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The removal of boron from aqueous solutions using natural and chemically modified sorbents

Mohsen Jalali, Fahimeh Rajabi, Faranak Ranjbar*

Department of Soil Science, College of Agriculture, Bu-Ali Sina University, Hamedan, Iran, emails: jalali@basu.ac.ir (M. Jalali), rajabi_fahimeh@yahoo.com (F. Rajabi), Tel. +98 81 34425292; Fax: +98 81 34424012; email: f_ranjbar1980@yahoo.com (F. Ranjbar)

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ABSTRACT

The presence of excessive amounts of boron (B) in water resources can endanger the health of organisms in an ecosystem. In this study, B removal from aqueous solutions was investigated using natural easily available materials including bentonite, kaolinite, zeolite, waste calcite, and residues of wheat, rice, and green shell of walnut as native and chemically modified with $FeCl_3$. The optimum values of pH and contact time for the B sorption were determined before isotherm experiments. The maximum sorption of B by mineral sorbents was observed at pH 9, while it was obtained at pH 7 for walnut shell and rice residues and at pH 8 for wheat residues. The optimum time obtained for mineral sorbents and organic sorbents was 24 and 48 h, respectively. The values of pHzpc measured for chemical sorbents were higher than those for organics. The sorption isotherms were performed using optimum parameters at three $CaCl_2$ concentrations as background electrolytes. Increasing $CaCl_2$ concentration caused to increase in B sorption. The chemical modification of sorbents by $FeCl_3$ had a positive significant effect on B sorption. The fit of Freundlich and Langmuir models to the experimental data was very well. The largest B sorption capacity among the mineral and organic sorbents was, respectively, observed in the waste calcite and rice residues. However, the extent of the B sorption by organics was much higher than by minerals. Therefore, the use of organic materials to remove excess amounts of B from water resources can be considered as an available, cost-effective, and environmentally friendly strategy.

Keywords: Boron removal; Natural sorbents; Sorption; Organic residues; Waste calcite

1. Introduction

Boron (B) compounds are widely used as raw materials in many industries such as fiberglass insulation, borosilicate glass, detergents, and even agricultural fertilizers. Increasing use of B in the industry and the subsequent discharge to the environment through industrial wastes is a serious threat for ecological systems, humans, animals, and plants. Therefore, the release of B to the environment can be occurred through the addition of waste waters resulted from glass, coal, and metal smelting factories as well as the application of agricultural fertilizers [1].

Although B is an essential nutrient required by plants in small amounts, its excessive amount has harmful effects on growth of many agricultural products. The World Health Organization (WHO) has given a recommendation of below 2.4 mg B L^{-1} for the

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*Corresponding author.

quality of drinking water [2]. Boron removal from water and waste waters is performed in order to reduce B concentration to the optimum range. The exchange resins, reverse osmosis, and activated carbon are common techniques for B removal despite the high costs. One of the most important characteristics for B removal is that the process must be cost-effective and easily available [3].

Sorption is a cost-effective process used for removal of a constituent from a multi component solution. There have been several investigations on the development of inorganic and organic selective sorbents for B and its adsorptive properties. Some of these sorbents used for B removal are pyrophyllite [4], some acidic soils [5], amorphous aluminum and iron oxides, allophane, kaolinite [6], hydrous ferric oxide [7], chitosan resin modified by saccharides [8], activated carbon [9], and clays and soils [10].

A significant fraction of boron can be bound by mineral surfaces present in the natural systems. Iron (hydr)oxides usually exhibit a strong affinity for oxyanions and may play an important role in boron adsorption due to the high surface area. Therefore, it seems the chemical modification of organic and mineral sorbents by iron components can increase their efficiency for B sorption.

Factors influencing the B sorption include pH, initial concentration of adsorbate, time, sorbent concentration, temperature, and chemical properties of the sorbent material. The relative abundance of main species of B in aqueous systems is pH dependent. B exists as trigonal unassociated boric acid complex $[\mathrm{B(OH)}]_3^0$ in acidic to slightly alkaline pHs, but it converts to the tetragonal borate anion complex $[\mathrm{B(OH)}]_4^-$ in alkaline pHs. The ligand exchange with surface hydroxyl groups and the subsequent formation of inner-sphere complexes is the main mechanism for the B sorption, so pH plays an important role in the chemical speciation of B in solution, and protonation and deprotonation of reactive surface sites of sorbents.

There is an increasing interest in the preparation of low-cost sorbents for water treatment, so usage of natural and abundant materials can be effective in reducing cost of the removal processes. The purpose of this study was to investigate the B removal from aqueous solutions using natural easily available materials including bentonite, kaolinite, zeolite, waste calcite, and residues of wheat, rice, and green shell of walnut as native and modified forms. Batch experiments were performed to determine the effects of several parameters such as initial solution concentration, pH, contact time, and ionic strength on B removal.

2. Materials and methods

2.1. Mineral sorbents

The mineral sorbents used were bentonite, kaolinite, zeolite, and waste calcite collected from power plant in Hamedan, Western Iran. Sorbent was air-dried and then ground until they passed through a 2 mm sieve. The pH, electrical conductivity (EC), and soluble cations and anions were measured in a 1:5 native sorbent to distilled water extract.

The chemical modification of mineral sorbents was performed using 0.1 M $\mathrm{FeCl_3}$ solution. 500 mL of this solution was added to 50 g of sorbents previously acid washed. After shaking for 1 h, pH of suspensions was adjusted on 9 using 6 M NaOH solution and then they were equilibrated for 24 h. After centrifuging and decanting the upper extracts, the sorbents were washed with distilled water until EC of extracts reached to $<50\ \mathrm{dS\,m^{-1}}$ and the color of leachates became lighter than the initial status [11].

2.2. Organic sorbents

Three organic materials including residues of walnut green shells and straw, stubble, and not harvested parts of wheat, and rice were oven-dried at 70°C, crushed, and then passed through a 2 mm sieve. The pretreatment of sorbent before using for sorption experiments was carried out by adding 2 L of 0.1 M NaOH to 100 g of organic residues. After 2 h of shaking, the suspensions were centrifuged and then the supernatants were gradually replaced with 2 L of distilled water. After shaking for 30 min and decanting the water, the residues were oven-dried at 50°C for 24 h and ground until they were passed through a 2 mm sieve [12]. The chemical modification of organic residues with $\mathrm{FeCl_3}$ was similar to mineral sorbents.

The pH values of zero point charge (ZPC) of native and modified forms of mineral and organic sorbents were determined using method given by Rivera-Utrilla et al. [13].

2.3. Optimizing pH for B removal by native sorbents

In order to optimize pH, $50\ \mathrm{g\,L^{-1}}$ of native mineral sorbents [14] was equilibrated with solutions containing $12\ \mathrm{mg\,B\,L^{-1}}$ (prepared from boric acid) at different pHs ranging from 5 to 10 for 24 h. The adjustment of pH was performed by adding appropriate amounts of 0.1 M HCl and NaOH solution. The values of solid to liquid (S:L) ratio and the initial B concentration used for organic sorbents were $2\ \mathrm{g\,L^{-1}}$ [15] and $62\ \mathrm{mg\,B\,L^{-1}}$, respectively. After equilibrium, the suspensions were centrifuged and upper extracts were collected for the measurement of the equilibrium B concentration using Azomethine-H method [16].

2.4. Optimizing contact time for B removal by native sorbents

In order to optimize the contact time, the experiments were performed using shaking times of 1, 3, 6, 12, 24, and 48 h. The values of S:L ratio and the initial B concentration were 50 g L^{-1} and 12 mg B L^{-1}, respectively, for mineral sorbents, while they were correspondingly 2 g L^{-1} and 62 mg B L^{-1} for organic sorbents. pH of solutions was adjusted on the optimum value obtained from the previous step.

2.5. B sorption isotherm

The sorption isotherm experiments were carried out using solutions containing 7–120 mg B L^{-1}. The S:L ratios were the same with the Section 2.3, and pH and contact time was adjusted on optimum values obtained from the Section 2.4. In order to investigate the effect of ionic strength on B sorption, the isotherm solutions were prepared in the presence of 0.001, 0.01, and 0.1 M $CaCl_2$ as background electrolyte. The empirical isotherm models were used in order to demonstrate the fit between experimental and modeled data. The most common isotherm models used to describe B sorption on oxides, clay minerals, and soils are Langmuir and Freundlich equations [17] with following equations, respectively:

$$Q_e = \frac{K_L C_e Q_{max}}{1 + K_L C_e} \tag{1}$$

$$Q_e = K_F C_e^{1/n} \tag{2}$$

where Q_e is B adsorbed (mg g^{-1}), C_e is the equilibrium B concentration (mg L^{-1}), Q_{max} is the maximum B sorption capacity of sorbent (mg g^{-1}), K_L is the Langmuir sorption constant (L mg^{-1}), K_F and n are Freundlich equation constants.

2.6. Physical characterization of sorbent surface

The scanning electron microscopy (SEM) measurements were performed using SEM (model: Philips XL30). All samples were of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Samples were cleaned ultrasonically using solvents like acetone or ethanol and then dried using oven or hot plate. Some electrically conductive black carbonic glue was placed on the specimen stub, as it covered the lower part of the sample. The surface of samples was coated with a gold coating of 10 nm thickness using sputtering method. The specific surface area of native sorbents was determined using Brunauer–Emmett–Teller (BET) method based on the nitrogen gas adsorption.

3. Results and discussion

3.1. Effect of pH on the B sorption

Fig. 1 indicates that pH strongly influences the B sorption on mineral and organic sorbents. Increasing pH from 5 to 9 caused to increase in the B sorption by mineral sorbents, while the more increase resulted in decreasing B sorption (Fig. 1(a)). So, pH 9 was the optimum pH for the maximum B sorption by mineral sorbents used. The maximum B sorption by waste calcite at pH 9 was higher than that observed in other mineral sorbents. At pH 9, 43% of B in solution is in the form of $B(OH)_4^-$ and this species includes about 87% of total adsorbed B [18]. On the other hand, the

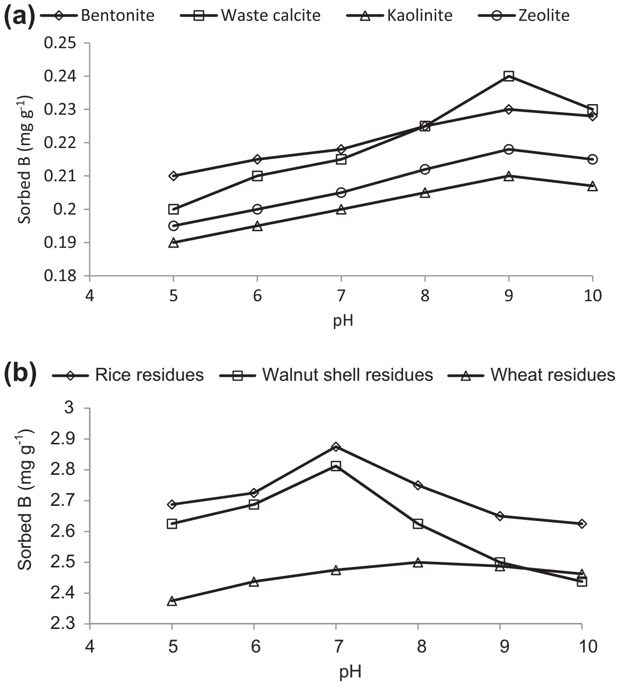

Fig. 1. The effect of pH on B sorption by native mineral (a) (S:L ratio: 50 g L^{-1}, C_0: 12 mg B L^{-1}) and organic (b) (S:L ratio: 2 g L^{-1}, C_0: 62 mg B L^{-1}) sorbents.

net negative charge of edge surfaces of clay minerals at this pH can be favorable for ligand exchange between $B(OH)_4^-$ and surface hydroxyl groups, as the affinity of the sorption sites for $B(OH)_4^-$ is much higher than that for unassociated H_3BO_3 [18–20].

Goldberg and Glaubig [21] reported that the maximum B removal from solution using three clay minerals including montmorillonite, illite, and kaolinite occurred at pHs 8–10, whereas the B sorption decreased with increasing pH from 10 to 12. The effective B removal by many sorbents has often been reported at pHs 6–9 [22–25], in that the concentration of OH^- is low enough to compete with $B(OH)_4^-$ which may be present in solution ($pK_a = 9.24$). Keren and Mezuman [19] studied B sorption by some clay minerals and reported that the maximum sorption occurred under alkaline conditions at pHs 9.0–9.7. Ichikuni and Kikuchi [26] suggested that the B sorption on $CaCO_3$ can likely occur through the precipitation of poorly soluble calcium borate, B replacement with the carbon in $CaCO_3$, and the B sorption on $CaCO_3$ surfaces. They also concluded that the main mechanism of B retention by $CaCO_3$ was sorption. In contrast with them, Hobbs and Reardon [27] indicated that B uptake by calcite mainly occurred through the co-precipitation process.

The maximum B sorption by walnut shell and rice residues occurred at pH 7, while the optimum pH for B removal by wheat residues was pH 8 (Fig. 1(b)). The comparison of Figs. 1 and 2 indicated that capacity of organic sorbents for B sorption was much more than mineral ones. The maximum values of B sorption by waste calcite and rice residues at the optimum pH were, respectively, about 0.24 and 2.88 mg g^{-1}. Liu et al. [15] reported that the optimum pH for the maximum B sorption by the cotton cellulose was 7. Lemarchand et al. [28] indicated that the B sorption by humic acid reached to the maximum at $5 < pH < 9$ and decreased sharply at $pH > 9$.

The change in the B sorption by pH is mainly due to the pH-dependence of protonation and deprotonation of reactive surface functional groups of clay minerals and organic materials. The increased pH causes to increase in: (1) negative surface charges on sorbents mainly attributed to the hydroxyl groups and (2) dissociation of H_3BO_3 to $B(OH)_4^-$ in solution which has more affinity to replace with surface OH^- groups through ligand exchange process. However, at $pH > 10$, the concentration of OH^- ions in solution reaches to a level in that $B(OH)_4^-$ ions are not able to compete for surface adsorbing sites.

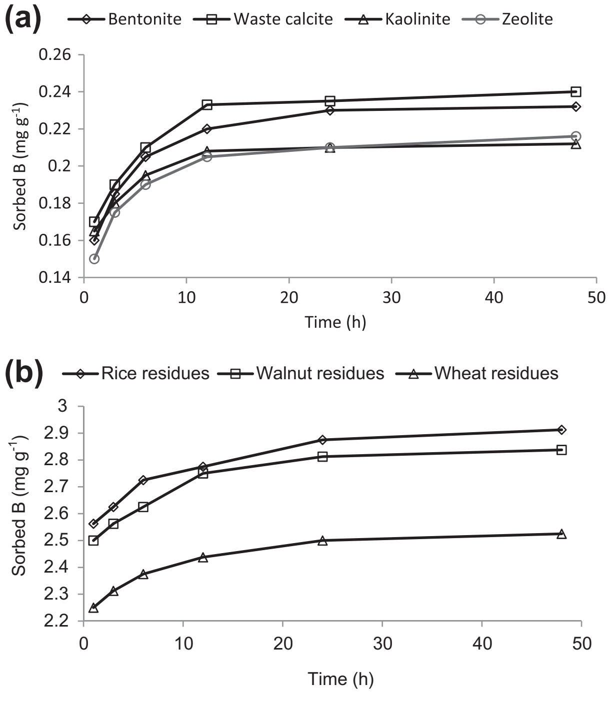

Fig. 2. The effect of contact time on B sorption by native mineral (a) (S:L ratio: 50 g L^{-1}, C_0: 12 mg B L^{-1}, equilibrium time: 24 h) and organic (b) (S:L ratio: 2 g L^{-1}, C_0: 62 mg B L^{-1}, equilibrium time: 48 h) sorbents.

3.2. Effect of contact time on the B sorption

Fig. 2(a) indicates that the B sorption by mineral sorbents reaches to the maximum value after a contact time of 24 h between solid and solution phases and subsequently there is no significant change in the quantity of B removal from the solution. Short-term experiments indicated that the optimum contact time for the B sorption was less than 2 h for montmorillonite and kaolinite, and 24 h for illite [14,19]. However, they used 24 h as equilibration time for sorption isotherm experiments. Keren et al. [18] also reported that the B sorption equilibrium occurred during one day.

Fig. 2(b) demonstrates that the B sorption equilibrium is established after 48 h for organic sorbents. The kinetic experiments by Lemarchand et al. [28] indicated that the B sorption by humic acid reached to the equilibrium within one day. However, they used two days as a typical contact time for the B sorption experiments. Dionisiou et al. [29] found that the equilibrium time was dependent on the initial B concentration and ranged from 6 h (for $B \leq 10$ mg L^{-1}) to 48 h (for $B \geq 50$ mg L^{-1}). Liu et al. [15] reported that the optimum contact time for the maximum B sorption by the cellulose cotton was 4 h.

Furthermore, Fig. 2 shows that the rate of B sorption is faster during the first 12 h indicating the B sorption on mineral and organic sorbents is initially a fast process and then becomes slower. Initially, the surface hydroxyl groups on the clay particle edges form B complexes through ligand exchange process. At the second step, B is slowly replaced by silicon and aluminum in tetrahedral sheets of clay minerals [30]. Ligand exchange is the main mechanism for the B sorption by organic sorbents. As different functional groups on organic surfaces mainly including carboxylic and phenolic acids vary in protonation and deprotonation constants, the rate of the B sorption changes with the time of reaction and may follow a two-(or multi) step process.

3.3. B sorption isotherms

The B sorption isotherms for native and modified forms of mineral and organic sorbents at three $CaCl_2$ concentrations as background electrolytes are presented in Figs. 3 and 4, respectively. The results indicated that the effect of ionic strength on the B sorption by all sorbents was relatively small at lower initial B concentrations, but it increased with increasing initial B concentration. The comparison of native and modified mineral sorbents at three background electrolyte concentrations showed that the largest amount of adsorbed B, which corresponded to the greatest initial B concentration (120 mg L^{-1}), was observed in the waste calcite, while it did not significantly differ among three clay minerals. Keren and Mezuman [19] reported that the extent of the B sorption by clay minerals followed this order: kaolinite < montmorillonite < illite. The hydroxyls are the most reactive surface functional groups on the edge surfaces of clay minerals. These functional groups are associated with Al and Si ions located on the octahedral and tetrahedral sheets, respectively. The hydroxyl groups associated with Al at the edge of the octahedral sheet act as Lewis acids. So, they can form an inner-sphere surface complex with H^+ at low pH values or with OH^- at high pH values. At the edge of the tetrahedral sheet, hydroxyl groups are individually coordinated to Si^{4+} cations. Therefore, the hydroxyl groups on octahedral sheets are the most likely available sites for the B sorption at pH 9. The ligand exchange is the main mechanism for the specific B sorption on the clay surfaces in that the adsorbed species displaces OH^- from the surface and forms covalent bonds with the structural Al. The distance between two adjacent hydroxyls in the octahedral sheet of the edge surface (0.22 nm) is nearly similar to the distance between two adjacent hydroxyls in the H_3BO_3 molecule (0.23 nm) and in the borate ion (0.19 nm) [31]. Therefore, B may form either two bonds or a single bond with the structural Al of clay minerals [32].

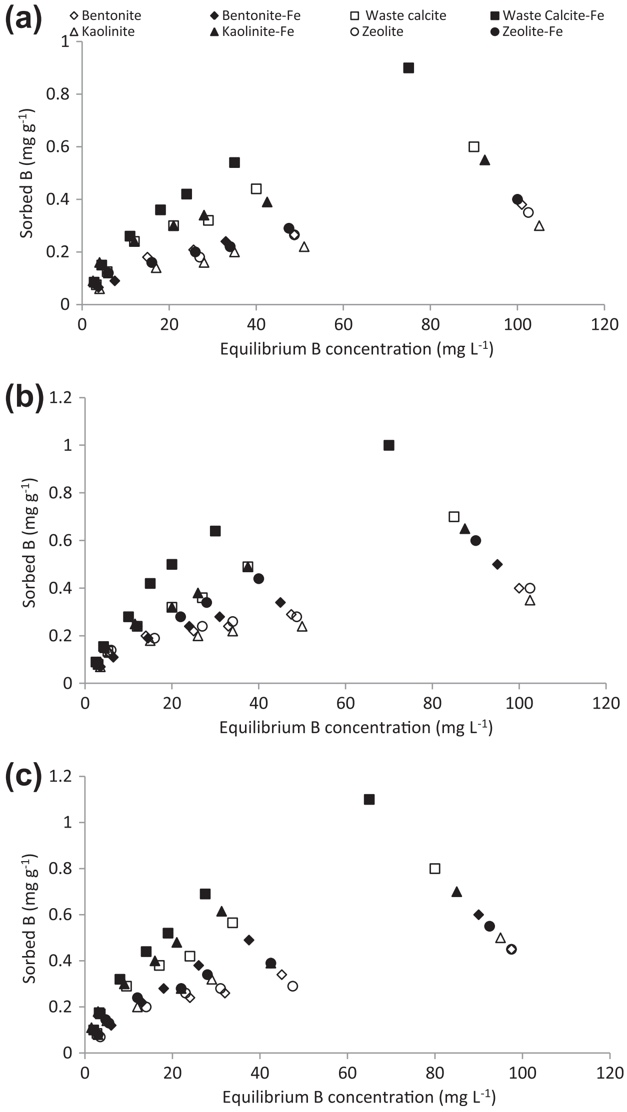

Fig. 3. B sorption isotherms for native and modified mineral sorbents in 0.001 (a), 0.01 (b), and (c) 0.1 M $CaCl_2$ solutions (S:L ratio: 50 g L^{-1}, C_0: 7–120 mg B L^{-1}, equilibrium time: 24 h).

Ichikuni and Kikuchi [26] suggested that the B sorption on the $CaCO_3$ can likely occur through: (1) the precipitation of the poorly soluble calcium borate, (2) the B replacement with carbon in $CaCO_3$, and (3) the B sorption on $CaCO_3$ surfaces. The B sorption by $CaCO_3$ occurs as two different types: (1) the electrostatic reaction of $B(OH)_4^-$ ions with positively charged sites on calcium carbonate and (2) the formation of a hydrogen bond between $H_3BO_3^0$ and carbonate [26]. Furthermore, B co-precipitation by calcite may be

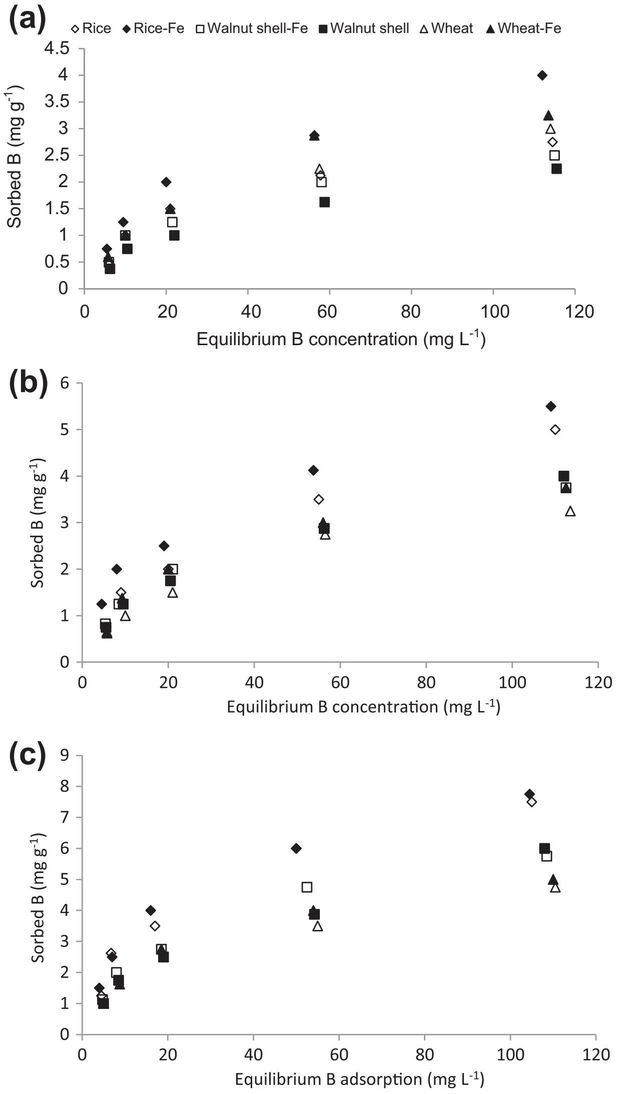

Fig. 4. B sorption isotherms for native and modified organic adsorbents in 0.001 (a), 0.01 (b), and (c) 0.1 M $CaCl_2$ solutions (S:L ratio: 2 g L^{-1}, C_0: 7–120 mg B L^{-1}, equilibrium time: 48 h).

anticipated which increases with increasing B concentration in solution [27].

The characterization results of mineral sorbents (Table 1) indicated that the pH values of ZPC of bentonite and in particular kaolinite were lower than the optimum pH for B removal (pH 9), so their surfaces were negatively charged. On the other hand, pH values below 9.24 are favorable for the sorption of $H_3BO_3^0$ as the predominant species on the mineral surfaces. The calcite surface was positively charged because of $pH_{ZPC} > 9$. Therefore, the B sorption by calcite may occur through three processes: (1) the electrostatic sorption of not dominant $B(OH)_4^-$ species at pH 9 on positively charged sites, (2) the sorption of $H_3BO_3^0$ as dominant B species at pH 9 through hydrogen bond with carbonate, and (3) co-precipitation of B by calcite.

The significant increase in the B sorption was observed in modified mineral sorbents in comparison with unmodified ones (Fig. 3). The pH_{ZPC} of modified bentonite, calcite, kaolinite, and zeolite were 8.0, 9.0, 8.8, and 8.5, respectively. So, the chemical modification of mineral sorbents resulted in decrease in pH_{ZPC} except for kaolinite. However, the values of $pH_{ZPC} < 9$ for all modified mineral sorbents resulted in formation of surfaces with net negative charges and the subsequent preferential sorption of the predominant $H_3BO_3^0$ species. Furthermore, the modification of sorbents with Fe may cause to form hydrous ferric (oxy) hydroxides reported as important for the B sorption [6,33,34]. Sims and Bingham [35] indicated that the amount of the B sorption by kaolinite and montmorillonite modified by Al and Fe was much more than that by unmodified clay minerals.

Figs. 3 and 4 indicate that the B sorption by mineral and organic sorbents increases with increasing the background electrolyte concentration. The increase in the B sorption on clays with increasing ionic strength of the solution has been previously reported [14,32]. The salt concentration is an effective factor in the B sorption due to the influence on the surface charge of minerals having pH-dependent charge [36]. At pH < ZPC, the increase of electrolyte concentration results in increasing the net positive charge on the surface, while at pH > ZPC, it causes to increase the negative charge. Therefore, the increasing pH gradually results in decreasing the sorption of anions due to the reduction in the surface potential [37]. The compression of the diffuse double layer affected by increasing ionic strength causes to increase in the movement of $B(OH)_4^-$ ions toward adsorbing sites located on the edge surfaces [32]. The increase in the sorption as a result of increased ionic strength indirectly indicates the formation of inner-sphere complexes [38].

The B sorption on mineral sorbents did not correlate with the specific surface area given in Table 1. This indicated that the other surface parameters including the type of reactive sites, the site density, and the amount of the surface charge may have more effect on the B sorption. The SEM images (Fig. 5) indicate that the surface of bentonite is composed of very fine needle-shaped crystals stuck together, while the surface of kaolinite and zeolite consists of layers tightly packed. The surface of waste calcite comprised of rough and irregular particles.

The largest B sorption (corresponded to 120 mg B L^{-1}) among organic sorbents was obtained in rice residues except for its native form at 0.001 M $CaCl_2$

Table 1
The characteristics of mineral adsorbents

Mineral adsorbents	pH^{a}	EC^{a}	Na^{+a}	K^{+a}	Ca^{2+a}	Mg^{2+a}	Cl^{-a}	PO_4^{3-a}	SO_4^{2-a}	HCO_3^{-a}	CO_3^{2-a}	NO_3^{-a}	$B–CaCl_2{}^{b}$	pH_{ZPC}	BET
	–	$dS\ m^{-1}$	$mg\ L^{-1}$										$mg\ kg^{-1}$		$m^2\ g^{-1}$
Bentonite	9.3^{c}	1.23^{c}	347.5^{c}	3.2^{c}	2.8^{c}	0.01^{c}	337.2^{c}	0.60^{c}	84.5^{c}	243.5^{c}	45.0^{c}	18.8^{c}	4.0	8.7	84.9^{c}
Kaolinite	9.0	0.13	33.3	5.2	1.7	0.08	53.5	0.61	23.5	0.0	0.0	0.0	2.5	9.6	3.6
Zeolite	8.0^{d}	1.82^{d}	299.0^{d}	16.6^{d}	98.4^{d}	15.90^{d}	455.7^{d}	0.61^{d}	197.8^{d}	124.3^{d}	0.0^{d}	10.5^{d}	1.5	8.0	13.8^{d}
Waste calcite	9.4^{e}	0.98^{e}	70.8^{e}	0.8^{e}	4.2^{e}	99.50^{e}	142.0^{e}	0.59^{e}	109.9^{e}	40.3^{e}	54.0^{e}	40.3^{e}	5.0	9.2	8.6

[a] Measured in a 1:5 solid to distilled water extract.
[b] B Measured in a 1:10 solid to 0.01 M $CaCl_2$ extract.
[c] Measured by [50].
[d] Measured by [51].
[e] Measured by [52].

concentration. The SEM analysis revealed the structural differences among three types of organic residues (Fig. 6). These images showed that the surface of rice, walnut shell, and wheat residues had porous and pitted positions, irregularly agglomerate structures, and regular cavities located side by side, respectively. The comparison of Figs. 3 and 4 indicated that the values of the B sorption by organic sorbents were much higher than those by mineral ones. The ligand exchange is a possible mechanism for the B sorption by the organic matter [39]. The B sorption by organic materials significantly occurs through the formation of bidendate and/or binuclear complexes. The H_3BO_3 species is preferentially forming tetrahedrally coordinated chelates with organic functional groups. The carboxylic and phenolic acids are two main reactive surface groups which play an important role in the B sorption on the organic matter [28]. The values of pH_{ZPC} were 8.0, 7.2, and 8.4 for of native rice, walnut shell, and wheat residues, respectively, while they reduced to 3.5, 4.0, and 3.3 for modified ones. Therefore, according to the pH of organic suspensions adjusted on the optimum values, the surface sites of rice residues were positively charged, while they were almost neutral in walnut shell and wheat residues. It can be concluded that $B(OH)_4^-$ anions were attracted by electrostatic forces associated with positively charged site, whereas the unassociated boric acid species were specifically adsorbed by reactive functional groups of organic materials through the ligand exchange process. Similar to mineral sorbents, B adsorption increased in modified organic sorbents, but the extent of variations was less than minerals (Figs. 3 and 4). Furthermore, the increased background electrolyte concentration caused to increase in the B sorption by native and modified organic sorbents (Fig. 4).

Figs. 3 and 4 indicate that the isotherms almost include two parts: at the low equilibrium concentration, the sorption increases almost linearly with increasing equilibrium concentration and then the rate of the sorption reduces with the increasing initial B concentration as a result of the saturation of sorption sites and the subsequent reduction in the sorption efficiency [24]. The parameters obtained from the fit of Freundlich and Langmuir models to the experimental data at 0.1 M $CaCl_2$ concentration are given in Table 2. The n values of Freundlich model above 1 (1.5–2.4) suggested a rapid decrease in the sorption capacity of the solid as the initial concentration is increased. According to the high values of coefficient of determination (R^2) and low values of standard error (SE), both empirical models fitted well to the experimental data. The Freundlich and Langmuir sorption isotherms have been previously used to describe the B sorption on clay minerals [30,40,41],

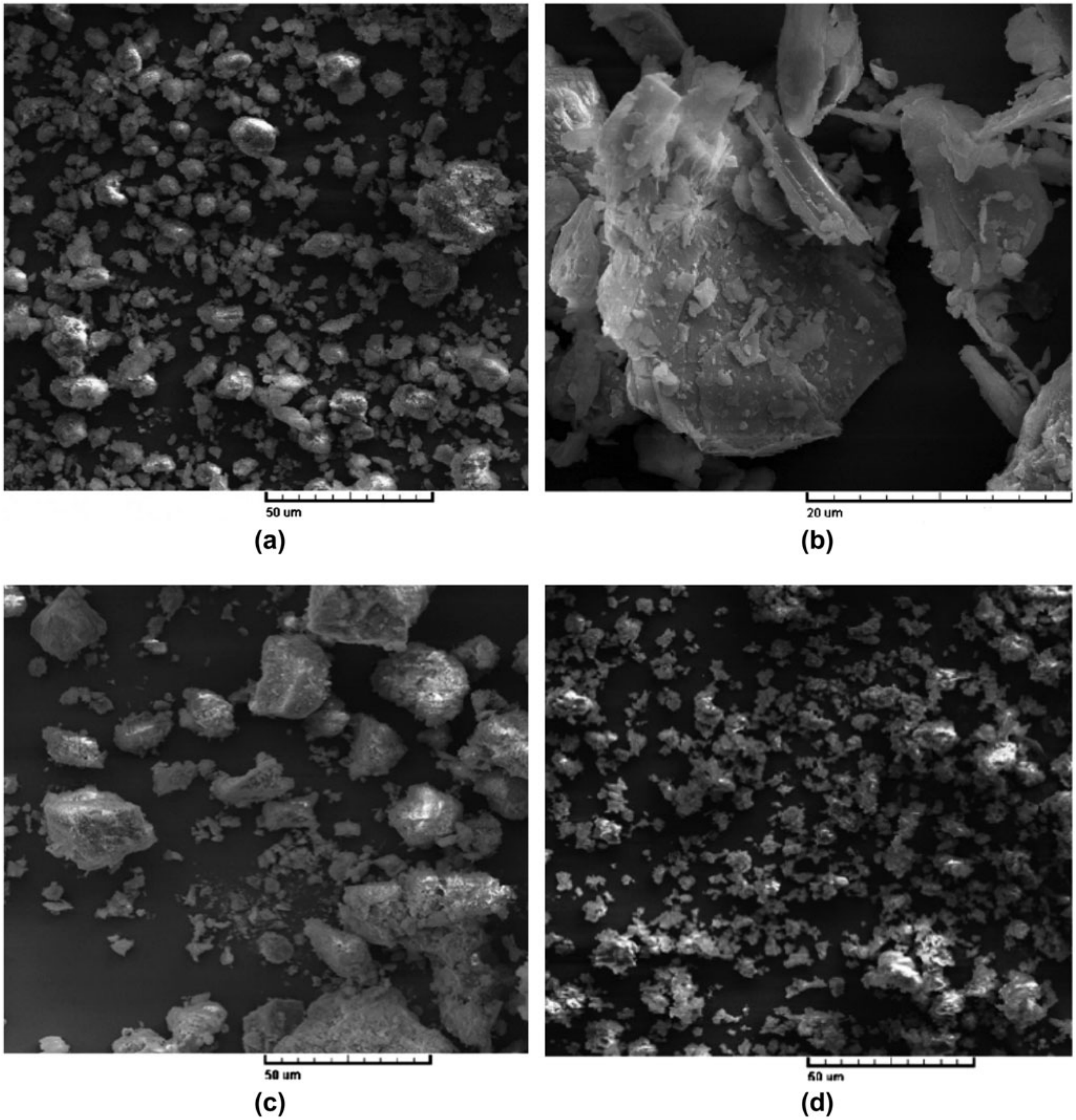

Fig. 5. SEM images of native mineral sorbents: (a) bentonite [50], (b) kaolinite, (c) zeolite [51], and (d) waste calcite [52]

humic acids [42], calcite [43], magnesia [29], calcined alunite [24], and clinoptilolite with and without ZrO_2 [25]. The maximum sorption capacity (Q_{max}) ranged from 0.51 to 1.60 mg g^{-1} for mineral sorbents and varied from 5.59 to 9.26 mg g^{-1} for organic ones. These results were in accord with the values reported in previous investigations. For example, the maximum sorption capacity (mg g^{-1}) reported for calcined alunite, humic acid, fly ash, neutralized red mud, activated sepiolite, Mg–Fe hydrotalcite, and bentonite was 3.39, 2.02, 20.9, 5.99, 178.60, 3.60, and 2.53, respectively [24,28,44–48]. In addition to natural sorbents, the commercial sorbents such as boron-selective resins have been used. Gazi and Bicak [49]

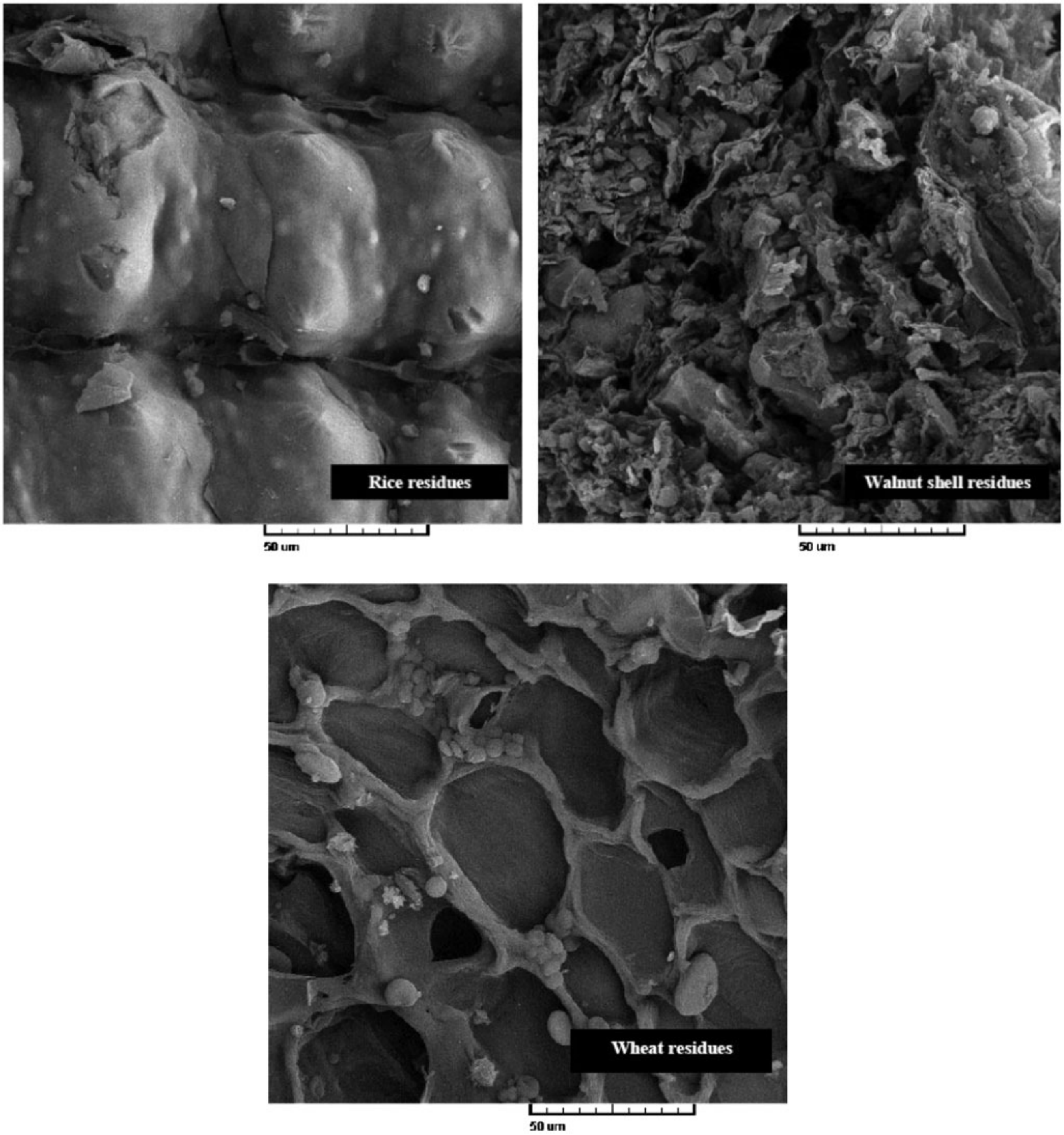

Fig. 6. SEM images of native organic sorbents.

reported that the pH-dependant B sorption capacity of an organic polymer varied from 9.30 to 18.16 mg g^{-1} at pHs ranging from 2 to 8. However, the goal of this study was to investigate the efficiency of natural mineral and organic components for B removal from aqueous solutions. According to the results, it can be said that the cheap and easily available organic components can be widely used to remove high concentrations of B from various water resources.

Table 2
The parameters obtained from fit of Freundlich and Langmuir models to experimental adsorption data in 0.1 M $CaCl_2$ solution

Adsorbents	Freundlich				Langmuir			
	n	K_F	R^2	SE	K_L (L mg^{-1})	Q_{max} (mg g^{-1})	R^2	SE
Bentonite	2.40	0.07	0.98	0.038	0.05	0.51	0.95	0.016
Waste calcite	1.66	0.06	0.94	0.087	0.04	1.05	0.96	0.006
Kaolinite	1.94	0.05	0.97	0.050	0.05	0.60	0.98	0.006
Zeolite	1.97	0.05	0.94	0.070	0.04	0.53	0.95	0.016
Bentonite-Fe	1.56	0.04	0.97	0.060	0.03	0.83	0.98	0.005
Waste calcite-Fe	1.50	0.07	0.98	0.041	0.03	1.60	0.95	0.003
Kaolinite-Fe	2.09	0.10	0.96	0.058	0.08	0.80	0.99	0.004
Zeolite-Fe	1.82	0.05	0.96	0.064	0.04	0.76	0.95	0.019
Rice residue	1.95	0.76	0.92	0.100	0.04	9.26	0.98	0.001
Walnut shell residue	1.99	0.61	0.96	0.065	0.04	7.04	0.99	0.001
Wheat residue	2.16	0.57	0.95	0.066	0.04	5.59	0.98	0.001
Rice-Fe	2.07	0.90	0.96	0.063	0.05	9.17	0.99	0.000
Walnut shell-Fe	1.85	0.48	0.97	0.054	0.03	7.58	0.95	0.002
Wheat-Fe	1.97	0.52	0.95	0.061	0.04	6.06	1.00	0.000

4. Conclusions

This study showed that the B sorption by natural mineral and organic sorbents was significantly affected by pH of solution, pH_{ZPC} of sorbents, the contact time between sorbate and sorbents, and ionic strength. Two empirical isotherm equations including Freundlich and Langmuir models fitted well to the experimental data. We concluded that both $H_3BO_3^0$ and $B(OH)_4^-$ species were adsorbed at optimum values of pH through the ligand exchange process. The waste calcite and rice residues adsorbed the greatest amount of B among the mineral and organic sorbents, respectively. However, the extent of B sorption was much higher in organic sorbents relative to the mineral ones. The B sorption by organic matter can be important in surface water reservoirs (seawater, groundwater, and soil waters) having either abundant organic surfaces or significant boron concentrations.

References

[1] C. Wells, J. Wood, K. Nicholson, Boron in the environment: An evaluation of the contribution from detergent, 16th European Environmental Geochemistry and Health Meeting, Derby, March 1998.

[2] WHO, Guidelines for Drinking Water Quality, fourth ed., World Health Organization, Geneva, Switzerland, 2011.

[3] L. Sütçü, Removal of boron from waters using fly ash, MSc. Thesis, Izmir Institute of Technology, Izmir, 2005.

[4] R. Keren, P.R. Grossl, D.L. Sparks, Equilibrium and kinetics of borate adsorption–desorption on pyrophyllite in aqueous suspensions, Soil Sci. Soc. Am. J. 58 (1994) 1116–1122.

[5] S.P. Datta, P.B.S. Bhadoria, Boron adsorption and desorption in some acid soils of West Bengal, India, J. Plant Nutr. Soil Sci. 162 (1999) 183–191.

[6] C. Su, D.L. Suarez, Coordination of adsorbed boron: A FTIR spectroscopic study, Environ. Sci. Technol. 29 (1995) 302–311.

[7] D. Peak, G.W. Luther, D.L. Sparks, ATR-FTIR spectroscopic studies of boric acid adsorption on hydrous ferric oxide, Geochim. Cosmochim. Acta 67 (2003) 2551–2560.

[8] M. Matsumoto, T. Matsui, K.J. Kondo, Adsorption mechanism of boric acid on chitosan resin modified by saccharides, J. Chem. Eng. Jpn. 32 (1999) 190–196.

[9] L.V. Rajaković, M.D. Ristić, Sorption of boric acid and borax by activated carbon impregnated with various compounds, Carbon 34 (1996) 769–774.

[10] S. Goldberg, H.S. Forster, S.M. Lesch, E.L. Heick, Influence of anion competition on boron adsorption by clays and soils, Soil Sci. Soc. Am. J. 161 (1996) 99–103.

[11] N. Haque, G. Morrison, I. Cano-Aguilera, J.L. Gardea-Torresdey, Iron-modified light expanded clay aggregates for the removal of arsenic(V) from groundwater, Microchem. J. 88 (2008) 7–13.

[12] P.J. Vaughan, P.J. Shouse, S. Goldberg, D.L. Suarez, J.E. Ayars, Boron transport within an agricultural field: Uniform flow versus mobile-immobile water model simulations, Soil Sci. 169 (2004) 401–412.

[13] J. Rivera-Utrilla, I. Bautista-Toledo, M.A. Ferro-Garcy'a, C. Moreno Castilla, Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption, J. Chem. Technol. Biotech. 76 (2001) 1209–1215.

[14] R. Keren, G.A. O'Connor, Effect of exchangeable ions and ionic strength on boron adsorption by montmorillonite and illite, Clays Clay Miner. 30 (1982) 341–346.
[15] R. Liu, W. Ma, C.Y. Jia, L. Wang, H.Y. Li, Effect of pH on biosorption of boron onto cotton cellulose, Desalination 207 (2007) 257–267.
[16] F.T. Bingham, in: A.L. Page (Ed.), Methods of Soil Analysis, Part 2, ASA, SSSA Inc., Madison, 1982, pp. 431–447.
[17] S. Goldberg, Reactions of boron with soils, Plant Soil 193 (1997) 35–48.
[18] R. Keren, R.G. Gast, B. Bar-Yosef, pH dependent boron adsorption by Na-montmorillonite, Soil Sci. Soc. Am. J. 45 (1981) 45–48.
[19] R. Keren, U. Mezuman, Boron adsorption by clay minerals using a phenomenological equation, Clays Clay Miner. 29 (1981) 198–204.
[20] S. Goldberg, R.A. Glaubig, Boron and silicon adsorption on an aluminum oxide, Soil Sci. Soc. Am. J. 52 (1988) 87–91.
[21] S. Goldberg, R.A. Glaubig, Boron adsorption and silicon release by the clay minerals kaolinite, montmorillonite, and illite, Soil Sci. Soc. Am. J. 50 (1986) 1442–1448.
[22] W.W. Choi, K.Y. Chen, Evaluation of boron removal by adsorption on solids, Environ. Sci. Technol. 13 (1979) 189–196.
[23] H. Polat, A. Vengosh, I. Pankratov, M. Polat, A new methodology for removal of boron from water by coal and fly ash, Desalination 164 (2004) 173–188.
[24] D. Kavak, Removal of boron from aqueous solutions by batch adsorption on calcined alunite using experimental design, J. Hazard. Mater. 163 (2009) 308–314.
[25] J. Kluczka, T. Korolewicz, M. Zolotajkin, W. Simka, M. Raczek, A new adsorbent for boron removal from aqueous solutions, Environ. Technol. 34 (2013) 1369–1376.
[26] M. Ichikuni, K. Kikuchi, Retention of boron by travertines, Chem. Geol. 9 (1972) 13–21.
[27] M.Y. Hobbs, E.J. Reardon, Effect of pH on boron co-precipitation by calcite: Further evidence for non-equilibrium partitioning of trace elements, Geochim. Cosmochim. Acta 63 (1999) 1013–1021.
[28] E. Lemarchand, J. Schott, J. Gaillardet, Boron isotopic fractionation related to boron sorption on humic acid and the structure of surface complexes formed, Geochim. Cosmochim. Acta 69 (2005) 3519–3533.
[29] N. Dionisiou, T. Matsi, N.D. Misopolinos, Use of magnesia for boron removal from irrigation water, J. Environ. Qual. 35 (2006) 2222–2228.
[30] E.L. Couch, R.E. Grim, Boron fixation by illites, Clays Clay Miner. 16 (1968) 249–256.
[31] E.L. Muetterties, The Chemistry of Boron and its Components, Wiley, New York, NY, 1967.
[32] R. Keren, D.L. Sparks, Effect of pH and ionic strength on boron adsorption by pyrophyllite, Soil Sci. Soc. Am. J. 58 (1994) 1095–1100.
[33] M.A. Elrashidi, G.A. O'Connor, Boron sorption and desorption in soils, Soil Sci. Soc. Am. J. 46 (1982) 27–31.
[34] M. McPhail, A.L. Page, F.T. Bingham, Adsorption interactions of monosilicic and boric acid on hydrous oxides of iron and aluminum, Soil Sci. Soc. Am. J. 36 (1972) 510–514.
[35] J.R. Sims, F.T. Bingham, Retention of boron by layer silicates, sesquoxides, and soil materials: II. Sesquioxides, Soil Sci. Soc. Am. J. 32 (1968) 364–369.
[36] R. Rahnemaie, T. Hiemstra, W.H. van Riemsdijk, A new surface structural approach to ion adsorption: Tracing the location of electrolyte ions, J. Colloid Interface Sci. 293 (2006) 312–321.
[37] R. Rahnemaie, T. Hiemstra, W.H. van Riemsdijk, Geometry, charge distribution, and surface speciation of phosphate on goethite, Langmuir 23 (2007) 3680–3689.
[38] M.B. McBride, A critique of diffuse double layer models applied to colloid and surface chemistry, Clays Clay Miner. 45 (1997) 598–608.
[39] U. Yermiyaho, R. Keren, Y. Chen, Boron sorption on composted organic matter, Soil Sci. Soc. Am. J. 52 (1988) 1309–1313.
[40] M. Singh, Equilibrium adsorption of boron in soils and clays, Geoderma 5 (1971) 209–217.
[41] B. Gu, L.E. Lowe, Observations on the effect of a soil polysaccharide fraction on boron adsorption by clay minerals, Can. J. Soil Sci. 72 (1992) 623–626.
[42] B. Gu, L.E. Lowe, Studies on the adsorption of boron on humic acid, Can. J. Soil Sci. 70 (1990) 305–311.
[43] S. Goldberg, H.S. Forster, Boron sorption on calcareous soils and reference calcites, Soil Sci. 152 (1991) 304–310.
[44] M.M.F.G. Soto, E.M. Camacho, Boron removal by means of adsorption with magnesium oxide, Sep. Purif. Technol. 48 (2006) 36–44.
[45] Y. Cengeloglu, A. Tor, G. Arslan, M. Ersoz, S. Gezgin, Removal of boron from aqueous solution by using neutralized red mud, J. Hazard. Mater. 142 (2007) 412–417.
[46] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption on waste sepiolite and activated waste sepiolite using full factorial design, Adsorption 10 (2004) 245–257.
[47] O.P. Ferreira, S.G. de Moraes, N. Durán, L. Cornejo, O.L. Alves, Evaluation of boron removal from water by hydrotalcite-like compounds, Chemosphere 62(1) (2006) 80–88.
[48] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by batch adsorption onto cerium oxide using full factorial design, Desalination 223 (2008) 106–112.
[49] M. Gazi, N. Bicak, Selective boron extraction by polymer supported 2-hydroxylethylamino propylene glycol functions, React. Funct. Polym. 67 (2007) 936–942.
[50] H. Merrikhpour, M. Jalali, Sorption processes of natural Iranian bentonite exchanged with Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} cation, Chem. Eng. Commun. 200 (2013) 1645–1665.
[51] H. Merrikhpour, M. Jalali, Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite, Clean Technol. Environ. Policy 15 (2013) 303–316.
[52] H. Merrikhpour, M. Jalali, Waste calcite sludge as an adsorbent for the removal of cadmium, copper, lead, and zinc from aqueous solutions, Clean Technol. Environ. Policy 14 (2012) 845–855.