Competitive adsorption of boric acid and chromate onto alumina in aqueous solutions

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ABSTRACT

The competitive adsorption of boric acid and chromate from aqueous solutions by alumina has been investigated by spectrophotometry at pH 8, ionic strength $\text{I} = 0.0, 0.1$ and $1.0 \text{ M NaClO}_4$, $T = 22 \pm 3 ^\circ \text{C}$ and under normal atmospheric conditions. The experimental data show that addition of excess boric acid in the system leads to the increase of Cr(VI) concentration in solution, indicating the replacement of adsorbed chromate by boron on the alumina surface. Data evaluation results in the determination of the competition reaction constant and the formation constant of the Cr(VI) surface complexes, which are $\log K_{\text{Cr(VI)-B(III)}} = -3.5 \pm 0.2$ and $\log^{\text{+ Cr}} = 7.6 \pm 0.3$, respectively.

Key words | adsorption, alumina, boric acid, chromate, competition, reaction constants

INTRODUCTION

Various pollutants (e.g. hexavalent chromium and boron) are introduced into the aquatic environment from a variety of industrial operations causing damages to the environment and affecting human health. Pollution of the environment with hexavalent chromium (Cr(VI)) and associated toxicity to microorganisms, plants, animals and humans is of major concern. Indeed, chromium in environmentally significant concentrations is found near to tanneries and chromium plating facilities and involves large volumes of wastewater (Mathur et al. 1977; Holdway 1988; Palmer & Wittbrodt 1991). Groundwater (with increased boron content) used in industrial activities (e.g. tanneries and chrome plating facilities) is associated with wastewaters containing both species, boron and chromium, which at pH 8 and normal atmospheric conditions exist predominantly as boric acid and chromate in aqueous solutions, respectively (Ayuso et al. 2007; Bouguerra et al. 2008). Boron in irrigation water is of particular interest because it can have beneficial or toxic effect on plants, depending on its concentration. For most plants boron levels above 1.0 mg l$^{-1}$ are considered toxic, but for sensitive crop (like citrus trees) the upper limit is even less (0.3 mg l$^{-1}$) (Nable et al. 1997).

One of the most effective remediation technologies used for the removal of Cr(VI) and B(III) from aquatic systems is their adsorption onto metal oxide surfaces (Goldberg & Glaubig 1985; Zachara et al. 1987; Hu et al. 2005; Garcia-Soto & Camacho 2006; Konstantinou et al. 2006; Ayuso et al. 2007; Bouguerra et al. 2008; Demetriou & Pashalidis 2009; Demetriou & Pashalidis 2011; Demetriou & Pashalidis 2012a, b). However, in order to understand better the mechanisms involved and improve the efficiency of remediation technologies, further fundamental studies are needed. In previous studies we have investigated parameters affecting the adsorption of boron on alumina and magnesia and compared the adsorption behaviour on the two different metal oxides (Konstantinou et al. 2006). For a further comparison, boron adsorption studies were performed also with iron oxide (Demetriou & Pashalidis 2012a, b). In addition to the experimental investigations and in order to better understand the adsorption of boron on alumina at molecular level, Raman spectroscopic and theoretical studies were performed (Stefani et al. 2008; Demetriou et al. 2012). Regarding the chromate adsorption, we have investigated the adsorption of chromate on dunite, obtained from a local igneous rock formation (Demetriou & Pashalidis 2011) and magnesia (Demetriou & Pashalidis 2009). In order to obtain information about the chemical affinity (e.g. values of the formation constant for surface complexes) and better understand the interaction mechanisms between chromate and the alumina surface,
studies based on competition reactions are very useful (Demetriou & Pashalidis 2012a, b). As a competitor species, boric acid has been used because boron is a common component of wastewaters and the adsorption of boric acid on alumina has been studied extensively.

The present study is focused on the competitive adsorption of chromate (CrO$_4^{2-}$) and boric acid (H$_3$BO$_3$) onto alumina at various ionic strengths ($I = 0.0$, $0.1$ and $1.0$ M NaClO$_4$), under normal atmospheric conditions, at $22 \pm 3$ C and pH 8 to investigate the adsorption mechanism and compare the individual affinities of CrO$_4^{2-}$ and H$_3$BO$_3$ for alumina. The concentration of chromate and boric acid in solution was determined spectrophotometrically by means of DPC (1,5-diphenylcarbazide) and azomethine-H, respectively.

**METHODS**

A periodically mixed batch technique was selected for the batch adsorption and competitive adsorption experiments. All experiments were performed at room temperature (22 ± 3 °C), under normal atmospheric conditions, in aqueous solutions, at pH 8 (except those related to the effect of pH) and three different ionic strengths ($I = 0.0$ M, $0.1$ M and $1.0$ M NaClO$_4$). The pH 8 was adjusted and maintained in solution by adding small amounts of $0.1$ M HClO$_4$ or NaOH in the test solutions. After adjustment the pH remained almost stable at pH 8 because this value corresponds to the point of zero charge (pzc) value of alumina. The experiments were performed in triplicate and the mean values have been used for data evaluation. The preparation of chromate and boron stock solutions was carried out by dissolution of a potassium chromate salt (K$_2$CrO$_4$, BDH Co) and a standard boron solution (99.99%, Aldrich Co), respectively. All experiments were performed in polyethylene screw-capped bottles since preliminary experiments have shown that adsorbate sorption onto the screw-capped bottle walls was negligible.

The ionic strengths 0.1 and 1.0 M in the test solutions were adjusted by the addition of sodium perchlorate (NaClO$_4$, Aldrich Co.), whereas $I = 0$ M indicates solutions without electrolyte addition. The adsorbent, alumina (Al$_2$O$_3$, 99.99%, 150 mesh, Aldrich Co.), was used without any further purification or other pre-treatment. The BET (Brunauer-Emmett-Teller) surface area and the average pore diameter was determined by N$_2$ adsorption (Micromeritics ASAP 2010 BET surface area analyser) and was found to be 169 m$^2$ g$^{-1}$ and 6 nm, respectively. The pzc value was determined by acid-base titration in solutions of various ionic strengths and was found to be ~8.0.

The potentiometric pH measurements were carried out by means of a glass electrode attached to a pH meter (Hanna Instruments, HI 8314, membrane pH-meter). The system was calibrated with buffer solutions (pH 2, 4, 7 and 10, Merck) before and after each measurement.

Experiments of the Cr(VI) sorption onto alumina were performed by addition of a Cr(VI) stock solution ([Cr(VI)] = 5·10$^{-5}$ mol l$^{-1}$ at pH = 8) to a test solution, which consisted of 0.05 g solid in 100 ml of $0.1$ M NaClO$_4$ aqueous solution. Several mixtures of constant amount of the adsorbent (0.05 g) and variable Cr(VI) concentration (5·10$^{-6}$ mol l$^{-1}$ < [Cr(III)] < 7·10$^{-4}$ mol l$^{-1}$) were prepared. Following three days equilibration, the concentration of the non-complexed Cr(VI) was determined spectrophotometrically at 543 nm using DPC (1,5-diphenylcarbazide) as chromophoric agent (Eckert et al. 1991; Hoshi et al. 1998). For comparison, parallel measurements were made for solutions of similar composition without solid (reference solutions).

Experiments of the B(III) adsorption onto alumina were performed by addition of B(III) stock solution ([B(III)] = 2·10$^{-4}$ mol l$^{-1}$ at pH = 8) to a test solution, which consisted of 1.0 g solid in 100 ml of $0.1$ M NaClO$_4$ aqueous solution. Several mixtures of constant amount of the adsorbent (1.0 g) and variable B(III) concentration (9·10$^{-6}$ mol l$^{-1}$ < [B(III)] < 7·10$^{-4}$ mol l$^{-1}$) were prepared. Following three days equilibration, the concentration of the non-complexed B(III) was determined spectrophotometrically using azomethine-H at 414 nm as chromophoric agent (Zenki et al. 1989; Rump & Krist 1992). For comparison, parallel measurements were made for solutions of similar composition without solid (reference solutions).

Competition reactions between chromate and boric acid regarding sorption on alumina were investigated by addition of a defined amount of a boron stock solution ([B(III)] = 5·10$^{-3}$ mol l$^{-1}$) to a 10 ml suspension containing alumina loaded with chromate, ($n$(Cr(VI)) = 5·10$^{-7}$ moles; 0.05 g alumina), at pH 8, $T = 22 \pm 3$ C and at three different ionic strengths ($I = 0.0$, $0.1$ and $1.0$ M NaClO$_4$). The competition reaction studies were performed in parallel and therefore several mixtures of Cr(VI)-loaded alumina (e.g. chromate was previously adsorbed on the alumina surface) and variable [B(III)] (5·10$^{-5}$ mol l$^{-1}$ < [B(III)] < 5·10$^{-4}$ mol l$^{-1}$) concentration were prepared. All spectrophotometric measurements were performed using a UV-visible recording spectrophotometer (UV-2401 PC/Shimadzu).
RESULTS AND DISCUSSION

Adsorption of Cr(VI) on alumina

pH effect

The pH of an aqueous solution is an important parameter that governs the adsorption of metal ions on metal oxide surface. Variation of pH affects both the stability of soluble species and the surface properties (e.g. the charge of functional groups responsible for surface sorption). Figure 1 shows the effect of pH (in the range 4 and 12) on the adsorption efficiency of Cr(VI) onto alumina at three different ionic strengths and \( T = 22 \pm 3 \) °C.

From Figure 1 it becomes evident that the optimum pH for the Cr(VI) adsorption onto alumina surface ranged between 5 and 7 for all the studied ionic strengths. There is an effect of the ionic strength on the relative adsorption of Cr(VI) on the surface, indicating the formation of outer-sphere complexes. However, this effect is relatively small particularly at pH 8 (~2%), indicating that the chromate adsorption on alumina is basically determined by the formation of inner-sphere complexes. The changes in Cr(VI) relative adsorption relating to pH are attributed mainly to changes of the surface charge (pzc value) of the adsorbent. At low pH values (pH < pzc), the relative adsorption increases because the surface of the adsorbent is positively charged and attracts the negatively charged chromate species (mainly HCrO\(_4\)). On the other hand, at high pH values (pH > pzc), the adsorption efficiency decreases because the surface of the adsorbent is negatively charged and repulses the negatively charged CrO\(_4^{2-}\) anions, which are the predominant Cr(VI) species at the respective pH range.

Cr(VI) initial concentration effect

Figure 2 shows the adsorption isotherm of Cr(VI) onto alumina at ionic strength 0.1 M NaClO\(_4\). According to Figure 2, the adsorption of Cr(VI) on alumina does not reach a plateau (surface saturation) but increases exponentially with increasing chromate concentration even at concentration values up to \( 7 \times 10^{-4} \) mol l\(^{-1}\). The isotherm behaviour indicates a chemical reaction occurring at the surface of the adsorbent that attracts and consumes species from the solution. Since no surface reduction of chromate is expected in the studied system, we assume a surface polynucleation of the adsorbed Cr(VI). Polynucleation of chromate on oxide surfaces (Weckhuysen et al. 1996) and ion-exchange resins (Sengljpta 1986) is described also in the literature.

Adsorption of B(III) on alumina

pH effect

Figure 3 illustrates the effect of pH on the relative adsorption/chemical recovery of B(III) on alumina at three different ionic strengths.

The optimum pH for the removal of boron by alumina is found to range from 7 to 9 with a maximum of about pH 8. This value is in agreement with the values given in the literature and related with boron adsorption onto amorphous and crystalline alumina (Goldberg 1997). This pH value is close to

**Figure 1** | Effect of pH on Cr(VI) adsorption onto alumina at ionic strengths 0.0, 0.1, and 1.0 M NaClO\(_4\), \( T = 22 \pm 3 \) °C, \([\text{Cr(VI)}]_0 = 5 \times 10^{-5} \) mol l\(^{-1}\) and \( m_{\text{alumina}} = 0.5 \) g l\(^{-1}\).

**Figure 2** | Adsorption isotherm of Cr(VI) on alumina at ionic strength 0.1 M NaClO\(_4\), pH 8, \( T = 22 \pm 3 \) °C and \( m_{\text{alumina}} = 0.5 \) g l\(^{-1}\).
the pzc value of alumina and is somewhat lower than the $pK_a$ (9.2) of the boric acid (H$_3$BO$_3$), indicating that the optimum conditions for boron removal are given when the surface has no charge and boronic acid is the predominant species in solution. The ionic strength has only a small impact on the adsorption processes, indicating that electrostatic interactions are of minor importance and that the adsorption occurs mainly via inner-sphere complex formation.

**B(III) initial concentration effect**

Figure 4 shows the adsorption isotherm of B(III) onto alumina at ionic strength 0.1 M NaClO$_4$. In contrast with the adsorption isotherm of chromate on alumina, which increases exponentially with increasing Cr(VI) concentration, the adsorption of boron onto alumina reaches a plateau, indicating the saturation of the adsorbent with the adsorbed species, and is described by the Langmuir model. The maximum adsorption capacity ($q_{\text{max}}$) is about 0.04 mol B(III) kg$^{-1}$ of solid and is significantly higher (about 0.02 mol B(III) kg$^{-1}$ of solid) than the corresponding value reported in the literature (Busseti et al. 1995).

**Competitive adsorption of Cr(VI) and B(III) on alumina**

To show the relative affinity of chromate for alumina and estimate a formation constant for the Cr(VI)–Al$_2$O$_3$ surface complex ($\log \beta_{\text{Cr(VI)-Al}_2\text{O}_3}$), we have performed experiments on the adsorption competition between Cr(VI) and B(III) for the adsorbent active binding sites. Boron (boric acid, H$_3$BO$_3$) was chosen as competitor because the adsorption of boric acid onto alumina is extensively studied and the formation constant of the B(III)–Al$_2$O$_3$ surface complex ($\log \beta_{\text{B(III)-Al}_2\text{O}_3}$) has been previously determined and found equal to 4.1 ± 0.1 (Demetriou et al. 2012). The primary experimental data obtained from competitions reactions between Cr(VI) and B(III) onto alumina performed at three different ionic strengths are plotted in the diagram shown in Figure 5. [Cr(VI)]$_{\text{aq}}$ and [B(III)]$_{\text{aq}}$ are the aqueous chromate and boron concentration, respectively, and determined by spectrophotometry.

From the diagram in Figure 5 it is evident that, under the given conditions, gradual addition of boron to the Cr(VI)–Al$_2$O$_3$ adsorption system saturated with chromate ions leads to the release of chromate and therefore to the increase of its concentration in solution. The chromate concentration in solution increases as the amount of boron is increased in the Cr(VI)–Al$_2$O$_3$ sorption system. This phenomenon is due to the replacement of Cr(VI) ions by B(III) on the surface of alumina.

For pH 8, the chemical competition reaction (1) and the corresponding competition constant (2) between Cr(VI) and B(III) for alumina active binding sites can be written as follows:

$$S - \text{Cr(VI)}_{\text{aq}} + n \cdot \text{B(III)}_{\text{aq}} \leftrightarrow S - \text{B(III)}_n + m \cdot \text{Cr(VI)}_{\text{aq}}$$

$$K_{\text{Cr(VI)-B(III)}} = \frac{S - \text{B(III)}_n \cdot \text{[Cr(VI)]}_{\text{aq}}^m}{[\text{B(III)}_{\text{aq}}]^m \cdot [S - \text{Cr(VI)}]^n}$$


Taking the logarithm and rearranging Equation (2), the following linear equation is obtained:

\[
\frac{n}{C_1} \log \frac{[\text{Cr(VI)}]_{\text{aq}}}{[\text{Cr(VI)}]_{\text{aq}}} = \frac{S}{C_0} \cdot \frac{[\text{B(III)}]_{\text{aq}}}{[\text{B(III)}]_{\text{aq}}} - m
\]

The competition reaction constant \( K_{\text{Cr(VI)-B(III)}} \) can be determined from the linear relationship given in Equation (3) and the relevant experimental data. The intercept of the line described by Equation (3) corresponds to the equilibrium constant of the competition reaction \( K_{\text{Cr(VI)-B(III)}} \), and the value of the slope corresponds to the stoichiometric factor of the competition reaction. \([=S-\text{Cr(VI)}] \) is the concentration of the surface-bound Cr(VI), which equals the total Cr(VI) concentration (initial Cr(VI) concentration) minus the aqueous Cr(VI) concentration \([\text{Cr(VI)}]_{\text{aq}}\) determined by spectrophotometry. \([-S-B(\text{III})] \) is the concentration of the surface bound B(III) and is assumed to equal the Cr(VI) concentration exchanged from the surface. The ‘concentration’ and consequently the numbers of alumina functional groups which are available for complexation are assumed to remain constant. In addition, \( n \) and \( m \) are the stoichiometric factors in the reaction Equation (1) for chromate and boric acid, respectively.

The experimental data obtained from competition reactions between Cr(VI)–B(III) regarding their surface binding by alumina and preformed at three different ionic strengths are plotted according to Equation (3) and the corresponding diagram is shown in Figure 6.

Evaluation of the data by linear regression results in a value for the slope corresponding to the Cr(VI)-alumina adsorption system equal to 2. This value indicates that one B(III) replaces two chromate ions \( (\text{CrO}_4^{2-}) \) or one dichromate \( (\text{Cr}_2\text{O}_7^{2-}) \). The latter is in agreement with the formation of polynuclear Cr(VI) species. The two possible surface reaction mechanisms which could describe the competition reaction between Cr(VI) and B(III) regarding their binding by the alumina active sites are shown schematically in Figure 7.
The logarithmic value of the competition constant for the Cr(VI)-alumina adsorption system (logK_{Cr(VI)-B(III)}) has been evaluated from the experimental data shown in Figure 6 and is equal to −3.5 ± 0.2. The negative sign indicates the higher affinity of chromate for the alumina surface. This value is similar to the corresponding one for the Cr(VI)-Fe(O)OH adsorption system (Demetriou & Pashalidis 2012a, b). Despite the higher affinity of chromate for alumina its replacement by boric acid occurs, because the concentration of the latter used in the competition experiments was up to two orders of magnitude higher than the chromate concentration.

Taking into account the value of the formation constant of B(III)–Al₂O₃ surface complex (logβ_{B} = 4.1 ± 0.1) and the value of the competition reaction constant (logK_{Cr(VI)-B(III)} = −3.5 ± 0.2), the formation constant for Cr(VI)–Al₂O₃ surface complexes is calculated to be logβ_{Cr(VI)} = 7.6 ± 0.3. This value is close to the value of the average intrinsic formation constant of the B(III)–α-Al₂O₃ surface complex which is given in the literature as logK_{int} = 5.84 (Zachara et al. 1988) and also to the value of the formation constant for a Cr(VI)–Fe(O)OH surface complex (logβ_{Cr(VI)} = 7.9 ± 0.2) (Demetriou & Pashalidis 2012a, b).

CONCLUSIONS

- The adsorption behaviour and the relative affinity of boron (boric acid) and chromium (chromate), two elements found in industrial wastewaters (e.g. tanneries, metal plating facilities), has been studied by batch adsorption and competition reaction experiments.

- The two species behave differently regarding their adsorption on alumina. In contrast to boron adsorption that is well fitted by a Langmuir isotherm, the chromate adsorption follows an exponential adsorption curve, indicating polynucleation reaction on the surface and preventing an evaluation of the formation constant of surface species.

- However, the relative affinity could be quantified by evaluation of the competition data, which indicate orders of magnitude higher affinity of alumina for chromate compared to boric acid (logK_{Cr(VI)-B(III)} = −3.5 ± 0.2). Further, the data indicate that two chromate species are replaced by one boric acid, and the formation constant for the Cr(VI)-alumina surface complex is calculated to be logβ_{Cr(VI)} = 7.6 ± 0.3.

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