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ORIGINAL PAPER

Surface complexation model of boron adsorption by calcareous soils

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Abstract This study aimed to evaluate boron (B) adsorption and the capacity of a surface complexation model for simulating this process in calcareous soils. Ten surface soils were collected from different land use areas in Hamedan, Western Iran, to characterize B sorption by soils. The mean B adsorbed by the sample soils varied from 8.9 to 32.8 %. Two empirical models including linear and Freundlich equations fitted well to the experimental data. The linear distribution (K_d) values varied from 1.32 to 6.86 L kg^{-1}, while the parameters of Freundlich equation including n and K_{Fr} ranged from 1.16 to 1.33 and 3.31–16.81, respectively. The comparison of two empirical models indicated that B adsorption followed a nonlinear pattern. The soil organic matter had positive correlations with Freundlich and linear distribution coefficients. However, empirical models were not suitable for explaining the mechanism of B adsorption, so a surface complexation model was used to simulate and predict the B adsorption process. B adsorption modeling was conducted using Visual MINTEQ and PHREEQC, based on the assemblage of major surface components (hydrous ferric oxides, aluminum hydroxides, calcium carbonate, and humic acids). B adsorption was successfully modeled by surface complexation. The significant contribution of organic matter to B complexes was resulted from both experimental data and mechanistic modeling.

Keywords Boron · Surface complexation · Adsorption · MINTEQ · PHREEQC

Introduction

Boron (B) is an essential nutrient that is required by plants in small amounts. The borate concentration in groundwater and surface water is typically low. However, it can be significantly increased by wastewater discharges, because borate compounds are common components of domestic detergents (ISO 1990). Boron naturally occurs in groundwater due to the leaching of rocks and soils containing borates and borosilicates. Groundwater B concentrations vary widely throughout the world from <0.3 to >100 mg L^{-1} (WHO 1998).

B adsorption reactions and the extent of soil sorption generally control the concentration of B dissolved in the soil. Chemical processes can also affect sorption reactions by controlling the dissolved B concentration, and consequently, they restrict B availability for plants. Distribution coefficients can be used to describe the relationship between the amount of B adsorbed by soil and that dissolved in water. Plants can only utilize or respond to B present in solution of soils, so B adsorbed on soil surfaces is nontoxic (Keren et al. 1985).

Important factors that are known to affect B adsorption and desorption in soils include the system pH (Hingston 1964), clay mineralogy (Hingston 1964; Keren and Mezuman 1981), the type of exchangeable ions (Parks and White 1952; Keren and Gast 1981), and wetting and drying cycles (Keren and Gast 1981).

There are various B adsorbing components with different adsorption capacities including clay minerals, Al and Fe oxides, $CaCO_3$, and humic particles (Goldberg and Glaubig 1985; Evans 1987; Goldberg and Glaubig 1988). Although Elrashidi and O'Connor (1982) reported no significant correlation between boron sorption and the soil $CaCO_3$ content, the highest level of B adsorption was

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found in the soils with the highest $CaCO_3$ content. Hingston (1964) found that the treatment of illite with $CaCO_3$ at the rate of 2 % resulted in decreasing B sorption capacity at pH 7.5 and 8.3; however, addition of $CaCO_3$ at pH 9.5 did not significantly influence B sorption when compared to untreated illite at pH 8.5. Ichikuni and Kikuchi (1972) suggested that B sorption on $CaCO_3$ can likely occur through precipitation of low-solubility calcium borate, B replacement with carbon in $CaCO_3$, and adsorption of B on $CaCO_3$ surfaces. They concluded that the main mechanism of B retention by $CaCO_3$ was adsorption.

Empirical models based on partition coefficients (K_d) or semiempirical Langmuir or Freundlich isotherms are often used to describe adsorbate partitioning between solutions and solid phases (Datta and Bhadoria 1999; Elrashidi and O'Connor 1982; Gupta et al. 2007, 2010; Mittal et al. 2010; Ranjbar and Jalali 2012). However, because partition coefficients depend on solution and solid composition, they cannot be utilized beyond the conditions for which they are measured. The ability of chemical models to describe the mechanism of B adsorption is obviously much more than empirical adsorption isotherm equations. Previous studies have investigated B adsorption using a constant capacitance model (CCM) as one of the mechanistic models (Goldberg et al. 2000, 2004, 2005). These models make a connection between surface complexation constants and some soil properties such as specific surface area, organic and inorganic carbon, and Al and Fe oxide contents (Goldberg et al. 2008). The empirical isotherm equations were used to predict B adsorption with changing pH (Goldberg et al. 2000) and equilibrium solution B concentration (Goldberg et al. 2004). Thus, in comparison with empirical equations, chemical models can be used to independently predict and describe B adsorption by soils.

The description of single-anion adsorption on oxide and hydroxide surfaces has mainly been performed by chemical complexation models. However, ion adsorption on soils or sediments is still problematic due to the competition for adsorption sites (Gustafsson 2001), the presence of various heterogeneous surfaces, and the heterogeneity of constituents as a consequence of the variety of organic and mineral components present on heterogeneous surfaces.

B adsorption modeling studies have been conducted with individual adsorbent materials such as aluminum and iron oxides/hydroxides, organic components, and goethite (Goldberg and Glaubig 1985; Toner and Sparks 1995; Goldberg 1999; Lemarchand et al. 2005; Goli et al. 2011). Although adsorption of B has been studied in numerous researches using empirical equations (Keren and Mezuman 1981; Elrashidi and O'Connor 1982; Goldberg and Forster 1991; Majidi et al. 2010), B surface complexation modeling of soil constituent assemblages has less been investigated (Goldberg 1999; Goldberg et al. 1993, 2000, 2004). The present study aimed to evaluate the utility of surface complexation modeling by using the Visual MINTEQ v.2.61 (Gustafsson 2006) and PHREEQC v.2.17 (Parkhurst and Appelo 1999) programs to describe B adsorption on hydrous ferric oxides (HFO), aluminum hydroxides, calcium carbonate, and humic acids. These are geochemical equilibrium speciation programs capable of computing equilibria among the dissolved, adsorbed, solid, and gas phases in an environmental setting. Furthermore, we compared the results predicted by mechanistic model with experimental data.

This study was conducted in June 2011 at Bu-Ali Sina University of Hamedan, western Iran.

Materials and methods

Physicochemical properties of soil samples

Ten soil surface samples (0–30 cm) were collected from different land use areas in Hamedan, western Iran. The main sampling points in each land use were selected at random locations generated with GPS; then, the soil samples were collected from these points and from the intervals specified in directions north, south, east, and west. Finally, all samples were combined and a composite sample for each land use was transferred to the laboratory. The geographical locations of soil sampling are given in Table 1. Soil samples were air-dried and ground until they passed through a 2-mm sieve, before their use in laboratory experiments. The physicochemical properties of soils were reported in detail by Ranjbar and Jalali (2012, 2013). The pH range was 6.8–7.8, and the quantities of soil electrical conductivity (EC) were low. The calcium carbonate equivalent content varied from 4.7 to 20.3 %, while the mean clay content was 29.1 % with a range of 14.5–43.2 %. The soil organic matter (SOM) varied from 0.66 to 3.9 %, while the mean total B in soils was

Table 1 Geographical positions of soil sampling points

Soil no.	Latitude	Longitude	Height
1	34°48′20.02″	48°28′35.00″	1,842
2	34°45′32.62″	48°26′21.91″	2,189
3	34°49′38.10″	48°25′24.10″	1,973
4	34°59′11.69″	48°24′13.61″	1,777
5	34°48′27.29″	48°30′26.32″	1,813
6	34°48′19.69″	48°28′57.00″	1,836
7	34°48′52.20″	48°30′26.60″	1,800
8	35°02′00.35″	48°19′55.09″	1,853
9	35°00′50.29″	48°22′11.71″	1,728
10	34°57′43.70″	48°24′54.79″	1,751

40.0 mg kg^{-1} with a range of 26.3–51.9 mg kg^{-1}. The oxalate reagent allows allophanes, iron and aluminum organic complexes, hydrated oxides of iron, and aluminum to be dissolved, whereas the dithionite–citrate–bicarbonate (DCB) reagent method (Mehra and Jackson 1960) extracts iron from the amorphous and crystalline compounds without significant modification of aluminosilicates or lithogenic hematite. Well-crystallized Al hydroxides are not extracted by the DCB method, and they are only partly extracted by the oxalate reagent (Parfitt and Childs 1988).

Isotherm experiments

These experiments were conducted using a batch method. One gram of each soil sample in duplicate was placed in polypropylene centrifuge tubes and equilibrated with 20 mL of different concentrations of B prepared from boric acid (0, 5, 10, 20, 30, 40, 50, and 100 mg B L^{-1}) in the presence of 0.01 M $CaCl_2$ solution for 24 h (Keren and O'Connor 1982). The suspensions were then centrifuged for 5 min and filtered. The equilibrium B concentration of each sample was measured using the colorimetric azomethine-H method (Bingham 1982). The difference between the amount of B in solution after equilibration and the initial concentration added was determined as the amount of B adsorbed by the soil. Jasmund and Lindner (1973) found that the presence of competing anions such as chloride, nitrate, and sulfate slightly influences B adsorption on clays, while phosphate remarkably causes to decrease B adsorption. Since the competitive adsorption was not aimed in this study, $CaCl_2$ was used as the background solution in the isotherm experiments.

Modeling of B adsorption

Empirical isotherm models

Empirical models including adsorption isotherm equations cannot describe adsorption process due to lack of mechanistic basis (Goldberg 1997). The most common models used to describe boron adsorption on oxides, clay minerals, and soils are Langmuir and Freundlich adsorption isotherms (Choi and Chen 1979; Elrashidi and O'Connor 1982; Goldberg and Forster 1991; Goldberg 1997).

We used the simple linear adsorption isotherm equation (K_d approach) and the nonlinear Freundlich equation to demonstrate the fit between experimental and modeled data:

$$Q_e = K_d C_e \tag{1}$$

where Q_e (mg kg^{-1}), C_e (mg L^{-1}), and K_d (L kg^{-1}) are the amounts of B adsorbed onto the solid phase, the equilibrium concentration of B in solution, and the linear distribution coefficient, respectively.

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

where Q_e (mg kg^{-1}) and C_e (mg L^{-1}) are the same as in Eq. (1), while K_{Fr} and n are empirical coefficients.

The Freundlich isotherm is based on two hypotheses: (1) adsorption occurs on a heterogeneous surface and (2) the heat of adsorption is exponentially distributed over the adsorbent surface (Gupta et al. 2010; Mittal et al. 2010).

The adsorbed B values for each step of the isotherm experiments in each soil sample were calculated using the following equation:

$$\text{Adsorbed B } (\%) = [(C_0 - C_e)/C_0] \times 100 \tag{3}$$

where C_0 (mg L^{-1}) is the initial B concentration.

Since empirical equations cannot predict B adsorption process with change in B concentration, pH, ionic strength in soil solution, etc., the parameters obtained from adsorption isotherm equations are only valid in specific experimental conditions (Goldberg 1997).

Chemical surface complexation models

The chemical mechanistic models are capable of describing the adsorption processes using an equilibrium approach. In case of boron adsorption, these models usually consider complex formation with surface hydroxyl groups on the variable charge sites of mineral and organic components in soils (Goldberg 1997).

Mass action and mass balance equations are two fundamental constituents in surface complexation models (Westall 1980). Some of the most important features of these models are consideration of chemical reactions, mass balances, and charge balance for the surface species as well as mathematical calculation of thermodynamic parameters including activity coefficients and equilibrium constants (Goldberg 1997). Furthermore, the main advantage of surface complexation models is that they can be widely used even with changing conditions such as adsorbate concentration in solution, pH, and ionic strength due to the consideration of charges on adsorbate ion and the adsorbent surface (Goldberg 1997).

In the present study, we considered HFO, aluminum hydroxides, calcium carbonate, and humic acids as the major soil surface components for B binding. Surface complexation modeling was performed using the Visual MINTEQ v.2.61 (Gustafsson 2006) and PHREEQC v. 2.17 (Parkhurst and Appelo 1999) programs. Table 2 shows the inorganic surfaces properties used in both programs. In MINTEQ, surface complexation was described using a diffuse double-layer model (DLM) with a 2-pK formalism. Since we considered four B-adsorbing surfaces in studied soils, the number of surfaces specified in surface complexation menu in MINTEQ program was selected to be 4.

Table 2 Inorganic surface properties used in MINTEQ and PHREEQC

Surface species	SSA† (m^2 g^{-1})	Site density (site nm^{-2})	Equations	
Hfo_wOH	600^a	2.256^a	$Hfo\_wOH + H^+ = Hfo\_wOH_2^+$	$\log K = 7.29^a$
			$Hfo\_wOH = Hfo\_wO^- + H^+$	$\log K = -8.93^a$
			$Hfo\_wOH + H_3BO_3 = Hfo\_wH_2BO_3 + H_2O$	$\log K = 0.62^a$
Hfo_sOH		0.056^a	$Hfo\_sOH + H^+ = Hfo\_sOH_2^+$	$\log K = 7.29^a$
			$Hfo\_sOH = Hfo\_sO^- + H^+$	$\log K = -8.93^a$
			$Hfo\_sOH + H_3BO_3 = Hfo\_sH_2BO_3 + H_2O$	$\log K = 5.63^e$
Alo_sOH	45^b	4.000^d	$Alo\_sOH + H^+ = Alo\_sOH_2^+$	$\log K = 7.38^e$
			$Alo\_sOH = Alo\_sO^- + H^+$	$\log K = -9.09^e$
			$Alo\_sOH + H_3BO_3 = Alo\_sH_2BO_3 + H_2O$	$\log K = 5.22^e$
Surf_wCaCO$_3$	0.22^c	4.402^c	$Surf\_wCaCO_3 + H_2O = Surf\_wCaOH_2^{2+} + CO_3^{2-}$	$\log K = -5.25^c$
			$Surf\_wcaCO_3 + HCO_3^- = Surf\_scaHCO_3 + CO_3^{2-}$	$\log K = 3.929^c$
			$Surf\_wCaCO_3 + H_3BO_3 = Surf\_wCaH_2BO_3^+ + HCO_3^-$	$\log K = -7.476^f$
Surf_sCaCO$_3$		0.554^c	$Surf\_sCaCO_3 + H_2O = Surf\_sCaOH_2^{2+} + CO3^{2-}$	$\log K = -5.25^c$
			$Surf\_scaCO_3 + HCO_3^- = Surf\_scaHCO_3 + CO_3^{2-}$	$\log K = 3.929^c$
			$Surf\_sCaCO_3 + H_3BO_3 = Surf\_sCaH_2BO_3^+ + HCO_3^-$	$\log K = 1.8^g$

w and s are representative of weak and strong sites, respectively

Hfo hydrous ferric oxides, *Alo* aluminum hydroxide

† Specific surface area

[a] MINTEQ and PHREEQC databases; [b] Manning and Goldberg (1996); [c] Sø et al. (2011); [d] Gustafsson (2001); [e] Goldberg (1999); [f] MINTEQA2 v.4 database; [g] Reardon (1976)

Then, the properties of each surface were added to program based on information given in Tables 2, 3, 4.

Complexation on organic matter can be modeled using WHAM, i.e., the Windermere Humic Acid Model of Tipping and Hurley (Tipping and Hurley 1992). In this model, the whole soil organic carbon is considered as humic acid and the complexation constants are defined for protons and cations at a number of monodentate and bidentate binding sites, which can be simply entered as SURFACE_SPECIES in PHREEQC. An empirical charge–potential relationship parameter for the (probably spherical) humic molecules is incorporated into the Gouy–Chapman relationship used in PHREEQC, by adjusting the specific surface area (SSA) using a function determined by the ionic strength of the solution (Appelo and Postma 2005):

$$SSA = 159{,}300 - 220{,}800/(I)^{0.09} + 91{,}260/(I)^{0.18} \quad (4)$$

where SSA (m^2 g^{-1}) and I (mol L^{-1}) are the specific surface area and ionic strength, respectively. The ionic strength was calculated using following equation (Griffin and Jurinak 1973):

$$I = 0.0127\ \mathrm{EC}. \quad (5)$$

The EC range of the soil samples was narrow (0.096–0.289 dS m^{-1}), so the mean value of EC (0.16) was used to calculate the ionic strength. Thus, the specific surface area of humic acids was assumed to be the same for all soils (52,332 m^2 g^{-1}).

Humic acid has a total charge of −7.1 meq g^{-1} in the WHAM model, which is distributed over four monoprotic carboxylic sites (nHA carrying a charge of −2.84 meq g^{-1} humic acid), four monoprotic phenolic sites (nHB, charge = −1.42 meq g^{-1} humic acid), and twelve diprotic sites combining carboxylic and phenolic charges (charge = −2.84 meq g^{-1} humic acid) (Tipping and Hurley 1992). Table 3 shows the organic B complexes with carboxylic, phenolic, and diprotic sites that were applied in PHREEQC. Only one monoprotic carboxylic site was considered in MINTEQ. The deprotonation constant of the surface site (log $K = -6.8$) and the B complex formation constant (log $K = 2.6$) were as given in Lemarchand et al. (2005).

To calculate the solid concentration on the surface sites, we converted the oxalate-extractable Fe and Al in each soil sample to HFO and aluminum hydroxide, based on their general formulae of FeOOH and Al(OH)$_3$, respectively. The measured calcium carbonate equivalent amounts were used to calculate the relevant solid concentration. The organic matter (OM) values were converted to organic carbon (multiplying by 1.72), and the charge values were calculated as stated above. Table 4 shows the solid concentrations on the surface sites that were used in both programs.

Statistical evaluation

To evaluate the model's efficiency in simulating the adsorption process, we calculated linear regressions for the

Table 3 Organic surface complexes used in PHREEQC

Equations		References
Monoprotic carboxylic sites		
$H\_aH = H\_a^{-} + H^{+}$	$\log K = -1.59$	Tipping and Hurley (1992)
$H\_bH = H\_b^{-} + H^{+}$	$\log K = -2.7$	
$H\_cH = H\_c^{-} + H^{+}$	$\log K = -3.82$	
$H\_dH = H\_d^{-} + H^{+}$	$\log K = -4.93$	
$H\_(a,b,c,d)H + H_3BO_3 = H\_(a,b,c,d)B(OH)_2 + H_2O$	$\log K = 2.5$	Lemarchand et al. (2005)
Monoprotic phenolic sites		
$H\_aH = H\_e^{-} + H^{+}$	$\log K = -6.88$	Tipping and Hurley (1992)
$H\_aH = H\_f^{-} + H^{+}$	$\log K = -8.72$	
$H\_aH = H\_g^{-} + H^{+}$	$\log K = -10.56$	
$H\_aH = H\_h^{-} + H^{+}$	$\log K = -12.4$	
$H\_(e,f,g,h)H + H_3BO_3 = H\_(e,f,g,h)B(OH)_2 + H_2O$	$\log K = 2.8$	Lemarchand et al. (2005)
Diprotic sites		
$H\_abH_2 = H\_ab^{2-} + 2H^{+}$	$\log K = -4.29$	Tipping and Hurley (1992)
$H\_adH_2 = H\_ad^{2-} + 2H^{+}$	$\log K = -6.52$	
$H\_afH_2 = H\_af^{2-} + 2H^{+}$	$\log K = -10.31$	
$H\_ahH_2 = H\_ah^{2-} + 2H^{+}$	$\log K = -13.99$	
$H\_bcH_2 = H\_bc^{2-} + 2H^{+}$	$\log K = -6.52$	
$H\_beH_2 = H\_be^{2-} + 2H^{+}$	$\log K = -9.58$	
$H\_bgH_2 = H\_bg^{2-} + 2H^{+}$	$\log K = -13.26$	
$H\_cdH_2 = H\_cd^{2-} + 2H^{+}$	$\log K = -8.75$	
$H\_cfH_2 = H\_cf^{2-} + 2H^{+}$	$\log K = -12.54$	
$H\_chH_2 = H\_ch^{2-} + 2H^{+}$	$\log K = -16.22$	
$H\_deH_2 = H\_de^{2-} + 2H^{+}$	$\log K = -11.81$	
$H\_dgH_2 = H\_dg^{2-} + 2H^{+}$	$\log K = -15.49$	
$H\_(ab,ad,bc,cd)H_2 + H_3BO_3 = H\_(ab,ad,bc,cd)BOH + 2H_2O$	$\log K = 5.0$	Lemarchand et al. (2005)
$H\_(af,ah,be,bg,cf,ch,de,dg)H_2 + H_3BO_3 = H\_(af,ah,be,bg,cf,ch,de,dg)BOH + 2H_2O$	$\log K = 5.3$	

Table 4 Solid concentration of surface sites used in both programs ($g\ L^{-1}$)

Soil no.	Hfo	$Al(OH)_3$	$CaCO_3$	Humic acid
1	0.022	0.0069	3.03	0.67
2	0.026	0.0036	2.87	1.13
3	0.026	0.0058	2.47	0.42
4	0.010	0.0039	8.60	0.19
5	0.025	0.0048	7.20	0.60
6	0.022	0.0051	4.88	0.34
7	0.039	0.0043	8.00	1.03
8	0.007	0.0036	2.38	0.36
9	0.009	0.0049	10.14	0.43
10	0.009	0.0044	7.27	0.44

measured values (y) on the modeled ones (x) and the coefficients of determination (R^2). This statistical parameter indicates the ratio between the scatter of simulated values and the average values of measurements. Thus, $R^2 = 1$, if the modeled values match the measured ones perfectly.

Results and discussion

Adsorption isotherms

Increasing the amount of B added to each soil increased the B sorption and the equilibrium solution B concentration (Fig. 1). The different studied soils exhibited a variable magnitude of B sorption. The effect of the initial B concentration on the B adsorption indicated that a greater proportion of added B was adsorbed at lower B concentrations.

The adsorbed values (%) obtained from Eq. (3) were decreased as the B concentration increased. The mean B adsorbed by the soil samples ranged from 8.92 % in soil no. 4 to 32.75 % in soil no. 7. Soil no. 4 had the minimum OM content compared to other soil samples. The percentage of adsorbed B was significantly positively correlated with the soil organic matter content ($r = 0.964$, $P < 0.01$). Therefore, the variable magnitudes of B adsorption in studied soils can be related to SOM as an important soil constituent that affects B availability. SOM binds B

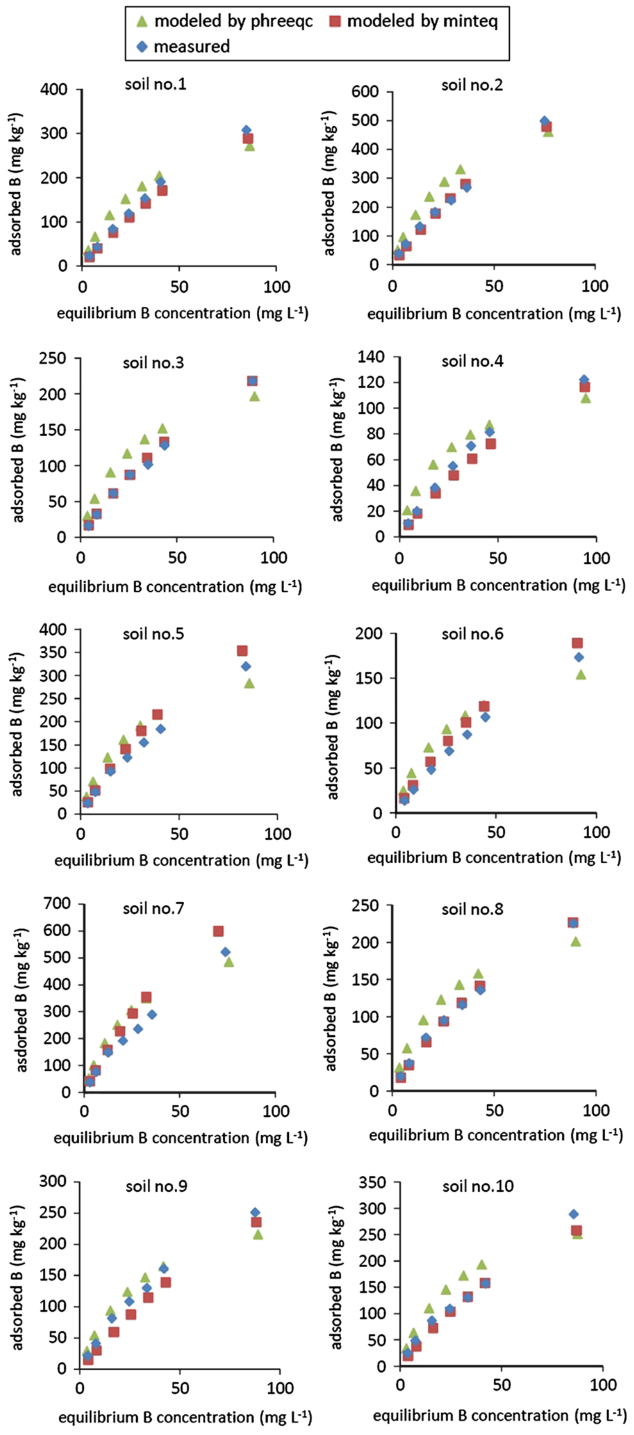

Fig. 1 Measured and modeled adsorption isotherms of boron in studied soils

Table 5 Parameters of empirical models fitted to experimental data

Soil no.	n	K_{Fr}	$R^{2\dagger}$	K_d	$R^{2\dagger}$
1	1.16	7.49	0.996	3.66	0.972
2	1.27	16.25	0.998	6.48	0.989
3	1.18	5.19	0.995	2.43	0.979
4	1.21	3.31	0.989	1.32	0.942
5	1.21	8.79	0.994	3.76	0.978
6	1.19	4.16	0.997	1.91	0.971
7	1.25	16.81	0.992	6.86	0.982
8	1.29	7.35	0.993	2.49	0.965
9	1.27	8.13	0.991	2.83	0.954
10	1.33	9.93	0.993	3.24	0.983

† Significant at $P < 0.01$

stronger and larger than mineral soil components at the same weight, and this interaction results in a reduction in B adsorption by minerals. The significant effect of organic components on B adsorption has been also reported by Parks and White (1952). Majidi et al. (2010) showed that the percentage of B adsorption by calcareous soils after application of 10 mmol B L^{-1} ranged from 3 to 20 %. This previous study also found no statistically significant relationship between the model parameters and soil properties, although soils with higher amounts of reactive particles (clay and OM) and higher pH adsorbed more B.

Table 5 shows the parameters of two linear and nonlinear equations that fitted well to the experimental data. The K_d values varied from 1.32 to 6.86 L kg^{-1}, while the parameters of Freundlich equation including n and K_{Fr} ranged 1.16–1.33 and 3.31–16.81, respectively. The comparison of R^2 values obtained from two equations indicated that B adsorption in our soil samples followed a nonlinear pattern, and the fit of nonlinear Freundlich equation to experimental data was better than simple linear equation. The empirical description of B adsorption on aluminum oxide (Choi and Chen 1979), clay minerals (Jasmund and Lindner 1973), calcite (Goldberg and Forster 1991), and soils (Elrashidi and O'Connor 1982; Evans 1987; Goldberg and Forster 1991; Wen-Ting et al. 2009) has been previously investigated using Freundlich equation. Arona and Chahal (2010) studied the effects of soil properties on B adsorption by arid and semiarid benchmark soils, and they reported that B adsorption data fitted successfully with Langmuir and Freundlich equations. Datta and Bhadoria (1999) studied B adsorption by acidic soils from India and reported n and K_{Fr} values ranging from 1.32 to 1.89 and 0.21 to 3.28, respectively. Soil pH can significantly influence B adsorption and thus B availability for plants. It has been reported that B adsorption increases with increasing pH from 3 to 9 (Bingham et al. 1971; Elrashidi and O'Connor 1982; Keren et al. 1985; Wen-Ting et al. 2009), whereas it decreases from pH 10 to 11.5 (Goldberg 1997). Therefore, higher K_{Fr} values indicating more B adsorption in this study in comparison with previous ones may be attributed to higher pH values in calcareous soil samples. The results also indicated that K_{Fr} ($r = 0.928$, $P < 0.01$) and K_d ($r = 0.982$, $P < 0.01$) were positively correlated with the soil organic matter content. There was also a significant correlation between K_d and oxalate-extractable Fe ($r = 0.690$, $P < 0.01$).

Although adsorption isotherm equations are widely used to describe B adsorption, they cannot be helpful for understanding adsorption mechanism due to the description of data using numerical relationships (Harter and Smith 1981). In other words, the experimental sorption data may be fit well with Langmuir and Freundlich equations, but they provide no information about the mechanism of the chemical reactions.

Surface complexation model

Tables 2, 3, and 4 show the surface properties used for B adsorption modeling. The pH range of the soil samples was <8, so B would mainly be present as $H_3BO_3^0$. Thus, log K values for surface complexation of this species were used. We selected surface characteristics from different sources with the greatest similarity to the conditions we used. Any variation in these properties will obviously give different results.

Figure 1 shows graphical evaluation of the modeling. The adsorbed values predicted by PHREEQC were higher than the actual values, with the exception of those corresponded to the highest initial added B concentration. The statistical evaluation of modeling obtained from linear regression of measured data and values modeled by PHREEQC and MINTEQ (data not shown) indicated that R^2 values ranged 0.910–0.967 and 0.987–0.999 (significant at $P < 0.01$), respectively. High coefficients of determination showed that surface complexation successfully predicted B adsorption in our soil samples, and both models were capable of simulating B adsorption on specified surface sites. The small difference between the results can be attributed to the various databases used in two programs.

The results of mechanistic modeling (Tables 6, 7) indicate that the contribution of surface constituents in B complexation follows this order: organic matter > aluminum hydroxide > Hfo > calcium carbonate. The soil organic matter which was considered as humic acid in modeling included more than 90 % of B adsorbed by surface complexes. As explained in material and method section, in order to mechanistically model the B adsorption, we supposed that all of soil organic carbon was in the form of humic acids. Furthermore, humic acid supposed to be composed of four monoprotic carboxylic, four monoprotic phenolic, and twelve diprotic sites to form complexes with B. However, due to the limitation in MINTEQ program, humic acid was not divided into different sites, while all of mentioned sites were defined in PHREEQC. So, organic complexes obtained from MINTEQ refer to B complexes formed with total humic acid that were nearly equal to sum of three types of organic complexes resulted from PHREEQC.

The significant effects of constituents such as iron and aluminum oxide/hydroxides, calcium carbonate, and organic matter on B adsorption and complexation have previously been reported. Goldberg and Glaubig (1988) investigated the B adsorption behavior of various crystalline and amorphous aluminum and iron oxides and found that sorption was enhanced by higher pH values. The maximum adsorption occurred at pH 6–7 with aluminum oxide and pH 8–9 with iron oxide. Hydroxyl Al-containing materials form stronger complexes with B in comparison with materials containing hydroxyl Fe (Adriano 1986).

The surface –OH groups on Al and Fe oxide minerals can bind B via ligand exchange process (McPhail et al. 1972; Goldberg et al. 1993; Su and Suarez 1995). The results of kinetic experiments conducted by Toner and Sparks (1995) showed that the ligand exchange of borate with surface –OH groups on Al oxide resulted in formation of inner-sphere surface complex. On the other hand, Su and Suarez (1995) by using the Fourier transform infrared (FTIR) spectroscopy indicated that adsorbed B species on amorphous Al and Fe oxides were composed of $B(OH)_3^0$ and $B(OH)_4^-$. It has been reported that B adsorption by goethite and birnessite was a pH-dependent process and the peak of B sorption occurred at $8 < pH < 9$ (Lemarchand et al. 2007). The results also indicated the higher value of linear distribution coefficient (K_d) for goethite than birnessite. On the other hand, these values were greater than those observed for clay minerals and humic acids.

B retention in soil may increase after addition of $CaCO_3$ due to the increasing soil pH. Calcium carbonate can play a significant role in B adsorption in calcareous soils (Elseewi 1974; Elseewi and Elmalky 1979; Goldberg and Forster 1991). Higher levels of B adsorption have been reported in soils with the high amount of calcium carbonate (Elseewi 1974; Elrashidi and O'Connor 1982). The main mechanism of B fixation by calcium carbonate is recorded to be adsorption (Ichikuni and Kikuchi 1972). Majidi et al. (2010) demonstrated a significant positive effect of calcium carbonate on B adsorption in calcareous soils. Removal of calcium carbonate from a soil sample in that study led to a 35 % reduction in B adsorption. The low effect of calcium carbonate and iron/aluminum oxides in this study may be related to their low levels in the soil samples.

Organic matter is an important soil component that affects the B availability. The proportionate B distribution among the four surface complexes was dependent on the initial added B concentration, as shown in Table 6 low B and high B. The contribution of organic matter (considered as humic acid) to B complex formation was significantly greater than other surface sites. The percentage of B complexation with hydrous ferric oxide and aluminum hydroxide was decreased by increasing the initial B concentration, whereas the proportion of organic complexes increased (Tables 6, 7). Yermiyaho et al. (1988) reported that B adsorption on composted organic matter is a rapid process and increased with increasing solution ionic

Table 6 The percentage of B distribution among different surface complexes modeled with initial concentration of 5 mg B L^{-1}

Soil no.	MINTEQ				PHREEQC					
								Organic complexes		
	$Hfo\_H_2BO_3$	$Alo\_H_2BO_3$	$Surf\_CaH_2BO_3^+$	Organic complexes	$Hfo\_H_2BO_3$	$Alo\_H_2BO_3$	$Surf\_CaH_2BO_3^+$	Monoprotic carboxylic complexes	Monoprotic phenolic complexes	Diprotic complexes
1	0.74	2.46	2.0×10^{-7}	96.80	0.69	0.96	0.31	53.02	45.01	–
2	0.59	0.82	9.0×10^{-8}	98.59	0.55	0.32	0.20	54.83	44.10	–
3	1.33	2.52	1.3×10^{-7}	96.15	1.01	1.03	0.33	42.11	55.52	–
4	0.33	3.13	6.5×10^{-7}	96.54	0.57	1.09	1.64	26.33	53.74	16.61
5	0.34	1.33	1.2×10^{-7}	98.34	0.73	0.62	0.67	43.01	54.97	–
6	0.80	2.31	4.3×10^{-7}	96.89	1.04	1.15	0.80	40.37	56.64	–
7	0.46	0.75	7.7×10^{-8}	98.79	0.77	0.35	0.48	44.62	53.77	–
8	0.14	1.49	7.1×10^{-8}	98.36	0.25	0.60	0.31	32.39	58.47	8.80
9	0.11	2.45	3.1×10^{-7}	97.43	0.27	0.52	0.81	78.81	19.51	–
10	0.14	1.65	2.3×10^{-7}	98.21	0.19	0.37	0.37	66.84	32.26	–

Table 7 The percentage of B distribution among different surface complexes modeled with initial concentration of 100 mg B L^{-1}

Soil no.	MINTEQ				PHREEQC					
								Organic complexes		
	$Hfo\_H_2BO_3$	$Alo\_H_2BO_3$	$Surf\_CaH_2BO_3^+$	Organic complexes	$Hfo\_H_2BO_3$	$Alo\_H_2BO_3$	$Surf\_CaH_2BO_3^+$	Monoprotic carboxylic complexes	Monoprotic phenolic complexes	Diprotic complexes
1	0.11	0.18	3.5×10^{-7}	99.71	0.11	0.17	0.05	68.29	31.38	–
2	0.08	0.06	1.5×10^{-7}	99.86	0.07	0.05	0.03	69.19	30.65	–
3	0.19	0.20	2.8×10^{-7}	99.61	0.19	0.20	0.05	58.38	41.17	–
4	0.13	0.26	1.1×10^{-6}	99.61	0.15	0.26	0.34	41.86	46.17	11.23
5	0.10	0.10	2.2×10^{-7}	99.79	0.12	0.11	0.11	59.00	40.66	–
6	0.17	0.21	9.5×10^{-7}	99.62	0.22	0.23	0.14	56.98	42.43	–
7	0.10	0.06	1.4×10^{-7}	99.84	0.11	0.06	0.07	60.03	39.73	–
8	0.05	0.12	1.4×10^{-7}	99.83	0.05	0.12	0.05	47.09	46.52	6.36
9	0.05	0.16	4.4×10^{-7}	99.78	0.05	0.12	0.19	86.71	12.91	–
10	0.05	0.13	4.2×10^{-7}	99.82	0.04	0.10	0.12	76.99	22.74	–

strength. It is obvious that these results have been obtained based on model prediction. Since the main purpose of this study was prediction of B adsorption mechanism using surface complexation models, we did not utilize any spectroscopic analysis to prove or validate our results. On the other side, the percentage of adsorbed B obtained from adsorption isotherm experiments was significantly positively correlated with the soil organic matter content. Therefore, it can be concluded that the consequences obtained from predicting mechanistic model are in the same side with experiment results.

The proportion of calcium carbonate complexes modeled by MINTEQ decreased with increasing initial B concentration from 5 to 100 mg L^{-1}; however, the reverse pattern was found with PHREEQC. The proportion of monoprotic carboxylic complexes increased with the initial 100 mg B L^{-1} level, although the monoprotic phenolic complexes decreased. The modeling results suggested that diprotic organic complexes may possibly have formed in soil nos. 4 and 8. Parks and White (1952) showed that B adsorption was significantly affected by humus extracted from soil. The positive correlation between adsorbed B and organic carbon content was also reported by other researchers (Elrashidi and O'Connor 1982; Evans 1987).

Yermiyaho et al. (1988) found that ability of SOM for complex formation with B was more than mineral soil components at the same weight. On the other hand, B reactive adsorption sites on soil minerals can be blocked by organic components (Marzadori et al. 1991; Gu and Lowe 1992). Lemarchand et al. (2005) demonstrated that B adsorption on the purified humic acid was a rapid, pH-dependant process which was significantly greater than that reported on clay minerals. The B adsorption curve was bell-shaped, and the maximum adsorption occurred at $9 < pH < 10$. Boron sorption by organic matter is mediated via ligand exchange (Yermiyaho et al. 1988). Parks and White (1952) found that carboxylic acid groups may have a role in monodentate and bidentate B-diol complex formation on organic matter. Datta and Bhadoria (1999) showed that organic carbon has a beneficial effect on the soil B retention capacity, which may be attributable to B forming a complex with dihydroxy organic compounds.

So, the results of both empirical and mechanistic modeling confirmed that organic matter is an important factor influencing B adsorption due to the high specific surface area and presence of reactive functional groups on its surface.

Conclusion

Empirical models can successfully be fit to experimental data, but they cannot explain the mechanism of B adsorption. Thus, we used a surface complexation model to simulate and predict the B adsorption process in ten soil samples. The modeled values were compared with the actual values using graphical and statistical methods. Boron adsorption was successfully modeled based on an assemblage of surface constituents, and it showed that HFO, aluminum hydroxides, calcium carbonate, and humic acids in particular were the major components that affected B adsorption in our ten soil samples. Thus, it can be concluded that chemical models of B adsorption have a more general predictive capability than empirical adsorption isotherm equations. Furthermore, since the parameters used in mechanistic models are composed of simple properties of adsorbing material, these models can be widely used in prediction of B adsorption in different types of soil, and mineral and organic components. This important advantage can be useful in reclamation of soils and waters contaminated with B based on prediction of B adsorption magnitude by any adsorbing component used as amendment. Organic materials can be applied as suitable amendments as they have more power for B adsorption in contrast to minerals.

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