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Adsorption of boron on iron-oxide in aqueous solutions

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ABSTRACT

The adsorption of boron on iron-oxide (FeO(OH)) has been investigated in aqueous solutions as a function of pH, ionic strength, temperature, boron concentration and amount of the adsorbent. Analysis of the experimental data indicates that boron adsorption on iron-oxide is based on the replacement of a water molecule by a boric acid molecule. Evaluation of the experimental data reveals that boron adsorption on iron-oxide is an exothermic process, which is not significantly affected by the ionic strength, indicating the formation of inner-sphere complexes. Furthermore, the maximum adsorption capacity of iron-oxide for boron has been determined using the Langmuir isotherm and is equal to 0.03 mol/kg. The conditional formation constant of the surface complexes under optimum conditions has been found to be $\log\beta^* = 4.5$, indicating the relative high affinity of iron-oxide for boron.

Keywords: Boron adsorption; Iron-oxide; Water solutions; Thermodynamic data; Surface complexes; Formation constant

1. Introduction

Boron is the first member of the main-group III elements in the periodic table with the chemical symbol B and atomic number 5. The element possesses a vacant p-orbital and all reactions are dominated by this electrophilic character of boron. Also boron compounds behave usually as Lewis acids, readily bonding with electron-rich Lewis bases to compensate for boron's electron deficiency [1]. Boron is a naturally occurring element that is found in oceans, sedimentary rocks, coal, shale, and some soils and is found mainly in the form of its oxygen compounds (e.g., borate minerals). There are hundreds of minerals that contain the element boron but few are found in great enough quantities to make them commercially valuable (e.g., colemanite, ulexite). In aqueous solutions boron exists predominantly as boric acid, which is a very weak Lewis acid with a pK of 9.2 and its dissociation is associated with the formation of $B(OH)_4^-$ and $H^+_{(aq)}$ through the addition of a water to a boric acid molecule as shown in Eq. (1) [1]:

$$B(OH)_{3(aq)} + H_2O \leftrightarrow B(OH)^-_{4(aq)} + H^+_{(aq)} \quad (1)$$

The acidity of boric acid can be increased by reacting $B(OH)_3$ with poly-alcoholic compounds (e.g., mannitol) to form esters. The strength of these new compounds is similar to that of acetic acid with a pK of about 4.7 [1]. It is also important to point out that, depending on the concentration of boric acid, different polyborate species formed by the condensation of several borate molecules may exist in solution. However, at boron concentrations below 0.025 mol/l the aquatic chemistry of boron is governed only by $B(OH)_3$ and $B(OH)_4^-$ [2].

Boron enters the environment mainly from the weathering of boron-containing rocks, from seawater in the form of boric acid vapour and from volcanic and other geothermal activities such as geothermal discharges. In natural waters the concentration of boron is usually less

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than 1 mg/l and seldom exceeds the boron concentration in seawater, which is relatively high and averages around 4.5 mg/l. However, depending on the hosting lithology boron concentration in regional ground waters can reach levels up to 8 mg/l [3]. Boron is also released, though to a lesser extent, from human activities, which include the use of borate-containing fertilizers and herbicides, the use of borates and perborates in the home and in industry, and the release of waste from borate mining and processing. Borate mining and use of boron in various manufacturing industries is associated with industrial effluents that can contain boron up to several grams per liter (g/l) and have to be treated before discharge in natural water bodies [4].

Several technologies have been proposed and applied for the removal of boron from waters and wastewaters [5–9]. In particular, several studies for the adsorption of boron by clays, soils, and other minerals have been carried out by several investigators [4,10–13]. Usually these studies are concerned with parameters that affect the efficiency of adsorption and only few studies have addressed the nature of the adsorbed boron species and the mechanism of the adsorption process [14–17]. In some cases (for example sorption on aluminum oxides) significant progress regarding the interaction mechanism has been made, but in other cases (like magnesium oxide) further investigations are needed in order to understand boron adsorption by solids and in particular metal oxides [16].

In addition, boron adsorption on iron-oxide (Fe(O)OH) is of particular interest because according to literature, aluminium and iron oxides are the primary boron adsorption surfaces in soils. Particularly, the content of iron oxide was a significant parameter explaining the variance in adsorbed, soluble and total boron for soils [10,11]. The present paper reports experimental results on the adsorption of boron by iron-oxide at various conditions (e.g., pH, ionic strength, temperature, boron concentration and amount of adsorbent), discusses the effect of these parameters on boron adsorption, suggests possible adsorption mechanisms and evaluates a formation constant of the surface complexes.

2. Experimental

A periodically mixed batch technique was selected for the batch adsorption experiments. All experiments were carried out under normal atmospheric conditions at 22 ± 3°C. Test solutions were prepared by dissolution of a standard boron solution (99.99%, Aldrich Co) in aqueous solution. The ionic strength (0.1 and 1.0 M) in the test solutions was adjusted by addition of sodium perchlorate ($NaClO_4$, Aldrich Co). The ionic strength values up to 1.0 M were selected to cover also ionic strength values corresponding to saline waters (e.g., seawater, ~0.7 M). Solutions without background electrolyte are denoted by $I = 0.0$ M. The adsorbent, iron-oxide (Fe(O)OH, mesh-325, Aldrich Co) was used without any further purification or other pre-treatment. The zero point of charge on the surface (pzc value) of the solid was determined by acid-base titration in solutions of varying ionic strength and was found to be ~8.0 [18].

Immediately after the addition of 100 ml of the test solutions to the adsorbent, the 100 ml polyethylene screw capped bottles were shaken and left for an equilibration time of three days. The solutions were then first centrifuged at 5000 rpm (Lab centrifuge, Memmert Co) and passed through a 0.20 µm Minisart RC 25 filter. The concentration of boron in solution was determined by spectrophotometry, using the azomethine-H method [19].

Four classes of experiments were conducted:

1) pH dependence: the pH value of the adsorption system (1.0 g adsorbent and 100 ml of the test solution: [B] = 0.55 mg/l) was varied between 4 and 12, by addition of perchlorate acid ($HClO_4$, Aldrich Co) or sodium hydroxide (NaOH, Aldrich Co).
2) Temperature dependence: the temperature of the sorption systems was varied between 25 and 70°C and after an equilibration time of three days at each adjusted temperature measurements were carried out. Amount of adsorbent (10 g/l), initial boron concentration (0.55 mg/l) and pH in the test solutions (100 ml) were kept constant.
3) Dependence on the initial boron concentration: the concentration of the adsorbate in the test solutions was varied between 0.1 and 7 mg/l, while a prefixed amount of adsorbent (adsorbent dosage = 1 g per 100 ml equivalent to 10 g/l) was weighted into 100 ml polyethylene screw capped bottles.
4) Dependence on the amount of adsorbent: various amounts of adsorbent (between 0.05 and 2.5 g) were weighted into a 100 ml polyethylene screw capped bottle, containing 100 ml of the test solutions. The concentration of the adsorbate in the test solutions was kept constant at 0.55 mg/l.

3. Results and discussion

3.1. pH

Fig. 1 shows the relative amount of boron adsorbed (B_{ads}) on iron-oxide as a function of pH, at three different ionic strengths. Moreover, Fig. 1 shows the pH area where the surface of the solid is predominantly positive or negative charged (point of zero charge, pzc ~ 8) and the area where boric acid (H_3BO_3) or borate ($B(OH)_4^-$) are the dominant boron species in solution. The optimum pH

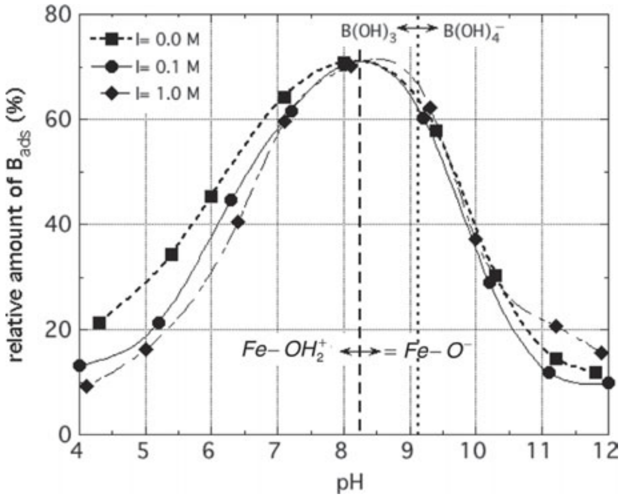

Fig. 1. Effect of pH on the removal efficiency of boron by iron-oxide. Conditions: amount of iron-oxide = 10 g/l, initial boron concentration 0.55 mg/l and temperature 22 ± 3°C.

for the removal of boron by iron-oxide is found to be close to the pzc value from 7 to 9 with a maximum at about pH 8 and this value agrees well with values given in the literature [20]. This pH value is close to the pzc value of iron-oxide and is somewhat lower than the pK_a (9.2) of the boric acid, indicating that the optimum conditions for boron removal occur when the surface has no charge and boric acid is the predominant species in solution.

This sorption behaviour is similar to the sorption behaviour of boron onto alumina, amorphous iron oxide, kaolinite, hematite and goethite and supports the mechanism involving a Lewis acid/base reaction of H_3BO_3 at the surface of the adsorbent resulting in the formation of an inner-sphere complex [20–22]. The adsorption mechanism is schematically shown in Fig. 2 and results in two possible surface complexes. The bi-dentate complex (2) is expected to be dominant at low boron concentrations, whereas the mono-dentate complex (1) is favoured at increased boron concentrations. Below pH 8 the surface sites become protonated, dissociation of the boric acid at the surface is unlikely to occur and thus the efficiency of boron removal is decreasing. At pH > 9, the surface is negative charged and repels borate anions which are at this pH area the dominant species in solution, resulting in lower removal efficiency. These results indicate that the adsorption of boron is affected by both the distribution of boron species and the type and/or number of active sites of the adsorbent that may vary with pH changes. The experiments of pH variation have shown that the optimum pH for boron adsorption on iron-oxide is at 8 and thus the following experiments have been performed at this pH.

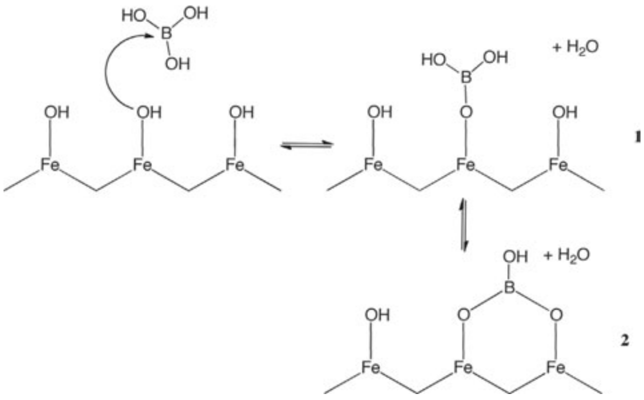

Fig. 2. Proposed mechanism for the adsorption of boric acid on iron-oxide surface, at pH 8.

3.2. Temperature

The effect of temperature on boron adsorption on iron-oxide was investigated at three different ionic strengths and various temperatures in order to validate the adsorption mechanism and estimate the apparent thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$). The thermodynamic parameters of the sorption reaction such as the free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were determined using the Eqs. (2) and (3):

$$\Delta G° = -RT \ln K_\mathrm{d} \tag{2}$$

and

$$\ln K_\mathrm{d} = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{3}$$

where T is temperature in Kelvin, R is the gas constant and K_s is the equilibrium constant of the adsorption reaction defined as:

$$K_\mathrm{d} = \frac{[B_\mathrm{ads}]}{[B_\mathrm{aq}]} \tag{4}$$

where $[B_\mathrm{ads}]$ is the amount of boron (in mg) adsorbed on iron-oxide per liter of the solution at equilibrium, and $[B_\mathrm{aq}]$ is the equilibrium concentration (in mg/l) of boron in solution.

The values of $\Delta H°$ and $\Delta S°$ were obtained from the slop and the intercept of the van't Hoff plot of lnK_d vs $1/T$, respectively. The graphical presentation of the van't Hoff plot is shown in Fig. 3 and the thermodynamic data evaluated are summarized in Table 1.

Negative values for $\Delta G°$ indicate that the adsorption is a spontaneous process. Furthermore, adsorption of

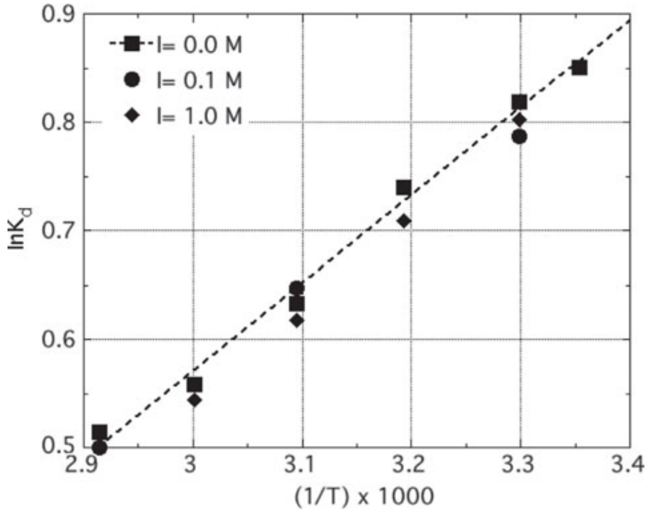

Fig. 3. Van't Hoff plot of the adsorption of boron by iron-oxide. Conditions: amount of adsorbent = 10 g/l, initial boron concentration 0.55 mg/l and pH 8.

Table 1
Thermodynamic data of the boron adsorption on Fe(O)OH

ΔH° (kJ/mol)	ΔS° (J/Kmol)	ΔG° (kJ/mol)					
		298K	303K	313K	323K	333K	343K
–15.5	–35.5	–4.9	–4.7	–4.4	–4.0	–3.7	–3.3

boron on iron oxide is based on surface complexation by species exchange, that is enthalpy-driven and the entropy effect is of minor importance. The almost similar thermodynamic values evaluated for the three different ionic strengths support the assumption that the boron adsorption on iron-oxide is based on inner-sphere complexation. In contrast to inner-sphere complexes, the stability of outer-sphere complexes, which are based on electrostatic interactions, are strongly affected by increasing ionic strength [23].

3.3. Boron concentration and amount of the adsorbent

The effect of the boron concentration on the adsorption efficiency of iron-oxide is shown in Fig. 4. According to Fig. 4 the removal efficiency of is higher at lower boron concentrations ($[B_{aq}]$) and this effect can be ascribed to the gradual occupation of certain types of active sites on iron-oxide where boron is adsorbed preferentially. Applying the Langmuir isotherm model on the experimental data results in a maximum adsorption capacity of about 0.03 mol/kg. The corresponding value for alumina is 0.04 mol/kg [21] and is somewhat higher because of the higher surface area of the former.

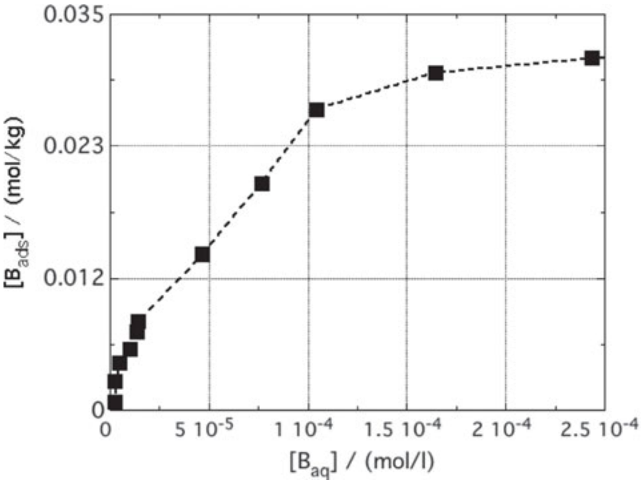

Fig. 4. Isotherm of the adsorption of boron by iron-oxide. Conditions: amount of iron-oxide = 10 g/l, pH 8, background electrolyte 0.1 M $NaClO_4^-$ and temperature 22 ± 3°C.

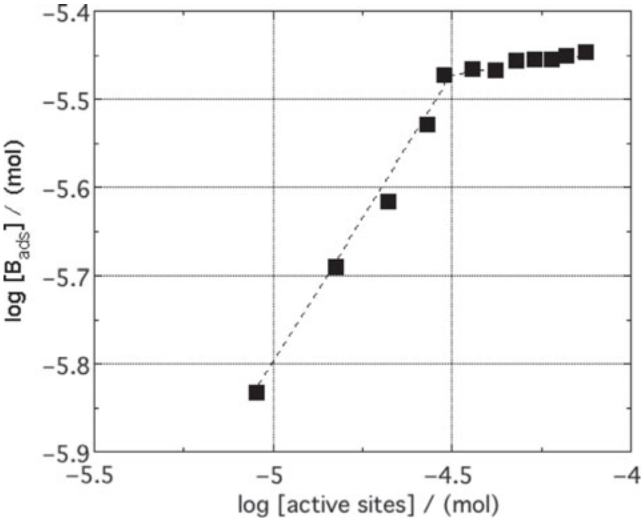

Fig. 5. Correlation between surface active sites and boron species adsorbed by iron-oxide. Conditions: Initial boron concentration 0.55 g/l, pH 8, ionic strength 0.1 M $NaClO_4$, amount of adsorbent 10 g/l and temperature 22 ± 3°C.

In Fig. 5 the adsorbent dosage is expressed in moles of active surface sites, as determined by the Langmuir isotherm. The removal efficiency (with initial boron concentration of 0.55 mg/l) increases linearly with increasing adsorbent dosage. The linear correlation between the moles boron adsorbed and the moles of active surface sites presents a slope close to 1 and indicates the formation of 1:1 complexes between boric acid or borate anions and the active surface sites. This behaviour is similar with boron adsorption on alumina, which also results in the formation of 1:1 inner-sphere complexes [21].

3.4. Stability of surface complexes

As already mentioned, the sorption of boron by iron-oxide occurs through the formation of inner-sphere surface complexes. These complexes are formed by acid/base interactions between of the boric acid and the hydroxyl groups of the surface. The boric acid, which is the predominant boron species under the given conditions in solution acts as the Lewis acid and the hydroxyl groups of the surface as the Lewis base. Schematically, the sorption of boron by the solid surface is illustrated in Fig. 2. Hereby the surface of the iron-oxide particles acts as cation exchanger, which binds boron through the oxygen active sites. In terms of a chemical equation, the interaction of the boric acid with Fe(O)OH is described by Eq. (5):

$$\mathrm{B(OH)_3} + (=\mathrm{Fe{-}OH})_2 \leftrightarrow (=\mathrm{Fe}-\mathrm{O}-)_2\,\mathrm{BOH} + 2\mathrm{H_2O} \tag{5}$$

and the corresponding equilibrium constant is given by Eq. (6)

$$K = \frac{[(=\mathrm{Fe{-}O{-}})_2\mathrm{BOH}]}{[\mathrm{B(OH)_3}]\cdot[(=\mathrm{Fe{-}OH})_2]} \tag{6}$$

at pH 8 Eq. (6) can be reformulated:

$$\beta^* = \frac{[(=\mathrm{Fe}-\mathrm{O}-)_2\mathrm{BOH}]}{[\mathrm{B(OH)_3}]\cdot[(=\mathrm{Fe{-}OH})_2]} \tag{7}$$

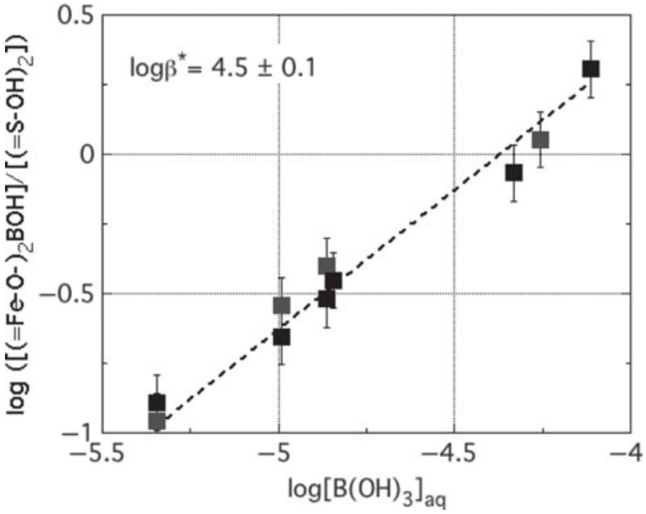

Fig. 6. log([(=Fe–O–B(OH)$_2$]/[(=Fe–OH)]) as a function of log[B(OH)$_3$]. The data were obtained from photometric measurements in aqueous solutions containing 10 g/l iron-oxide at different boron concentrations, 0.1 M NaClO$_4$ as background electrolyte and at 22 ± 3°C under normal atmospheric conditions.

where, β^* is the conditional formation constant, $[(=\mathrm{Fe{-}O{-}})_2\mathrm{BOH}]$ is the concentration of the complexed boron and equals to the total boron concentration (initial boron concentration) minus the non-complexed boron concentration determined by photometry. The non-complexed boron concentration equals to the boric acid concentration ($[\mathrm{B(OH)_3}]$) in solution because the latter is the predominant species under the given conditions. $[(=\mathrm{Fe{-}OH})_2]$ is defined as the total concentration of active sites on the solid surface minus the complexed active sites ($[(=\mathrm{Fe{-}OH})_2]=[(=\mathrm{Fe{-}OH})_2]_{tot}-[(=\mathrm{Fe{-}O{-}})_2\mathrm{BOH}]$). The total concentration of active sites ($[(=\mathrm{Fe{-}OH})]_{tot}$) corresponds to the total number of the surface sites available for boron complexation and is determined using the Langmuir isotherm. Taking the logarithm and rearranging Eq. (7) results in Eq. (8):

$$\log\left(\frac{[(=\mathrm{Fe{-}O{-}})_2\mathrm{BOH}]}{[(=\mathrm{Fe{-}OH})_2]}\right) = \log\beta^* + n\cdot\log([\mathrm{B(OH)_3}]) \tag{8}$$

The intercept of the line described by Eq. (8) corresponds to the logarithmic value of the conditional constant ($\log\beta^*$) and the value of the slope corresponds to the stoichiometric factor of $[\mathrm{B(OH)_3}]$, which here by definition equals to unit. Fig. 6 presents the experimental data in a $\log([(=\mathrm{Fe{-}O{-}})_2\mathrm{BOH}])/([(=\mathrm{Fe{-}OH})_2])$ vs $\log[\mathrm{B(OH)_3}]$ diagram. Linear regression analysis of the experimental data obtained at pH 8 based on Eq. (8) results in a $\log\beta^*$ of 4.5 ± 0.1 and in slope of 1.0 ± 0.1. The value of the slope is consistent with the equation proposed for the surface complexation of boron by iron-oxide. On the other hand comparing the value of the formation constant for the adsorption of boron on iron-oxide ($\log\beta^*$ of 4.5) with the corresponding data for the adsorption of boron on alumina ($\log\beta^*= 4.5$) [21], reveals a similar affinity of the two oxides for boron, indicating similar type of surface complexes (e.g., inner-sphere complexes). Although there are several papers dealing with the adsorption of boron on iron oxides, there are no formation constants given for comparison. However, reports on similar behavior between aluminum- and iron-oxides indicate that the similar values of the formation constants could be correct [13,20].

4. Conclusions

The results obtained from this study lead to the following conclusions:

- The optimum pH for boron removal by sorption on iron-oxide is pH ~ 8
- The adsorption is based on inner-sphere complexation and is an exothermic reaction.

- The maximum removal capacity, which is calculated from the Langmuir isotherm, is found to be 0.03 mol/kg.
- The formation constant of the boron surface complexes has been evaluated from experimental sorption data and is equal to $\log\beta^* = 4.5$, indicating an increased affinity of the iron-oxide for boric acid.
- Iron-oxide is an important adsorbent for boric acid, which could affect the chemical behaviour and migration of boron in natural environment, and in industrial water treatment processes related to boron removal.

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