

Application of iron-rich natural clays in Çamlica, Turkey for boron sorption from water and its determination by fluorimetric-azomethine-H method

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Abstract

In this study, iron-rich natural Çamlica Bentonites, CB1 and CB2, were used for the sorption of boron in water samples. Boron was determined by newly progressed fluorimetric azomethine-H method. The optimum conditions found using factorial designs are pH 10, 45 °C, 0.250 g of clay and 20 mL of sample volume. It was found that 180 min is enough time for the equilibrium state to be reached in boron adsorption. At these conditions, boron sorption percentage was 80% for CB1 and 30% for CB2. The adsorption isotherms are well described by linear Freundlich model. Various geothermal waters in our country were also studied for boron sorption.

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1. Introduction

Boron and boron compounds are widely used in industrial applications [1]. During the production of boron compounds, much of these are introduced into the environment in the form of waste. They form some complexes with heavy metals so that the potential toxicity of heavy metals increases. Thus, boron compounds cause some serious health and environmental problems, when the complexes pass to groundwater [2]. A very low boron content is required in irrigation water for certain metabolic activities, but if its concentration is only slightly higher, plant growth will exhibit effects of boron poisoning, which are yellowish spots on the leaves and fruits, accelerated decay and ultimately plant expiration [3,4].

Clays are the main components of the mineral fraction of soils. They are efficiently natural in consequence of both their particle size lower than 2 µm and their lamellar structures which give them a very large reactive surface area [5]. The important source of boron adsorbing surfaces is clay minerals. The boron adsorption on clay minerals is fast but fixation is slow [6]. Up

to now, many different materials such as modified or unmodified clay minerals, oxides, polymeric gels and active carbon were used for the removal of boron from waters and wastewaters by adsorption technique. Certain clays having mostly SiO₂ and Al₂O₃ such as sepiolite [7], modified bentonite [8], siral samples [9], and siral-30 and pural [10] have been used in the application of boron sorption.

Boron adsorption is a pH dependent process. The species of B(OH)₃, B(OH)₄⁻ and OH⁻ compete for the sorption sites. At low pH values, B(OH)₃ is the dominant component in solution. Therefore, the amount of adsorbed is lower due to low affinity of B(OH)₃ to the clay surface at present pH values. However, at higher pH values, B(OH)₄⁻ is the major component and its affinity to the clay surface at higher pH values is relatively higher. Therefore, the amount of boron adsorbed increases with increasing of solution pH [11].

The application of statistical experimental design techniques in adsorption process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements, and reduced development time and overall costs [12,13]. It is also possible to reduce the number of experiments.

The study aims to determine the adsorption capacity of two kinds of iron-rich bentonite clays for boron using full factorial

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design and its determination by newly derivatized fluorimetric-azomethine-H method.

2. Materials and methods

2.1. Apparatus

Fluorescence was monitored with a Varian Cary Eclipse model spectrofluorometer, equipped with xenon arc lamp and a photomultiplier tube. All measurements were performed in a standard 10 mm path length quartz cell. The boron measurements using ICP atomic emission spectrometer were carried out with Perkin Elmer model DV 3300 (Norwalk, CA, USA). The used emission line of boron was B I 249.773 nm. The line of internal standard indium (In I 325.609 nm) and copper (Cu I 324.754 nm) were used for matrix effect correction [14]. The operating condition was as followed: plasma power supply 1.3 kW, observation height 6 mm, plasma gas flow 15 L min⁻¹, auxiliary gas flow 0.5 L min⁻¹, nebuliser gas flow 0.8 L min⁻¹, photomultiplier voltage 600 V, sample uptake rate 1.7 mL L⁻¹, integration time 1 s, sample time delay 30 s. A WTW InoLab pH meter was used for all pH measurements. Adsorption experiments were carried out in an isothermal water-bath circulator (Lindberg Blue, USA) at 150 rpm. For adsorption experiments, the water used throughout the work was deionized by Millipore Milli-Q system.

2.2. Chemicals and materials

Boric acid (Merck) was used without treatment. Boron standard stock solution as 1000 mg L⁻¹ was prepared using boric acid in deionized water. Further solutions were freshly prepared from stock solution for each experimental run. The ICP standard solutions of In and Cu as 10 mg mL⁻¹ in HNO₃ from Aldrich were used. For pH adjustment, 0.1–1.0 mol L⁻¹ NaOH or HCl solutions were used. One gram of azomethine-H sodium salt (Fluka) and 3 g of L(+)-ascorbic acid were dissolved by deionized water up to 100 mL. Citrate buffer (pH 5.9) was prepared using citric acid (0.002 M) and sodium citrate (0.001 M). Reagent solution having equal volumes of azomethine-H and buffer solution was freshly prepared for determination of boron. Stock solution of sodium dodecylsulfate (SDS, Merck) as 5 × 10⁻² mol L⁻¹ was prepared in deionized water.

Iron-rich clays were provided by a local place located in Çamlica/Mustafakemalpaşa. They were dried, and then washed with deionized water for many times to remove any dust and other water-soluble impurities. Before use in adsorption experiments, the processed clays were oven-dried at 105 °C for 2 h and stored in a desiccator for further studies.

2.3. Sampling of water samples

Tap water was taken from Chemistry Laboratory in Dokuz Eylül University. Geothermal water samples were collected from Dikili and Balçova, İzmir. The water samples were filtered through 0.45 µm membrane filter before sorption experiments. Sampling and analysis were performed within the same day.

Table 1
Factors and levels used in Factorial Design

| Factor | Level | |
|--|-------|-------|
| | (-) | (+) |
| Temperature (<i>T</i> , °C) | 25 | 45 |
| pH | 5.7 | 10.0 |
| Volume of sample solution (<i>V</i> , mL) | 20 | 50 |
| Mass of adsorbent (<i>m</i> , g) | 0.100 | 0.250 |

2.4. Batch adsorption experiments

In batch adsorption experiments, adsorbent was put onto tightly switched erlenmeyer flask each of which contain 10 mg L⁻¹ boron solution and shaken at 200 rpm for 3 h in a temperature-controlled water bath circulator. After adsorption, samples were centrifuged at 4000 rpm for 15 min and the amount of boron in supernatant solution analyzed spectrofluorimetrically.

2.5. Determination of boron with azomethine-H-fluorimetric method

In boron determination method, reagent solution and 1 × 10⁻² mol L⁻¹ of SDS as micelle were mixed with 2–20 mg boron containing supernatant solution and was diluted to 10 mL with deionized water using calibrated flask. The complexation reaction was completed within 10 min and the final solution was measured at emission wavelength 486 nm with excitation at 416 nm using spectrofluorometer with excitation and emission slits as 5 nm [15].

2.6. Statistical design of experiments

The parameters involved in the adsorption experiments were optimized by a full factorial design (2⁴) using statistical software, MINITAB (Version 13.32) of Minitab, Inc., USA. Minimum (-) and maximum (+) levels used for boron adsorption system was defined from previous assays. The levels -1 and +1 in the adsorption of boron for temperature (*T*), pH, volume of sample solution (*V*) and mass of adsorbent (*m*) are given in Table 1. All the experiments were carried out in random order in duplicates using 10 mg B L⁻¹ and contact time as 3 h.

3. Results and discussion

3.1. Characterization of clays

The surface area, pore size distribution and chemical compositions of Çamlica Bentonites (CB) are summarized in Table 2. Major constituents of the clays are SiO₂, Al₂O₃ and Fe₂O₃ and some metal oxides with small amounts are also present. Specific surface area and pore size distribution of the samples were determined according to the BET method after adsorption of N₂ gas at 77 K by using Quantachrome Autosorb 3B. The adsorption-desorption data was evaluated by using Autosorb for Windows for AS-3 and AS-6 Version 122 software.

Table 2
Chemical composition of iron-rich CB clays

| | CB1 | CB2 |
|--|----------------------|-------|
| Surface area (m^2/g) | 107.2 | 111.2 |
| Average pore diameter (\AA) | 50.03 | 53.51 |
| Chemical composition | Percentage by weight | |
| SiO ₂ | 48.21 | 44.55 |
| Al ₂ O ₃ | 13.10 | 11.91 |
| Fe ₂ O ₃ | 9.97 | 12.12 |
| MgO | 3.17 | 2.82 |
| CaO | 2.59 | 1.92 |
| Na ₂ O | 0.06 | 0.06 |
| K ₂ O | 0.47 | 0.45 |
| TiO ₂ | 0.46 | 0.40 |
| P ₂ O ₅ | 0.01 | 0.01 |
| MnO | 0.02 | 0.03 |
| Cr ₂ O ₃ | 0.04 | 0.04 |
| Ignition loss | 21.92 | 25.85 |

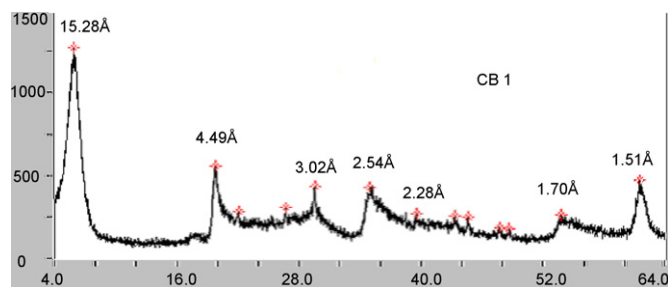


Fig. 1. XRD pattern of CB1.

The mineralogical contents of the bentonite clay samples were determined using XRD patterns. The XRD pattern of CB1 clay in Fig. 1 shows the characteristic d-spacings for smectites: 15.28, 4.49, 3.02, 2.54, 2.28, 1.70, 1.51 Å. Also, the peaks represented quartz at 3.34 Å and opal-CT at 4.03 Å. The XRD pattern of CB2 clay in Fig. 2 demonstrated the characteristic peaks for smectites: 15.17, 4.47, 3.03, 2.59, 1.71 and 1.51 Å and for quartz at 3.34 Å. As can be seen from the XRD patterns these two clays are highly purified, and consist of more than 95% smectite.

3.2. Factorial design

The relative importance and possibility of interactions between temperature, pH, sample volume and mass of sorbent

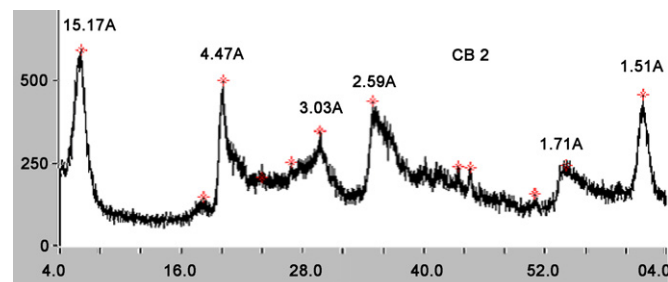


Fig. 2. XRD pattern of CB2.

Table 3
Design of trial runs for boron removal from aqueous solution in two replicate experiments for CB1

| Trial | <i>T</i> | pH | Sample volume | Mass of clay | Sorbed B (%) | |
|-------|----------|----|---------------|--------------|--------------|------|
| | | | | | (1) | (2) |
| 1 | – | – | – | – | 63.5 | 63.3 |
| 2 | – | + | – | – | 71.4 | 71.1 |
| 3 | – | – | + | – | 57.9 | 57.5 |
| 4 | – | + | + | – | 62.8 | 62.8 |
| 5 | – | – | – | + | 69.5 | 70.0 |
| 6 | – | + | – | + | 74.5 | 74.3 |
| 7 | – | – | + | + | 61.8 | 61.8 |
| 8 | – | + | + | + | 66.4 | 66.6 |
| 9 | + | – | – | – | 71.4 | 70.5 |
| 10 | + | + | – | – | 73.3 | 73.8 |
| 11 | + | – | + | – | 64.4 | 64.9 |
| 12 | + | + | + | – | 68.3 | 69.0 |
| 13 | + | – | – | + | 77.6 | 77.0 |
| 14 | + | + | – | + | 79.8 | 80.2 |
| 15 | + | – | + | + | 66.8 | 67.5 |
| 16 | + | + | + | + | 70.2 | 70.0 |

were studied using the full factorial design method. For four variables with two levels for each variable experimental design matrix, 16 possible combinations, with the recovery of boron for CB1 and CB2 were tabulated in Tables 3 and 4. The significance of the effects was checked by analysis of variance (ANOVA, statistical software, MINITAB (Version 13.32) of Minitab, Inc., USA) and using *p*-value significance levels.

The ANOVA results for boron on CB1 and CB2 produced the Pareto chart of main effects shown in Figs. 3 and 4. Bar lengths are proportional to the absolute value of the estimated effects, which help in comparing the relative importance effects. Also, according to Tables 3 and 4, 2⁴ factorial-design allows obtaining the model-function equation that represents the relationship between the variables studied as the response. The

Table 4
Design of trial runs for boron removal from aqueous solution in two replicate experiment for CB2

| Trial | <i>T</i> | pH | Sample volume | Mass of clay | Sorbed B (%) | |
|-------|----------|----|---------------|--------------|--------------|-------|
| | | | | | (1) | (2) |
| 1 | – | – | – | – | 5.70 | 5.80 |
| 2 | – | + | – | – | 12.00 | 12.20 |
| 3 | – | – | + | – | 2.60 | 2.60 |
| 4 | – | + | + | – | 9.30 | 9.30 |
| 5 | – | – | – | + | 11.50 | 11.30 |
| 6 | – | + | – | + | 17.50 | 17.30 |
| 7 | – | – | + | + | 9.10 | 9.30 |
| 8 | – | + | + | + | 15.10 | 15.30 |
| 9 | + | – | – | – | 17.50 | 17.80 |
| 10 | + | + | – | – | 24.00 | 24.20 |
| 11 | + | – | + | – | 9.80 | 10.00 |
| 12 | + | + | + | – | 18.00 | 18.20 |
| 13 | + | – | – | + | 24.00 | 23.80 |
| 14 | + | + | – | + | 30.00 | 29.90 |
| 15 | + | – | + | + | 17.70 | 17.70 |
| 16 | + | + | + | + | 22.10 | 22.10 |

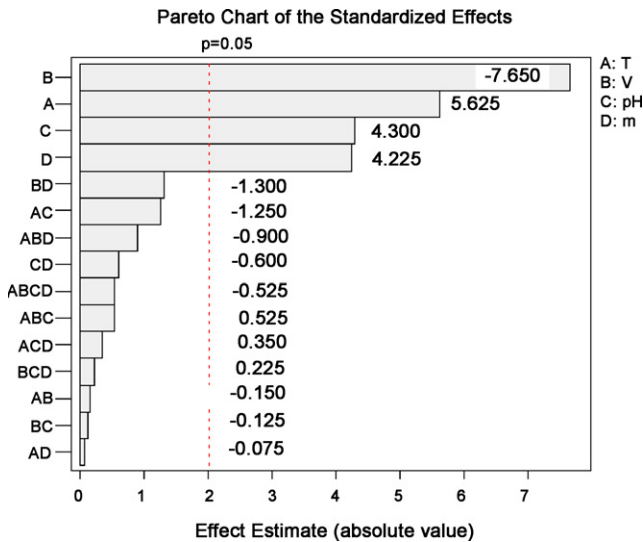


Fig. 3. Pareto Chart of standardized effects for variable in boron adsorption onto CB1. (A) temperature (T), (B) sample volume (V), (C) pH, (D) mass of clay (m).

model-function equations for B adsorption on clays are:

B adsorption on CB1

$$= +5.625 T - 7.650 V + 4.300 \text{ pH} + 4.225 m$$

B adsorption on CB2

$$= +10.075 T + 6.275 \text{ pH} + 5.925 m - 4.775 V \\ - 2.200 TV - 0.650 \text{ pH } m$$

It was concluded that four factors were effective individually for CB1. The sample volume was highest but has only negative effect and the others were slightly lower and have positive effects. The interactions among the others are not so significant. For CB2, each factor individually and the interaction between

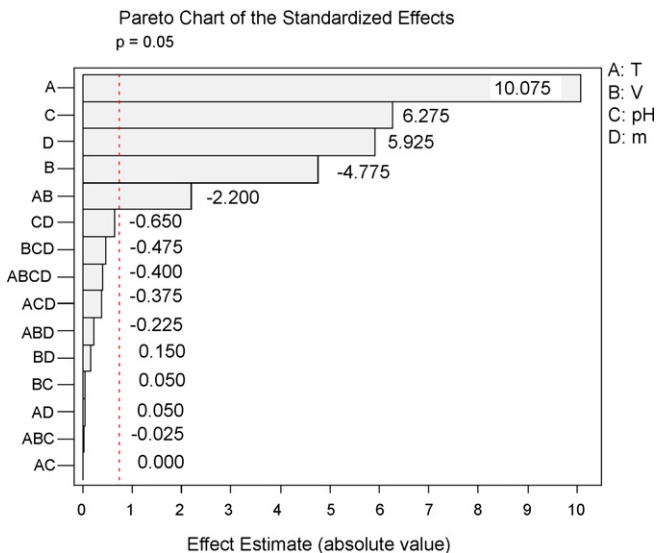


Fig. 4. Pareto Chart of standardized effects for variable in boron adsorption onto CB2. (A) temperature (T), (B) sample volume (V), (C) pH, D) mass of clay (m).

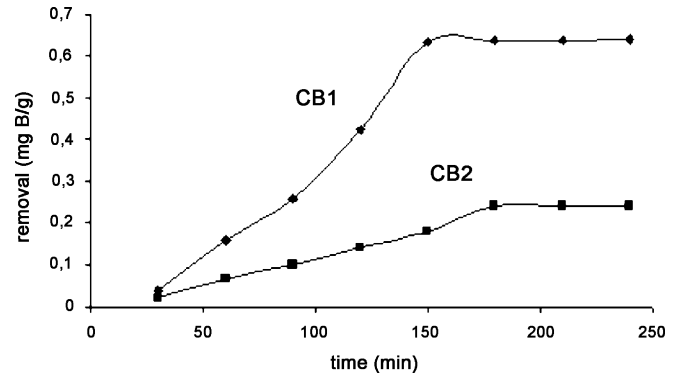


Fig. 5. Kinetics of B (10 mg L^{-1}) adsorption for CB1 and CB2 clays at 45°C .

temperature and sample volume were seen significant. In this clay, temperature has the highest effect, so it seems that adsorption increases when temperature increases. Similar effect was seen with the parameters of pH and mass of clay. Their effects are approximately equal but slightly lower than temperature effect. As it was seen in CB1, the effect of sample volume is negative but lower. The interaction between temperature and sample volume has negative small degree. As a consequence, the best adsorption conditions for CB1 and CB2 were obtained; 45°C , pH 10.0, 20 mL of sample volume and 0.25 g of sorbent.

3.3. Adsorption kinetic

The kinetic curve for B/clay system at 45°C in 10 mg B L^{-1} solution at pH 10.0, is given in Fig. 5 for CB1 and CB2. From the curves, the distribution coefficient k_d was estimated:

$$k_d = \frac{rV}{(100 - r)m} \quad (1)$$

where r is the percentage removal of boron, V is the volume of sample solution and m is the mass of adsorbent. The distribution coefficient k_d expresses the ratio of boron in the solid phase over that in the liquid phase. It defines the selectivity of the adsorbents towards the boron and is depended on the ratio V/m . Changes in the ratio V/m affect the removal of boron from solution and subsequently k_d values. The higher the maximum adsorption, expressed as percentage removal r , the greater the adsorption coefficient value [16]. Boron removal was achieved to a higher extent by CB1 clay as indicated by k_d values (320.0 mL g^{-1} for CB1 and 34.3 mL g^{-1} for CB2). Presumably, the large difference in k_d values may be due to the differences in the structural or the associated iron content and the oxidation levels of iron atoms found in these bentonite clays.

3.4. Adsorption isotherm

In order to a reasonable mechanism for boron adsorption, the adsorption isotherms were obtained. Initial boron concentrations used in this study are in the range of 1–10 ppm. Two replicates of each experiment were conducted. Isotherm profiles can give information about the nature of the adsorbed species. Data obtained from the adsorption isotherms was fitted to linearized

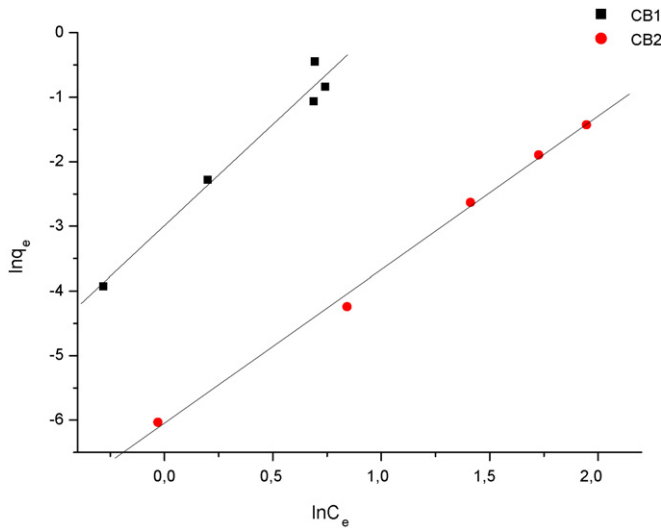


Fig. 6. Freundlich isotherm of boron sorption onto CB1 and CB2 (pH 10, $T=45\text{ }^{\circ}\text{C}$, mass of clay = 0.25 g, $V=20\text{ mL}$).

form of Freundlich (Fig. 6):

$$\ln q_e = \ln K_f + n_f \ln C_e \quad (2)$$

where q_e is the amount adsorbed per gram of adsorbent, C_e the adsorbate equilibrium concentration, n_f the isotherm constant (a measure of the deviation of the adsorption from linearity) and K_f relative adsorption capacity. Our data fit the linear form of Freundlich equations; $\ln q_e = -2.991 + 3.136 \ln C_e$ for CB1 and $\ln q_e = -6.047 + 2.377 \ln C_e$ for CB2 with $r^2 = 0.997$. The relative adsorption capacities are 0.050 mg g^{-1} for CB1 and $2.36 \times 10^{-3}\text{ mg g}^{-1}$ for CB2. Since n_f values are greater than 1, this indicates that adsorption bond becomes weak.

3.5. Salt effect

The salt effect was controlled using Na_2SO_4 and CaCl_2 at two different concentrations and results are given in Table 5. The sorption percentage was affected negatively by increasing concentration of salts. The sorption percentage for CB1 and CB2 was decreased about 7–14%. Na_2SO_4 was more effective in adsorption of boron.

3.6. Application

To show the applicability of this clay for removal of boron several geothermal water samples having in the range of

Table 5
Salt effect on boron adsorption

| | Sorption (%) | |
|------------------------------|--------------|-----|
| | CB1 | CB2 |
| 1 M Na_2SO_4 | 70 | 21 |
| 5 M Na_2SO_4 | 66 | 16 |
| 1 M CaCl_2 | 73 | 24 |
| 5 M CaCl_2 | 67 | 18 |

18–38 mg L^{-1} (Dikili, Balçova, Bigadiç) in Turkey were used. The boron removal from these geothermal water samples were achieved using only CB1 as 80% (Table 6). The analytical data given in this table indicate a high degree of correlation between the results of ICP-OES and azomethine-H-fluorimetric method. The adsorption percentage obtained in real samples was same with the synthetic adsorption batch studies. It can be concluded that when this iron-rich clay is used for treatment of water containing up to 2.5 mg L^{-1} of boron (in the adsorption isotherms) it is possible to reach the limit of recommended by WHO for boron concentration in drinking water, 0.5 mg L^{-1} [17].

4. Conclusion

In this study, iron-rich clays, CB1 and CB2 can be used as adsorbents for boron sorption $[\text{B}(\text{OH})_4^-]$ from aqueous media. It was found that 180 min is enough for the equilibrium state in the adsorption studies.

The boron removal was found dependent of the adsorbent dose, pH, sample volume and temperature. From the factorial experimental design, the optimum conditions for the best adsorption results of 10 mg L^{-1} of boron were pH 10, $45\text{ }^{\circ}\text{C}$, 0.250 g of clay and 20 ml of sample volume. At these conditions, boron sorption percentage was 80% for CB1 and 30% for CB2. Adsorption isotherms were performed for initial B concentrations ranging from 1 to 10 mg L^{-1} . The linearized Freundlich isotherms are indicating a physical adsorption for both adsorbents. The maximum adsorption capacities are according to linearized Freundlich model, 2.534 and 0.1184 mg g^{-1} for CB1 and CB2, respectively. Therefore, the adsorption capacity of CB1 is much higher than that of CB2. By these clays, boron content in geothermal water samples from Bigadiç, Balıkesir and Dikili, İzmir were also studied. As summary, this work shows that iron-rich clays could be used as adsorbent for the treatment of natural waters containing boron or to participate in one of the stage of treatment process.

Table 6
The results of determination of B in geological samples ($n=3$)

| Geothermal samples | B (mg L^{-1}) | | B sorbed (mg L^{-1}) | |
|--------------------|--------------------------|------------------|---------------------------------|------------------|
| | Fluorimetric method | ICP-OES | Fluorimetric method | ICP-OES |
| Balçova 1 | 18.63 ± 0.11 | 18.52 ± 0.10 | 14.90 ± 0.10 | 14.84 ± 0.06 |
| Balçova 2 | 20.12 ± 0.08 | 20.06 ± 0.08 | 16.32 ± 0.08 | 16.27 ± 0.09 |
| Dikili 1 | 38.08 ± 0.10 | 38.15 ± 0.12 | 30.84 ± 0.12 | 30.77 ± 0.05 |
| Dikil 2 | 36.04 ± 0.08 | 36.18 ± 0.06 | 28.83 ± 0.03 | 28.84 ± 0.04 |

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