

Removal of boron from aqueous solution by clays and modified clays

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Abstract

In order to increase the adsorption capacities of bentonite, sepiolite, and illite for the removal of boron from aqueous solution, the clay samples were modified by nonylammonium chloride. Specific surface areas of the samples were determined as a result of N₂ adsorption–desorption at 77 K using the BET method. X-ray powder diffraction analysis of the clays and modified clays was used to determine the effects of modifying agents on the layer structure of the clays. The surface characterization of clays and modified clay samples was conducted using the FTIR technique before and after the boron adsorption. For the optimization of the adsorption of boron on clays and modified clays, the effect of pH and ionic strength was examined. The results indicate that adsorption of boron can be achieved by regulating pH values in the range of 8–10 and high ionic strength. In order to find the adsorption characteristics, Langmuir, Freundlich, and Dubinin–Radushkevich adsorption isotherms were applied to the adsorption data. The data were well described by Freundlich and Dubinin–Radushkevich adsorption isotherms while the fit of Langmuir equation to adsorption data was poor. It was reached that modification of bentonite and illite with nonylammonium chloride increased the adsorption capacity for boron sorption from aqueous solution.

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1. Introduction

The largest boron sources in the world exist in Turkey for which boron contamination of water is a common environmental problem. For instance, a big area around Mendere River in West Anatolia suffers from the boron pollution caused by geothermal sources and boron mines [1]. Currently the most common minerals used in the boron industry are colemanite and tincal. During the production of boron compounds, many of these are introduced into the environment in the form of waste [2]. Boron is an essential micronutrient for plants, but the range between deficient and toxic boron concentrations is similar for any other nutrient element [3]. In excess of 2.0 mg/dm³ in irrigation water is deleterious to certain plants. Some plants may be affected adversely by concentrations as low as 1.0 mg/L [4].

Monomeric boric acid that is the dominant form of inorganic boron in natural aqueous solution is a very weak monobasic acid and has the p*K*_a value of 9.2. The conjugate base of boric acid in aqueous solution, tetrahydroxyborate [B(OH)₄⁻] ions have strong affinity for hydrogen ions.

Clays are the main components of the mineral fraction of soils. They are effective natural adsorbents due to their particle size (lower than 2 μm), lamellar structure [5]. Clay minerals are an important source of boron adsorbing surfaces in soils [6]. The rate of boron adsorption on clay minerals consists of a fast adsorption reaction and a slow fixation reaction [3]. The ionic strength, temperature, and pH of the aqueous solution are important factors which influence the sorption of boron.

Numerous works have been done for removal of boron from aqueous solution. Some of the processes that have been used in these studies were: (a) use of boron selective resins Amberlite IRA 743 [7–9], chitosan resin modified by saccharides [10], and N-methylglucamine-type cellulose derivatives [11], (b) adsorption on active carbon [4], soils [3], and

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Table 3
Isotherm constants for boron adsorption onto bentonite, NB, sepiolite, NS, illite, and NI

| Sample | Bentonite | NB | Sepiolite | NS | Illite | NI |
|---|-----------|--------|-----------|--------|--------|--------|
| DR isotherm | | | | | | |
| R | 0.968 | 0.998 | 0.997 | 0.969 | 0.997 | 0.990 |
| k (mol ² J ⁻²) | 0.0101 | 0.026 | 0.027 | 0.014 | 0.007 | 0.046 |
| E (kJ mol ⁻¹) | -7.010 | -4.390 | -4.310 | -6.040 | -8.450 | -3.300 |
| Linear form of Freundlich | | | | | | |
| K_f (mmol g ⁻¹) | 0.117 | 0.345 | 0.034 | 0.115 | 0.058 | 0.046 |
| n_f | 1.091 | 2.217 | 2.361 | 1.091 | 0.607 | 3.509 |
| R | 0.991 | 0.999 | 0.998 | 0.978 | 0.998 | 0.999 |
| Nonlinear form of Freundlich | | | | | | |
| K_f (mmol g ⁻¹) | 0.001 | 0.035 | 0.004 | 0.008 | 0.006 | 0.005 |
| n_f | 1.000 | 2.170 | 2.105 | 1.687 | 0.617 | 3.443 |
| R | 0.977 | 0.995 | 0.989 | 0.997 | 0.998 | 0.986 |

Note. NB, nonylammonium bentonite; NI, nonylammonium illite; NS, nonylammonium sepiolite.

provides a mathematically rigorous method for determining isotherm parameters using the original form of the equation. These parameters were determined from the linear form of Freundlich and the original form of equation fitted using Sigmaplot version 4 program [26].

The Freundlich equation has the form of

$$C_s = K_f C_e^{n_f}, \quad (1)$$

where n_f is the adsorption intensity, K_f is the relative adsorption capacity (mmol/g).

The linear form of Freundlich equation was used to interpret the results in the following form,

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

The Freundlich parameters with the corresponding correlation coefficient were given in Table 3. The data found are well described by the Freundlich isotherm equation when plotted as $\ln C_e$ versus $\ln C_s$.

The n_f values are related to the Giles classification, S, L, and C type isotherm. $n_f > 1$ correspond to S shape, $n_f = 1$ to C type, and $n_f < 1$ to L type [27]. As can be seen from the results of nonlinear and linear form of Freundlich equation, the n_f values of the boron sorption isotherms on clays and modified clays confirm S-shape for B, S, NB, NI, NS samples and L-shape for illite sample. As can be observed from Table 3, linear and nonlinear forms of Freundlich equation gave a high level of conformity with the experimental data of boron sorption for all adsorbents. The correlation coefficients were in all cases greater than 0.978, this being significant at the 0.0001 probability level. Based on the linear form of Freundlich equation, the greatest K_f value belongs to bentonite among the clay samples. It is noticeable that NB has the greatest relative adsorption capacity among the modified clays. In addition, it has been also reached that the values of K_f for clay samples rose after the modification of clay samples with nonylammonium cations.

Dubinin–Radushkevich equation was used to determine the type of adsorption for the removal of boron from aqueous

solution by adsorption. The equation can be expressed as

$$\ln C_s = \ln X_m - k\varepsilon^2, \quad (3)$$

where X_m is the adsorption capacity (mol/g), C_s is the amount of boron adsorbed per unit weight of adsorbent (mol/g), k is the constant related to adsorption energy (mol²/kJ²). From the plots of $\ln C_s$ versus ε^2 , the values of X_m and k were computed by using the values of intercept and slope. Polanyi potential (ε) can be calculated from the equation

$$\varepsilon = RT \ln(1 + 1/C_e), \quad (4)$$

where C_e is the equilibrium concentration of boron in aqueous solution (mol/L), T is the temperature (K), and R is the gas constant.

The value of k is used to find the mean free energy E (kJ/mol) of sorption:

$$E = -(2k)^{-0.5}. \quad (5)$$

The magnitude of E gives information about the type of adsorption. If this value is between 8 and 16 kJ/mol, adsorption type can be explained by ion-exchange [28]. It has been found that the adsorption energy for the adsorption of As(III) on activated alumina was 7.45 kJ/mol, assuming the adsorption type as physical adsorption [29]. The mean free energy values were summarized in Table 3. As was observed from Table 3, E values were calculated to be -7.01, -4.39, -4.31, -6.04, -8.45, and -3.30 kJ/mol for B, NB, S, NS, I, and NI, respectively. It can be reached that the type of adsorption of boron can be mostly considered as physical adsorption.

3.2. FTIR results

In order to identify the coordination of adsorbed boron species on the surfaces of clay and modified clay samples, FTIR spectroscopy was used. The vibrations of the Si–OH bond result in a broad band at 3700 cm⁻¹ together with a doublet due to O–H deformation at approximately 800 cm⁻¹

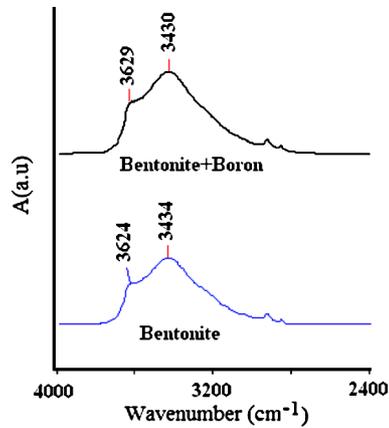


Fig. 5. FTIR spectrum of bentonite and boron adsorbed bentonite.

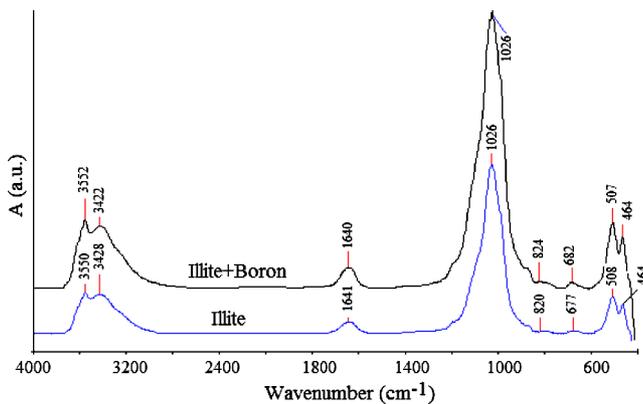


Fig. 6. FTIR spectrum of illite and boron adsorbed illite.

[30]. When the shifts or changes occur in these bands, it indicates that there are interactions of boron species with the silanol groups.

As can be seen in the spectra of bentonite (Fig. 5), there is an absorption band in the range of 3200–3600 cm^{-1} because of the stretching band of OH groups. Boron treated bentonite displays two bands, at 3629 and 3430 cm^{-1} . Intensities of these bands increased as compared with the range 3200–3600 cm^{-1} of spectrum of bentonite sample. Hydrogen bond may occur between hydroxyl group of bounded water and boron species.

In the spectrum of illite (Fig. 6), the absorption bands at 3550 and 3428 cm^{-1} can be assigned to lattice OH and bound water stretching vibrations. After boron adsorption, these bands shifted to 3552 and 3422 cm^{-1} . As was mentioned above, hydrogen bonding may occur between water molecules and boron species. Water deformation band is located at 1641 cm^{-1} that is almost the same as boron adsorbed illite. A strong and sharp band is detected at 1026 cm^{-1} that corresponds to Si–OH stretching vibrations, which is similar to Si–OH absorption band of boron treated illite. From this point of view, distortion of the symmetry of the tetrahedral sheet could not occur by treating boron at that temperature. The bands near 820 and 677 cm^{-1} can be evaluated as Si–O–Si stretching vibrations. There is lit-

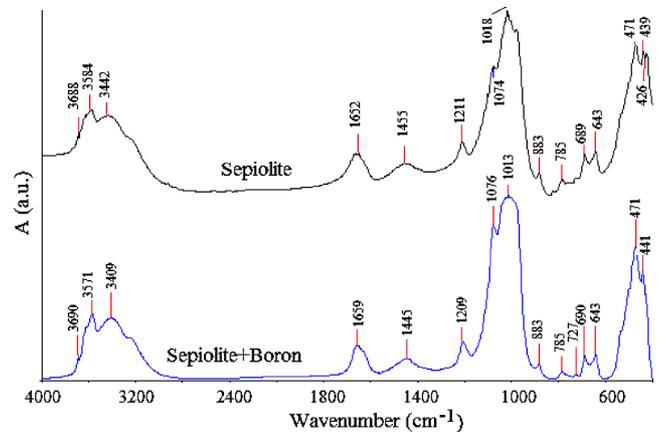
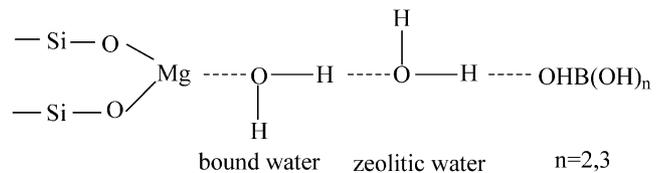


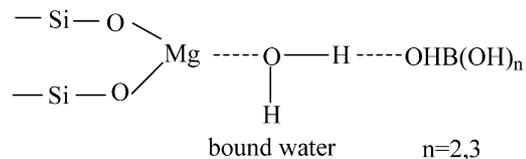
Fig. 7. FTIR spectrum of sepiolite and boron adsorbed sepiolite.

tle change after the boron adsorption. The spectra from illite and boron treated illite were similar in the 600–400 cm^{-1} region. The weak absorption bands at 507 and 464 cm^{-1} can be identified as Si–O–Al (octahedral) and Si–O–Si bending vibrations, respectively.

In the spectra of sepiolite (Fig. 7), zeolitic water gives a broad adsorption band at 3442 cm^{-1} that shifted to 3409 cm^{-1} in the spectra of boron treated sepiolite. The entrance of boron species inside channels may affect the structure of residual zeolitic water. Possible association of boron species and zeolitic water via hydrogen bond may occur, as depicted below,



As can be seen in the spectrum of sepiolite, bound water gives two stretching absorptions, located at 3688 cm^{-1} (relatively weak) and 3584 cm^{-1} , that shifted to 3690 and 3571 cm^{-1} , respectively, in the case of boron adsorbed sepiolite. These small shifts in absorption bands may be indication of the hydrogen bonds between bound water and boron species.



It has been argued that the appearance of two stretching bands is due to the fact that two water molecules coordinated to each of the octahedral cations exposed to the channels are not identical [31–33]. HOH deformation vibration shifted from 1652 to 1659 cm^{-1} with the treated boron. The stretching band at 1018 cm^{-1} as a sharp band is replaced by a broad band at about 1013 cm^{-1} . It indicates that the symmetry of the tetrahedral sheet is probably distorted. This distortion is accompanied with the evolution of bound water. Sepiolite

shows absorption maxima at 883, 785, 689, 643, 471, 439, 426 cm^{-1} . Most of the bands were the same in the case of boron treated sepiolite (Fig. 7).

It has been stated that essentially there is no polymer boron specie present in solution at concentrations ≤ 25 mmol/L and polynuclear species are less than 5% at pH 7 [34]. The boron solutions used in our study are less than 25 mmol/L. The pH values of solutions were about 8.8–9.0 for sepiolite; 7.7–8.3 for illite; 6.9–7.8 for bentonite; 8.6–9.0 for NB; 6.9–7.2 for NI; 7.8–8.2 for NS, corresponding to adsorption isotherms shown in Figs. 1 and 2. The pK_a value of boric acid is 9.2, where half of the total boron is in the form of boric acid and half is in the form of borate anion. As the pH decreases below 9, the $\text{B}(\text{OH})_3$ is the dominant aqueous species. As can be seen in Table 3, the relative adsorption capacities are increasing in the order of S, NI, I, NS, B, NB. According to K_f values (Table 3) calculated from Freundlich equation, after the modification of sepiolite and bentonite, the relative adsorption capacities increased. However, the relative adsorption capacity of illite decreased after the modification with nonylammonium chloride. As could be revealed before, the amounts of adsorbed boron are increasing with the pH to a maximum point for each clay and modified clay minerals. After the maximum point, adsorption of boron is decreasing. It is clear that the proportion of boron species in the equilibrium solution varies with pH values. At high pH, the clay surfaces are negatively charged. Due to formation of OH^- group, competitive adsorption can be observed between $\text{B}(\text{OH})_4^-$ and OH^- groups for the sorption sites of clay samples. It reveals the reason of decrease in adsorbed boron with the increase of pH after a maximum point. The vital point here is that repulsion between negatively charged clay surface and negatively charged ions (OH^- , $\text{B}(\text{OH})_4^-$) occurs at high pH values. This result is supported by FTIR results, since Si–OH stretching vibrations change after the adsorption of boron. The edge of each clay platelet has a hydroxide group which may react with boron species as well.

As was presented in Table 2, organic carbon content of NS is lower than the others. There is no further difference with the d_{001} values of sepiolite and NS. Nonylammonium ions could not enter the interior channels of sepiolite. Silanol groups presented at the border of each block are usually accessible to organic species. According to FTIR results of NS (data not shown here), the stretching vibrations of $-\text{CH}_2$, $-\text{CH}_3$ group is very weak. Small variations were observed in the OH stretching region, Si–O absorption bands and ammonium absorption bands. The adsorbed amounts of boron species on B and NB are shown in Figs. 1 and 2, and the shape of the isotherms are of S type which indicates physical adsorption. The adsorption capacities of B and NB are shown in Table 3. It can be inferred that little adsorption of boron species was observed on bentonite alone, whereas modifying the surface of bentonite from hydrophilic to hydrophobic using nonylammonium cation occurred a drastic increase in the adsorbed amounts of boron species. Among

the modified samples, the highest organic carbon content belongs to NB. So when the FTIR spectrum was examined, the bands due to antisymmetry and symmetry of $-\text{CH}_2$ group, scissoring mode and rocking mode of $-\text{CH}_2$ group was almost the same in NB and boron adsorbed NB. However, ammonium stretching mode was extremely sensitive to adsorption of boron on NB. It was deduced that formation of organo-boron complexes may have appeared between nonylammonium ions and boron species.

The effect of ionic strength to adsorption of boron species was also examined. Adsorption capacities of the clay samples for boron species increase with the increase in ionic strength. This result is in agreement with a previous report [19]. The amount of positive ions on the clay surface increases with the increase of ionic strength. Since the possibility of ionic attraction between positive ions presented on the surface and boron species enhances, the amount of adsorbed boron is at high level.

4. Conclusion

It was found that based on relative adsorption capacity values, adsorption of boron onto clays (bentonite and sepiolite) was enhanced by changing the clay surface from hydrophilic to hydrophobic by modifying with nonylammonium chloride. The optimization of boron adsorption can be achieved by sustaining the pH in the range 8–10 and a constant ionic strength. Thus, modification of bentonite and sepiolite with nonylammonium chloride can be advantageously utilized to remove and recover high levels of boron concentration in the aqueous environment in stead of clay samples. The results of the present work seem to assert the conclusion that modification of clay minerals (bentonite and sepiolite) with long alkyl chains such as nonylammonium ion may increase the relative adsorption capacities. The experimental results were analyzed by using Langmuir, Freundlich, and Dubinin–Radushkevich equations. Langmuir equation did not show good agreement with our experimental data. From the shape of isotherms corresponding to bentonite, sepiolite, NB, NI, NS, it is inferred that adsorption occurs physically. Furthermore, this result was supported by the mean free energy values (lower than 8 kJ/mol) calculated from DR isotherm. In addition, from the shape of the isotherm for illite, it is derived that the type of adsorbent cannot be considered as S type isotherm and these results were also supported by the mean free energy values obtained from DR isotherm (greater than 8 kJ/mol).

As far as K_f values concerned, as indicated in Table 3, sorption capacity of boron onto adsorbents was increasing in the order of sepiolite, NI, illite, NS, bentonite, and NB. From the standpoint of industrial applications, bentonite is suitable adsorbent due to low price and high adsorption capacity among the clays investigated. However, nonylammonium modified bentonite is the most attractive adsorbent due to a high adsorption capacity among the samples studied.

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