration and was unclear for solid-pH interaction.

3.8. Isotherm and kinetic 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 reactor. 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 follows [23]:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \quad (7)$$

Table 1
Low and high levels of parameters for optimization

Parameters	Abbreviation	Low level	High level
Modified talc			
pH	pH	3	7
Solid amount (g/50 mL)	S	1.5	3
Concentration (mg/L)	C	100	500

Table 2
Experimental matrix for optimization and responses (25°C, 50 mL, 150 rpm, 24 h)

Experimental parameters				Boron removal
Run	Concentration	Solution pH	Solid	Adsorption capacity (mg/g)
1	100	7	1.5	0.674
2	100	3	1.5	0.851
3	100	7	3	0.426
4	100	3	3	0.426
5	500	7	1.5	2.604
6	500	3	1.5	1.91
7	500	7	3	1.244
8	500	3	3	0.84

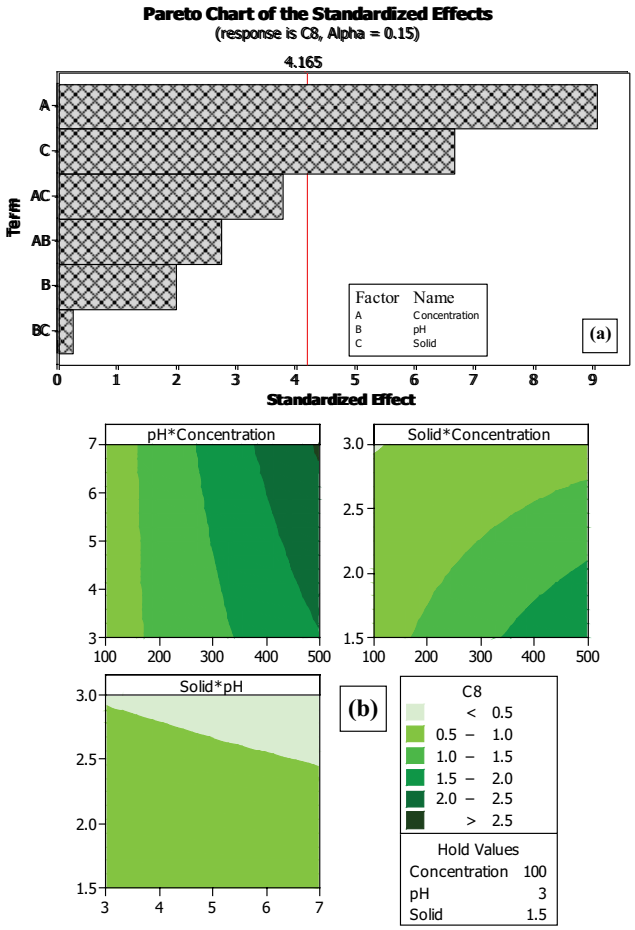

Fig. 5. (a) Pareto chart of analysis and (b) surface plots for boron removal.

where C_e is the equilibrium concentration in the liquid phase (mg/L). q_e is the maximum amount of the boron adsorbed (mg/g). q_m is q_e for a complete monolayer (mg/g). k_L 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 [23]:

$$\ln q_e = \ln k_F + \left(\frac{1}{n}\right)\ln C_e \tag{8}$$

where C_e is the equilibrium concentration in the liquid phase (mg/L). q_e is the maximum amount of boron adsorbed (mg/g). k_F is the Freundlich adsorption capacity. $1/n$ is the sorption equilibrium constant.

The isotherm data fitted to the Langmuir isotherm model indicating monolayer adsorption of boron ions. The coefficient of determination values for the Freundlich isotherm and Langmuir isotherm were calculated as 0.833 and 0.950, respectively. The q_m and k_L values for the Langmuir isotherm were calculated as 3.953 mg/g and 0.0096 L/mg. The k_F and n values were calculated as 10.2 and 1.6. The isotherm data belong to Fig. 2b. Kinetics of boron removal by aluminum loaded talc mineral is important for boron removal in a batch reactor and kinetics of removal determines the retention time of solution in the batch reactor and diffusion model establishes the mechanism of removal. The widely used kinetic models are pseudo-second-order and pseudo-first-order models.

Lagergren's first-order kinetic model is given as follows [24].

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{9}$$

Ho's pseudo-second-order kinetic model is given as follows [25].

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \tag{10}$$

where k_1 is the rate constant of the pseudo-first-order equation (min^{-1}). k_2 is the rate constant of the pseudo-second-order equation (g/mg min). q_e is the theoretically sorbed amount at equilibrium (mg/g). q_t is the sorbed amount at any time t (mg/g). The fitness of the equations is determined from coefficients of determination values.

The kinetic plot of boron removal by modified talc is given in Fig. 6a. The experimental parameters were pH = 7, 500 mL, 25°C, 10 gram, 180–425 μm, 500 mg/L boron, 500 rpm. Kinetic data could be described with the pseudo-second-order kinetic model and the coefficient of determination value for the model was 1.0. The pseudo-first-order equation is widely used but its applicability may be questionable due to the heterogeneity of the sorbent surfaces and diversity of sorption phenomena (transport, surface reaction) as pointed out by Ho and Mckay [26]. Also, as stated by Mckay et al. [27], the pseudo-first-order equation may be valid only for a short time of a reaction or multiple series of the pseudo-first-order may occur. A general acceptance was also suggested by Azizian [28], which assumes that the pseudo-first-order and the pseudo-second-order equations can be employed with high and low initial concentrations of solutions, respectively. It was investigated which step was controlling the diffusion of boron into the modified talc clay. Assuming adsorption of boron as a liquid-solid phase reaction, which includes the diffusion of boron through the liquid film, the diffusion of boron within the clay pores and chemical reaction between boron and clay surface, three possible adsorption mechanisms can be proposed as follows [29];

A fractional approach to the equilibrium:

$$F = \left[\frac{\left(C_0 - C_t\right)}{\left(C_0 - C_e\right)}\right] \tag{11}$$

Film-diffusion controlled process:

$$\ln\left(1 - F\right) = -k_f t \tag{12}$$

Particle-diffusion controlled process:

$$\ln\left(1 - F^2\right) = -k_p t \tag{13}$$

Moving boundary process:

$$3 - 3\left(1 - F\right)^{2/3} - 2F = k_m t \tag{14}$$

where F is the fractional approach to the equilibrium. k_f is the film diffusion rate constant. k_p is the particle diffusion rate

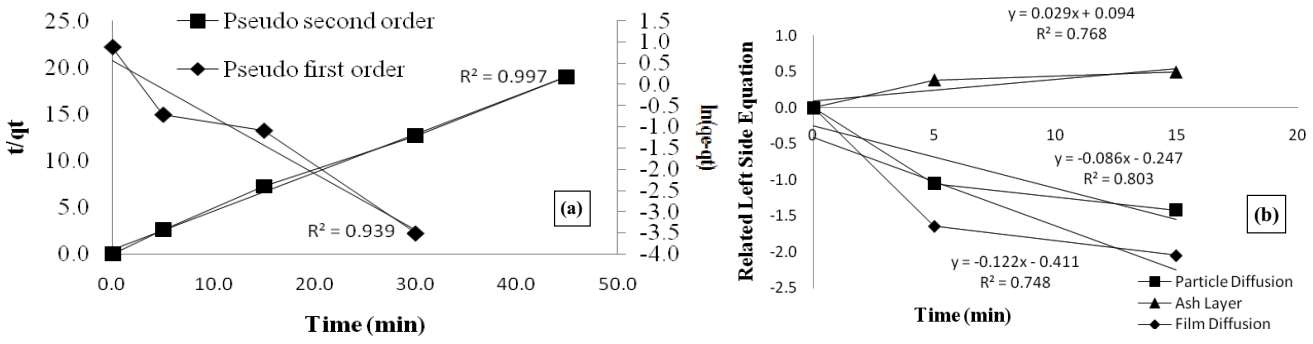

Fig. 6. (a) Kinetic models and (b) diffusion models.

Table 3
Factorial fitness and ANOVA analysis for boron removal from solutions

Source	Seq SS	Adj SS	Adj MS	F	p
Main effects	3.53671	3.53671	1.17890	43.24	0.111
Concentration	2.22711	2.22711	2.22711	81.70	0.070
pH	0.10603	0.10603	0.10603	3.89	0.299
Solid	1.20358	1.20358	1.20358	44.15	0.095
Concentration × pH	0.20320	0.20320	0.20320	7.45	0.224
Concentration × solid	0.38588	0.38588	0.38588	14.15	0.165
pH × solid	0.00160	0.00160	0.00160	0.06	0.849
Residual error	0.02726	0.02726	0.02726		
Total	4.15465				

constant. k_m is the moving boundary process rate constant. The fitness of kinetic data to the diffusion model is given in Fig. 6b and the data fitted to the partial particle diffusion model.

3.9. Mechanism of removal and novelty of findings

The treated talc clay with aluminum cation caused to exchange of structural magnesium with aluminum and adsorption of aluminum to the negative surface of talc. Thus the interior sites and surface of the talc gained positive charge and boron binding occurred at that sites and also probably boron adsorption by inner-sphere and outer-sphere binding in pores of the adsorbent and at surface, aluminum hydroxide groups occurred. The crystal structure of talc is given in Fig. 7 [30] and boron adsorption also occurred at broken edges (aluminum or silicon) forming after grinding. The molecular size of boric acid is several hundred picometers. The ATR-FTIR spectrums of modified talc and boron adsorbed modified talc clay are given in Fig. 8. As can be seen in Fig. 8a, the bands between 3,675 and 3,660 cm^{-1} are associated with the stretching of OH associated with magnesium (Mg–OH and Mg_3–OH) [31]. Also, the pics between 3,000 and 3,660 cm^{-1} are probably due to the aluminum hydroxide and water-OH groups [32]. The band at 1,639 cm^{-1} is associated with the deformation vibration of water molecules.

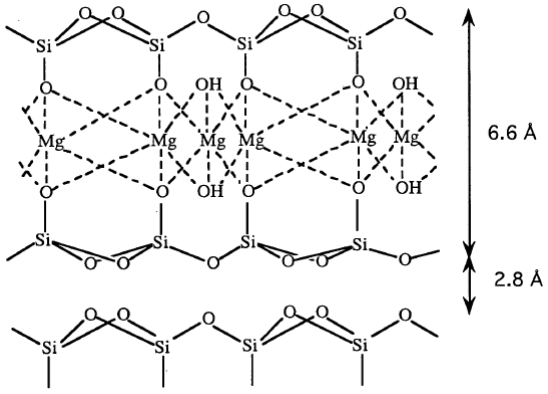

Fig. 7. Crystal structure of talc clay.

One can observe the vibration bands attributed to the Si–O–Si at 987 cm^{-1} [31]. The Si–O bands are seen at 755 cm^{-1} [31]. The 3,401 cm^{-1} vibration decrease in Fig. 8b is probably due to boron adsorbed on aluminum hydroxide.

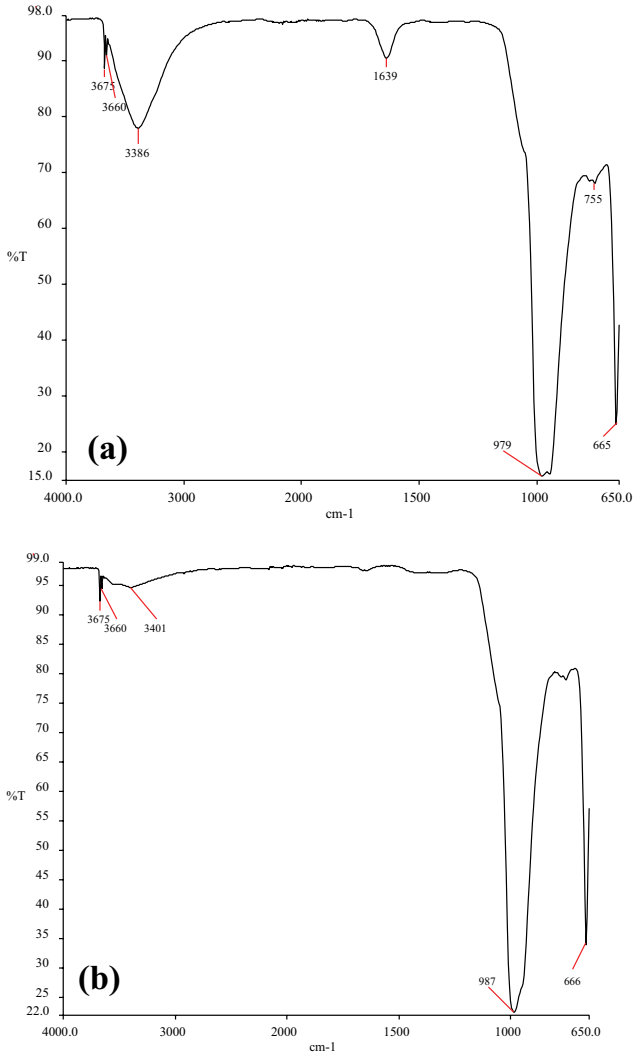

Fig. 8. (a) ATR-FTIR spectrum of aluminum talc clay and (b) ATR- FTIR spectrum of boron adsorbed aluminum talc clay.

As can be seen in Fig. 2b, the capacity of modified talc was increased with concentration increase between 0 to 500 ppm and boron removal percentage by modified talc was found as insufficient for 0–500 ppm at 0.8 g/50 mL solid amount. However, the findings for 10 and 50 ppm (Fig. 4a) which are quite high for common drinking water concentrations are found as quite appropriate for drinking water treatment. The boron removal percentages for 10 and 50 ppm concentrations were 53.01 and 42.86% at 0.4 g/10 mL and 1 g/10 mL dosages, respectively. The boron is a problematic contaminant for removal from drinking water sources. The boron concentration for drinking water usage is 2.4 ppm according to the report of the World Health Organization [33]. For instance, one of the boron problematic regions of Turkey is the Kütahya-Emet region due to boron deposits and the highest boron and arsenic concentrations in underground water and surface waters are between 2.4–3.25 ppm for boron and 1 ppm for arsenic [34]. On the other hand, the borated talc clay may be found usage field in ceramic, lightweight building materials and insecticide production [35]. If the modified talc clay is used for boron removal from low concentration drinking water sources, the sludge production will be low and it may find industrial usage.

4. Conclusion

The feasibility of boron removal from solutions by raw and aluminum modified talc clay was investigated using classical single parameter experiments and factorial experimental design. The raw talc had low adsorption capacity than modified talc and further experiments were carried out by modified talc except for pH experiments. Optimum pH value for boron adsorption to modified talc was calculated as 7 and optimum concentration was 500 mg/L. The process had exothermic nature and the adsorbent amount providing to maximum capacity was 0.8 g/50 mL for modified talc. The boron adsorption process was found as unspontaneous and isotherm data fitted to the Langmuir isotherm. The kinetic data fitted to the pseudo-second-order model and particle diffusion model. The significant row of the factors and their interactions for factorial design were obtained as follows: Model constant, concentration, solid amount, concentration-solid amount, concentration-pH, pH, pH-solid amount. The maximum adsorption capacity of the modified talc was calculated as 3.1 mg/g. The ATR-FTIR analysis of modified talc confirmed the boron adsorption onto $Al(OH)_3$.

Acknowledgment

The authors are grateful for financial support of Balıkesir University Scientific Research Project Department

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