

SPECTOPHOTOMETRIC STUDIES ON THE COMPETITIVE ADSORPTION OF BORIC ACID (B(III)) AND CHROMATE (Cr(VI)) ONTO IRON (OXY) HYDROXIDE (Fe(O)OH)

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ABSTRACT

Various pollutants (e.g. boron and hexavalent chromium) are introduced into the aquatic environment from a variety of industrial operations causing damages to environment and affecting human health. Boron in irrigation water is of particular interest because it can have beneficial or toxic effect on plants, depending on its concentration. 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 involves large volumes of wastewater. One of the most effective remediation technologies used for the removal of B(III) and Cr(VI) from aquatic systems and wastewater is their sorption on metal oxide surfaces. However, in order to understand better the mechanisms involved and improve the efficiency of remediation technologies further fundamental studies are needed. The present study is focused on the adsorption of H_3BO_3 and CrO_4^{2-} onto Fe(O)OH at various ionic strengths ($I = 0.0, 0.1$ and 1.0 M $NaClO_4$), under normal atmospheric conditions, at 22 ± 3 °C and pH 8. Additionally, competitions studies were carried out to investigate the ion-exchange mechanism and compare the individual affinities of H_3BO_3 and CrO_4^{2-} for Fe(O)OH. The concentration of H_3BO_3 and CrO_4^{2-} in solution was determined spectrophotometrically by means of azomethine-H and DPC (1,5-diphenylcarbazide), respectively. The results obtained indicate that the release of Cr(VI) and therefore its concentration in solution increases as the amount of B(III) is increased in the sorption system. This phenomenon is due to the replacement of Cr(VI) ions by ions B(III) on the surface of Fe(O)OH. Evaluation of the experimental data results in a value for the competition constant which is equal $\log K = -3.5 \pm 0.2$, indicating that the adsorbent surface has greater affinity for Cr(VI) than for B(III) species. The formation constant for the Cr(VI)-Fe(O)OH surface complex is calculated to be $\log \beta_{Cr} = 7.9 \pm 0.2$.

KEYWORDS: boron; chromate; adsorption; metal oxides; competition reaction; formation constants.

INTRODUCTION

Removal of toxic metal ions and other chemical species from contaminated waters by adsorption on solid surfaces (minerals and metal oxides) is compared to other water treatment technologies (e.g. precipitation, ion exchange and reverse osmosis) a cost-effective, simple regarding design and operation, and insensible to toxic substances. Moreover, adsorption water treatment technologies meet environmental protection requirements (Kurniawan *et al.*, 2006). There are several studies on the adsorption of boron (Konstantinou *et al.*, 2006; Demetriou and Pashalidis, 2012; Bouguerra *et al.*, 2008; Goldberg and Glaubig, 1985; Goldberg, 1999) and chromate (Alvarez-Ayuso *et al.*, 2007; Bhutani *et al.*, 1992; Tel *et al.*, 2004; Demetriou and Pashalidis, 2011; Erdem *et al.*, 2004) on metal oxides and other minerals, however these studies

are usually concerned with parameters that affect the efficiency of adsorption and only few studies have addressed the nature of the adsorbed species and the mechanism of the adsorption process (Goldberg *et al.*, 1993; Corwin *et al.*, 1999; Chunming and Suarez, 1995; Peak *et al.*, 2003; Weerasooriya and Tobschall, 2000). Adsorption studies of contaminants on iron-oxide (Fe(O)OH) is of particular interest because besides aluminium oxides, iron oxides are the primary 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 (Goldberg and Glaubig, 1985; Bloesch *et al.*, 1987; Goldberg *et al.*, 1993).

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). In aqueous solutions boron exists predominantly as boric acid, which is a very weak Lewis acid with a pK of 9.2 (Garcia-Soto and Camacho, 2005). In natural waters the concentration of boron is usually less than 1 mg l⁻¹ and seldom exceeds the boron concentration in seawater, which is relatively high and averages around 4.5 mg l⁻¹.

Boron is released to the environment mainly from human activities. 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⁻¹) and have to be treated before discharge in natural water bodies (Weinthal *et al.*, 1985). Humans can be exposed to boron through vegetables, water, air and consumer products. Due to potential adverse health effects of boron on human beings international regulatory bodies (e.g. WHO, EU) have set up standards/guidelines (0.5 mg l⁻¹) for boron in drinking water (WHO, 1994; Weinthal *et al.*, 2005). Furthermore, increased boron levels in irrigation waters can have deleterious effects on boron-sensitive crops (e.g. citrus plants). According to Keren and Bingham (Keren and Bingham, 1985) the safe B concentration ranges are 0.3 to 1 mg l⁻¹ for sensitive crops, 1 to 2 mg l⁻¹ for semi-tolerant crops, and 2 to 4 mg l⁻¹ for tolerant crops. In order to achieve the desired boron levels, often removal of boron from drinking and irrigation waters is required (Nikolai, 1996; Kotas and Stasicka, 2000).

Chromium is also a naturally occurring element that enters the human environment through various natural processes and human activities. Contamination of soil and waters occurs mainly due to the disposal of products/waste containing chromium and untreated industrial effluents. In aqueous solution chromium exists usually in the form of trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) ions. Cr(VI) is the most important species of chromium and it is highly soluble in water and as anionic species very mobile in the geosphere. In aqueous solutions Cr(VI) exists depending on the pH and its concentration in different forms such as chromic acid (H₂CrO₄), chromates (HCrO₄⁻ and CrO₄²⁻) and dichromate (Cr₂O₇²⁻), besides chromic acid (H₂CrO₄) [26]. At increased concentrations and in the neutral and alkaline pH, dichromate is the predominant form of Cr(VI). In the acidic pH range, chromate or chromic acid become the most dominant species and Cr(VI) becomes a strongly oxidizing because its redox potential increases significantly. In contrast to Cr(III), which is an essential trace element in human and animal diets (Anderson 1989), Cr(VI) has been reported to be carcinogenic and cytotoxic effects for human beings and animals (Kotas and Stasicka, 2000). Therefore wastewater containing Cr(VI) have to be treated before discharge in natural water bodies.

Pollution of the environment with hexavalent chromium (Cr(VI)) and associated toxicity to microorganisms, plants, animals, and humans is of major concern (Palmer and Wittbrodt, 1991; Mathur *et al.*, 1997; Holdway *et al.*, 1988). Indeed, chromium in environmentally significant concentrations is found near to tanneries and processing facilities and usually involves large volumes of wastewater. Removal of Cr(VI) from such large volumes of wastewater require a cost effective remediation technology. Conventional wastewater treatment technologies usually rely on metal oxide and mineral adsorbents (Zachara *et al.*, 1987; Davis and Leckie, 1980; Bhutani *et al.*, 1992; Demetriou and Pashalidis, 2009). On the other hand, chemical behavior and migration of Cr(VI) species in the geosphere is strongly governed by adsorption/desorption phenomena on the underlying rock formations (Davis and Leckie, 1980). Hence, studies regarding Cr(VI) adsorption on metal oxides and natural minerals and the evaluation of the corresponding thermodynamic data is of fundamental importance with respect to the treatment

of Cr(VI) contaminated waters and environmental impact assessments related to Cr(VI) disposal and migration in the geosphere (Richard and Bourg, 1991)

The chemistry during Cr(VI) removal by activated sludge is of particular interest. The highest adsorption of Cr(VI) in these systems is observed at pH 7 and 8 and the removal is more efficient under anaerobic conditions. The latter can be attributed to the reduction of Cr(VI) to Cr(III). The aerobic activity of Cr(VI) reduction is associated with a soluble protein fraction utilizing NaDH as an electron donor, whereas under anaerobic condition Cr(VI) may act as a terminal electron acceptor through a membrane bound reductase activity (Stasinakis and Thomaidis, 2010).

This paper presents a study on the adsorption of Cr(VI) species and the competitive adsorption of Cr(VI) and B(III) on iron (oxy)hydroxide by means of photometry using chromophoric organic reagents. The study aims to compare the affinity of two different pollutants for iron (oxy)hydroxide and provide further insight into the B(III) and Cr(VI) adsorption on metal oxide and mineral surfaces. Boron and chromium can be found simultaneously in acid mine drainage according to previous investigations (Demetriou *et al.*, 2010).

EXPERIMENTAL

All experiments were performed at room temperature (22 ± 3 °C) under atmospheric conditions in aqueous solutions at pH 8 and constant ionic strength ($I=0.1$ M NaClO₄). The experiments were performed in duplicate and the mean values have been used for data evaluation. The preparation of boron and chromate stock solutions was carried out by dissolution of a standard boron solution (99.99%, Aldrich Co) and a potassium chromate salt (K₂CrO₄, BDH 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.

Iron(Oxy)hydroxide

The material for the adsorption experiments (Fe(O)OH, 50-80 mesh, 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 various ionic strengths and was found to be ~8.0.

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

Experiments of B(III) sorption on iron(oxy)hydroxide were performed by addition of a B(III) stock solution ($[B(III)] = 5 \cdot 10^{-5}$ mol l⁻¹ at pH = 8) to a test solution, which was consisted of 1.0 g solid in 100 ml of 0.1 M NaClO₄ aqueous solution. Several mixtures of constant amount of the adsorbent (1.0 g) and variable B(III) concentration ($9 \cdot 10^{-6}$ mol l⁻¹ < $[B(III)]$ < $7 \cdot 10^{-4}$ mol l⁻¹) were prepared. After three days equilibration, the solutions were first centrifuged at 5000 rpm (Lab centrifuged, Memmert Co) and passed through a 0.20- μ m Minisart RC 25 Filter. The concentration of the non-complexed B(III) species was determined by photometry using azomethine-H as chromophoric reagent. For comparison, parallel measurements were made for solutions of similar composition without iron(oxy)hydroxide (reference solutions).

Experiments of the Cr(VI) sorption onto iron(oxy)hydroxide were performed by addition of a Cr(VI) stock solution ($[Cr(VI)] = 5 \cdot 10^{-5}$ mol l⁻¹ at pH = 8) to a test solution, which was consisted of 0.05 g solid in 100 ml of 0.1 M NaClO₄ aqueous solution. Several mixtures of constant amount of the adsorbent (0.05 g) and variable Cr(VI) concentration ($5 \cdot 10^{-6}$ mol l⁻¹ < $[Cr(VI)]$ < $7 \cdot 10^{-4}$ mol l⁻¹) were prepared. Following three days equilibration, the concentration of the non-complexed Cr(VI) species was determined spectrophotometrically by means of DPC (1,5-diphenylcarbazide). For comparison, parallel measurements were made for solutions of similar composition without solid (reference solutions). The three days equilibration time has been chosen based on experience obtained by previous experiments (Konstantinou *et al.*, 2006; Demetriou and Pashalidis, 2011).

The K_d values have been determined by equation (1):

$$K_d(\text{l.kg}^{-1}) = \frac{[\text{Cr(VI)}]_{\text{ads}}}{[\text{Cr(VI)}]_{\text{free}}} \quad (1)$$

where, K_d is the conditional linear distribution coefficient, $[\text{Cr(VI)}]_{\text{ads}}$ is the amount of chromate adsorbed on Fe(O)OH (in mol kg^{-1}) and $[\text{Cr(VI)}]_{\text{free}}$ is the equilibrium concentration of chromate (in mol l^{-1}), as it determined by photometry.

Competition reactions between Cr(VI) and B(III) regarding sorption on iron(oxy)-hydroxide were carried out by addition of a defined amount (1, 2, 3, 4, 6, 8, 10 and 11 ml) of a B(III) stock solution ($[\text{B(III)}] = 5.10^{-3} \text{ mol l}^{-1}$), to a suspension containing iron(oxy)hydroxide loaded with Cr(VI) , ($[\text{Cr(VI)}] = 5.10^{-5} \text{ mol l}^{-1}$), at $\text{pH } 8$, $T = 22 \pm 3^\circ\text{C}$ and at three different ionic strengths ($I = 0.0, 0.1$ and 1.0 M NaClO_4). Several mixtures of constant amount of Cr(VI) (10ml) loaded iron(oxy)hydroxide (0.05 g) and variable $[\text{B(III)}]$ ($5.10^{-5} \text{ mol l}^{-1} < [\text{B(III)}] < 5.10^{-4} \text{ mol l}^{-1}$) concentration were prepared. Competition reactions between B(III) and Cr(VI) regarding sorption on iron(oxy)hydroxide were carried out by addition of a defined amount (1, 2, 3, 4, 5, 8, 10 and 11 ml) of a stock solution ($[\text{Cr(VI)}] = 5.10^{-3} \text{ mol l}^{-1}$), to a suspension containing iron(oxy)hydroxide loaded with B(III) ($[\text{B(III)}] = 5.10^{-5} \text{ mol l}^{-1}$). Several mixtures of constant amount of B(III) loaded iron(oxy)hydroxide (1.0 g) and variable $[\text{Cr(VI)}]$ ($5.10^{-5} \text{ mol.l}^{-1} < [\text{Cr(VI)}] < 5.10^{-4} \text{ mol l}^{-1}$) concentration were prepared.

The experiments were performed in 100mL screw capped polyethylene vials. After three days equilibration, the pH was measured and amount of the species exchanged determined spectrophotometrically. The LOD (limit of detection) of the method has been determined to be $9.10^{-6} \text{ mol l}^{-1}$ and $1.10^{-6} \text{ mol l}^{-1}$ for boron and chromate, respectively.

RESULTS AND DISCUSSION

Adsorption of Cr(VI) on Fe(O)OH

Figure 1 shows the isotherm for Cr(VI) adsorption on Fe(O)OH at ionic strength 0.1 M NaClO_4 ($\text{pH}=8$ and $T= 22 \pm 3^\circ\text{C}$). From Figure 1 becomes evident that the isotherm doesn't reach a plateau (surface saturation) but increases exponentially with increasing chromate concentration even at concentration values up to $7.10^{-4} \text{ mol l}^{-1}$. This isotherm behavior indicates a chemical reaction occurring at the surface that attracts and consumes chromate species from solution. Since no surface reduction of Cr(VI) is expected in the studied system, we assume a surface polynucleation of the adsorbed Cr(VI) , which is described also in literature for chromate adsorption/binding on oxide surfaces (Weckhuysen *et al.*, 1996) and ionexchange resins (Sengljpta,1986).

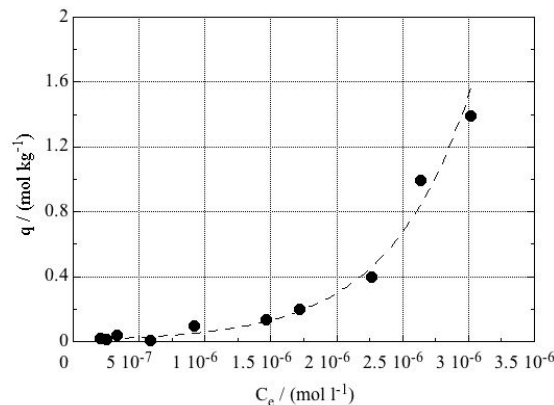


Figure 1. Adsorption isotherm of Cr(VI) on Fe(O)OH at ionic strength 0.1 M NaClO_4 , $\text{pH}=8$, $T= 22 \pm 3^\circ\text{C}$ and $m_{\text{Fe(O)OH}}= 0.5 \text{ g l}^{-1}$

The relatively high values of K_d over a wide pH range (Figure 2) indicate also the occurrence of polynuclear surface complexes. On the other hand the ionic strength has only small impact on the adsorption process indicating that electrostatic interactions are of minor importance and that

the adsorption occurs mainly via inner-sphere complex formation, supporting also the formation of polynuclear surface species. The change of the pH dependence of K_d for $\text{pH} > 6$ is attributed to the second dissociation of the chromic acid ($\text{p}K_2 \sim 6.5$).

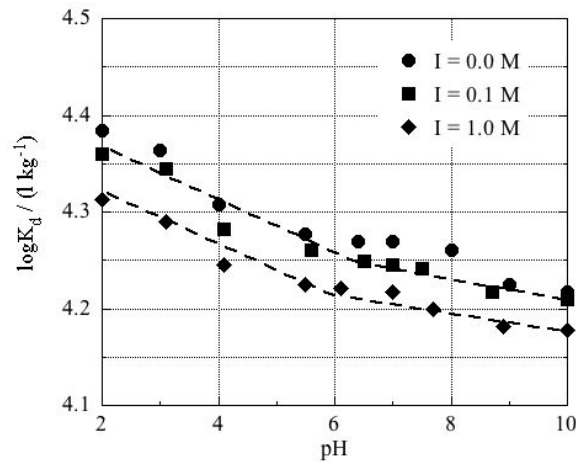


Figure 2. $\log K_d$ values as a function of pH for the Cr(VI) adsorption on Fe(O)OH at three different ionic strengths, $T=22 \pm 3^\circ\text{C}$, $[\text{Cr(VI)}] = 5.10^{-5} \text{ mol l}^{-1}$ and $m_{\text{Fe(O)OH}}=0.5 \text{ g l}^{-1}$

Competitive Adsorption of Cr(VI) and B(III) on Fe(O)OH

To show the relative affinity of Cr(VI) for Fe(O)OH but also estimate a formation constant for the Cr(VI) surface complexes we have performed competition adsorption experiments between Cr(VI) and B(III) . B(III) (boric acid) was chosen as competitor because the adsorption of boric acid on Fe(O)OH is extensively studied and the formation constant of the B(III) surface complexes on Fe(O)OH have been previously determined [3]. Figure 3 shows the Cr(VI) concentration in solution when the concentration of B(III) in the solution of a Cr(VI)/Fe(O)OH adsorption system is increased.

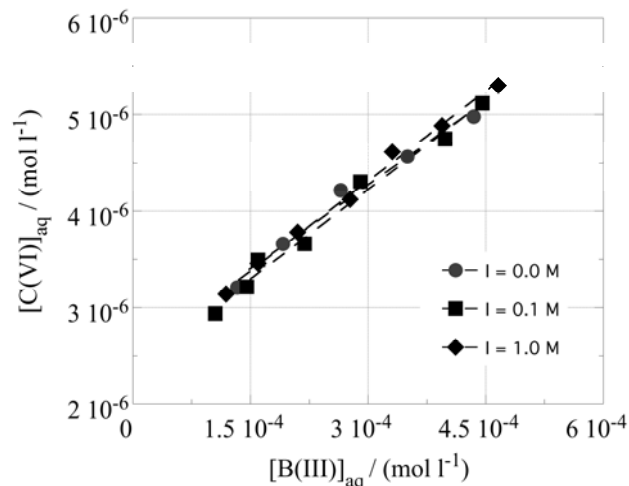
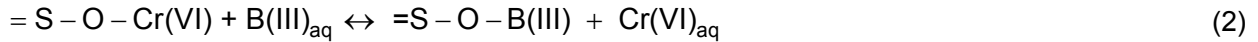


Figure 3. $[\text{Cr(VI)}]_{\text{aq}}$ as a function of $[\text{B(III)}]_{\text{aq}}$ when B(III) is added to a Cr(VI)/Fe(O)OH adsorption system at three different ionic strengths, $\text{pH}=8$, $T=22 \pm 3^\circ\text{C}$ and $m_{\text{Fe(O)OH}}=0.5 \text{ g l}^{-1}$

From the experimental data shown in Figure 3 it becomes evident that under the given conditions, B(III) replaces Cr(VI) on the solid surface resulting in the increase of the Cr(VI) concentration in solution. The correlation between the B(III) - and Cr(VI) - concentration in solution is linear within the investigated concentration range and for the three different ionic strengths. The correlation coefficient for the three lines in Figure 3 is $R^2 \sim 0.99$ indicating very good linear correlation and the slope, which corresponds to the $[\text{Cr(VI)}]_{\text{aq}}/[\text{B(III)}]_{\text{aq}}$ ratio is calculated to amount 0.0062, 0.0060 and 0.0062 for $I=0.0 \text{ M}$, 0.1 M and 1.0 M NaClO_4 ,

respectively. The values of the $[\text{Cr(VI)}]_{\text{aq}}/[\text{B(III)}]_{\text{aq}}$ ratio indicate two orders of magnitude higher affinity of the Fe(O)OH surface for Cr(VI) compared to B(III) independent of the ionic strength. In the form of a chemical equation this competition reaction can be written as follows:



and the corresponding equilibrium constant is given by Equation (3)

$$K = \frac{[= \text{S} - \text{O} - \text{B(III)}] \cdot [\text{Cr(VI)}]_{\text{aq}}}{[\text{B(III)}]_{\text{aq}} \cdot [= \text{S} - \text{O} - \text{Cr(VI)}]} \quad (3)$$

Assuming linearity also when the $[= \text{S} - \text{O} - \text{B(III)}]/[= \text{S} - \text{O} - \text{Cr(VI)}]$ ratio equals to unity, the average value for K is calculated to be 0.0061 ± 0.0002 . Since the formation constant of the B(III)-Fe(O)OH surface complex at pH 8 has been determined in previous experiments [3] assuming surface complexation reaction (4):



with the corresponding formation constant equation (5):

$$\beta_{\text{B}} = \frac{[= \text{S} - \text{O} - \text{B(III)}]}{[\text{B(III)}]_{\text{aq}} \cdot [= \text{S} - \text{OH}]} \quad (5)$$

The formation constant for the Cr(VI)-Fe(O)OH surface complex can be calculated by dividing equation (5) by equation (3):

$$\beta_{\text{Cr}} = \frac{[= \text{S} - \text{O} - \text{Cr(VI)}]}{[\text{Cr(VI)}]_{\text{aq}} \cdot [= \text{S} - \text{OH}]} \quad (6)$$

Equation (6) is defined as the formation constant of following surface complexation reaction, which corresponds to the Fe(O)OH surface binding of chromate:



Taking into account the value of the formation constant of B(III)-Fe(O)OH surface complex ($\log \beta_{\text{B}} = 4.4 \pm 0.1$) and the value of the competition reaction constant ($\log K = -3.5 \pm 0.2$), the formation constant for Cr(VI)-Fe(O)OH surface complex is calculated to be $\log \beta_{\text{Cr}} = 7.9 \pm 0.2$.

CONCLUSIONS

Cr(VI) e.g. chromate presents higher affinity for the Fe(O)OH surface than B(III) e.g. boric acid and if both present in solution in increased concentrations Cr(VI) is preferentially adsorbed on the Fe(O)OH surface. The corresponding competition constant is evaluated to amount $\log K = -3.5 \pm 0.2$ and the formation constant for the Cr(VI)-Fe(O)OH surface complex is calculated to be $\log \beta_{\text{Cr}}$ of 7.9 ± 0.2 . The applied treatment process is simply and economic with relatively high removal capacity and hence could be effectively used for detoxification of water/wastewater containing Cr(VI) and B(III).

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