

ADSORPTION OF Cr(VI) AND As(V) ON CHITOSAN-MONTMORILLONITE: SELECTIVITY AND pH DEPENDENCE

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Abstract—Montmorillonite modified with the cationic biopolymer, chitosan, has, in weak acidic solutions, protonated amine groups which act as anion-adsorption sites. Due to the specific surroundings of the adsorption sites and diffusion paths in the interlayer of chitosan-montmorillonite, preferential adsorption of certain anions is likely. In the present study, the adsorption properties for the inorganic anions Cr(VI) and As(V) were determined, taking into account solution pH and competitive adsorption in the presence of Cl^- and SO_4^{2-} . Chitosan-montmorillonite was prepared by adding an amount of chitosan equivalent to 500% of the cation exchange capacity (CEC) at pH 5 and 75°C. The resulting anion exchange capacity was ~ 0.34 mol_e/kg. The adsorption properties for As(V) and Cr(VI) were determined with the batch technique at pH 3 to 9. Adsorption isotherms were fitted to the Langmuir and Dubinin-Radushkevich equations and judged quantitatively by the correlation coefficient. To describe the competitive adsorption, the selectivity (*S*) was determined by the ratio of amounts of anions A and B adsorbed (q_A/q_B) in a binary system. The ionic species adsorbed, *i.e.* either Cr(VI) or As(V), depended on the pH, as did the degree of protonation of the amine groups, and this played a decisive role in the amount of anions adsorbed. The maximum amount of Cr(VI) adsorbed was 180 mmol/kg at pH 3.5, whereas for As(V) it was 120 mmol/kg at pH 4.0 to 5.0. The adsorption process of Cr(VI) and As(V) fit well to the Langmuir isotherm. By increasing the concentration of the competitive anion, Cl^- , in solution, the amount of Cr(VI) and As(V) adsorbed remained almost constant, whereas SO_4^{2-} had a more pronounced competitive effect. At concentration ratios of 0.5 and 1 for SO_4^{2-} to Cr(VI) and As(V), respectively, the sorption capacity decreased by 10 and 25%, respectively. The sequence of the selectivity was: Cr(VI) > SO_4^{2-} > As(V) > Cl^- . Chitosan-montmorillonite showed a high selectivity for Cr(VI), which adsorbed chemically. Despite the lower affinity for As(V) and physical adsorption, the adsorption capacity was relatively high.

Key Words—Anion Adsorption, Arsenate, Chitosan-montmorillonite, Chromate, Selectivity.

INTRODUCTION

Permanent, negatively charged clay minerals are good adsorbents for cations, but, in general, their adsorption capacity for neutral and anionic compounds is small. Many attempts have been made to improve the adsorption capacities of clay minerals for anions by modifying them with organic cations (Beall, 2003; Bors *et al.*, 2000; Li and Bowman, 1998; Mortland *et al.*, 1986; Krishna *et al.*, 2001). The resulting organo-clays adsorb neutral organic compounds (Mortland *et al.*, 1986) but they also adsorb anions if the organic cations are adsorbed in amounts exceeding the CEC. Ion pairs with inorganic cations in the interlayer of organo-clay minerals may also contribute to anion exchange (Meleshyn and Bunnenberg, 2006). Montmorillonite modified with hexadecylpyridinium (HDPy⁺) was suggested as an adsorbent for I^- and TcO_4^- (Bors *et al.*, 2000) and, in the case of modification with hexadecyltrimethylammonium (HDTMA⁺), as an adsorbent for CrO_4^{2-} (Krishna *et al.*, 2001).

Chitosan, a natural non-toxic biopolymeric cation, was recently found to adsorb on external surfaces and in the interlayer of montmorillonite in amounts up to 157% of the CEC (Darder *et al.*, 2003). As a consequence of the uptake of positively charged sites exceeding the CEC, chitosan-montmorillonite is an adsorbent for anions and has an anion-exchange capacity (AEC) which is greater than half of the CEC (An and Dultz, 2007a). Relatively few studies have focused on chitosan-modified montmorillonite as an adsorbent for anions. As for organo-clay minerals modified with monovalent cations, preferential adsorption of anions is also reported for chitosan-montmorillonite. Chitosan-coated montmorillonite exhibits selectivity for inorganic anionic tungsten species (Gecol *et al.*, 2005). In other experiments, a physical mixture of chitosan and activated clay was used for the adsorption of tannic acid and humic acid and also reactive dyes (Chang and Juang, 2004). The adsorption capacity of the adsorbent was found to be relatively large, 1490 g/kg for tannic acid, 243 g/kg for humic acid, and 1912 g/kg for the reactive dye. However, as chitosan is highly swelling in water, it is difficult to handle in aqueous suspensions. It is also susceptible to microbial decomposition.

As chitin, the raw material of chitosan, is a very abundant polymer in nature, chitosan is – from an economic point of view – a relatively cheap material

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(Chang and Juang, 2004). However, its pronounced swelling in water and its small specific gravity limits the use of chitosan in geotechnical applications. Its handling is improved, however, if adsorbed on clay minerals. Despite the fact that chitosan is a polycation, it is also adsorbed in the interlayer of montmorillonite and desorption is very limited (Darder *et al.*, 2003). Whereas some of the chitosan amine groups neutralize the negative layer charge in the montmorillonite, under weak acidic conditions, a distinct number of free protonated amine groups are in the interlayer and on the external surfaces, which act as adsorption sites for anions.

The pollution of surface- and ground-water by the toxic anionic contaminants Cr(VI) and As(V) from both anthropogenic wastes and natural sources is a serious problem (Seki *et al.*, 2005; Manning and Goldberg, 1996). The use of ion-exchange resins to remove Cr(VI) from waste waters (Krishna *et al.*, 2001; David *et al.*, 1998) is very expensive, which often limits their use.

For the multivalent anions chromate and arsenate, the kind of anionic species in solution depends largely on the pH. At $\text{pH} > 7$, the bivalent anionic form of chromate, CrO_4^{2-} , is dominant in solution (Seki *et al.*, 2005). At $\text{pH} < 7$, monovalent HCrO_4^- is formed and, up to $\text{pH} 5.5$, two chromate anions, HCrO_4^- , and dichromate $\text{Cr}_2\text{O}_7^{2-}$ co-exist. As(V) is the most stable As species in oxidizing environments, though microbial reduction of As(V) to As(III) might occur (Masscheleyn *et al.*, 1991). As(V) exists in solution as the pH-dependent protonated oxyanions of arsenic acid, H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} (Manning and Goldberg, 1996; Seki *et al.*, 2005). As(V) is present as bivalent monohydroarsenate HASO_4^{2-} at $\text{pH} > 7.5$. At lower pH (7.5 to ~ 6.0), the monovalent dihydroarsenate, H_2AsO_4^- , is formed.

Due to the effect of pH on the kind of anionic species of Cr(VI) and As(V), previous studies considered the effect of solution pH on the adsorbed amount (Krishna *et al.*, 2001; Seki *et al.*, 2005; Manning and Goldberg, 1996). In the case of chitosan, where anion adsorption depends on the protonation of the amino-group, the pH dependency of the adsorption also has received much attention (An and Dultz, 2007a; Darder *et al.*, 2003; Gecol *et al.*, 2005).

MATERIALS AND METHODS

Preparation of chitosan-montmorillonite

Wyoming-bentonite (MX-80) was used in the preparation of chitosan-montmorillonite. The CEC, determined using the Cu-triene-complex, is $0.822 \text{ mol}_c/\text{kg}$. The exchangeable cations are Na^+ ($\sim 65\%$) and Ca^{2+} ($\sim 35\%$). Chitosan of high molecular weight (MW average = $342,500 \text{ g/mol}$), containing an average number of 2130 glucosamine units with a MW of 161 g/mol (Darder *et al.*, 2003), was purchased from Kraeber GmbH&Co (Germany). The deacetylation degree, deter-

mined by polyelectrolyte titration in the cell of a particle charge detector (PCD), was 74.5% ($4.6 \text{ mol}_c/\text{kg}$).

Chitosan-montmorillonite was prepared by the method of Darder *et al.* (2003), in which, briefly, chitosan solutions were prepared first by the addition of corresponding amounts of polysaccharide to 1% (v/v) acetic acid. Then the pH of the suspension was adjusted to 5.0 by adding 1 M NaOH before shaking for 5 days at 75°C in a temperature-controlled water bath. After washing with deionized water until free of acetate, the sample was freeze-dried. According to X-ray diffractometry (XRD) (Siemens D500) a bilayered structure of chitosan in the interlayer of montmorillonite was obtained (d_{001} at 2.6 nm). The charge of the weakly bound fraction of counterions on the external surfaces, determined by the streaming potential (electrokinetic charge) (Böckenhoff and Fischer, 2001), was found to be slightly positive ($6.5 \text{ mmol}_c/\text{kg}$ at $\text{pH} 5.0$). The electrokinetic charge of the external surfaces, referred to here as surface charge, was quantified in the cell of a particle charge detector (PCD 03, Müttek) by combining the electrokinetic signal with polyelectrolyte titration (Böckenhoff and Fischer, 2001). The calculated AEC, determined from C content obtained by a CNS analyzer (elementar, vario EL III), was $0.43 \text{ mol}_c/\text{kg}$. In comparison, the effective AEC determined by anion exchange was $0.34 \text{ mol}_c/\text{kg}$, which is $\sim 80\%$ of the calculated value (An and Dultz, 2007b). Comparing the effective AEC with the surface charge revealed that most of the anion-adsorption sites of chitosan-montmorillonite were located in the interlayer.

Determination of anion adsorption

Adsorption experiments of chitosan-montmorillonite for Cr(VI) and As(V) were carried out using the batch technique. Different amounts of chitosan-montmorillonite (0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 g) were weighed into centrifuge tubes containing 30 mL of Cr(VI) or As(V) solution at concentrations of 2 mmol/L or 1 mmol/L, respectively. The solutions were prepared from the K- and Na-salts, respectively, and adjusted to $\text{pH} 4.5$ with 0.1 M HCl. The suspensions were shaken at 200 rpm for 24 h at room temperature. The pH of 4.5 of the suspensions was adjusted with 1 M HCl and 1 M NaOH, respectively. The adsorption experiments were terminated by centrifugation. The supernatant was passed through a $0.45 \mu\text{m}$ acetate membrane filter and used to determine the amount of anions adsorbed. To assess the effect of adsorption sites located on the external surface and in the interlayer space on anion adsorption, a series of chitosan-montmorillonites with different amounts of chitosan applied (0, 20, 60, 100, 200, and 500% of the CEC) was prepared and used for the adsorption of Cr(VI).

As(V) in solution was assumed to be equal to total As measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS – Agilent 7500C). The amount

of Cr(VI) adsorbed was determined using a UV-VIS spectrophotometer (Varian Cary 50 Scan) according to Li and Zou (1999). Five milliliters of the solution was added to a 10 mL volumetric flask with 0.2 mL of a 0.5 M $\text{H}_3\text{PO}_4\text{-KH}_2\text{PO}_4$ buffer solution (pH 2.1) and 0.3 mL of diphenylcarbazide solution (1.0 g dissolved in 100 mL of acetone). The flask was filled with de-ionized water up to a total volume of 10 mL. For full color development, the mixture was allowed to stand for 0.5 h. The absorbance at the wavelength of 540 nm was measured by the UV-VIS spectrophotometer. If the concentration was found to be >5 mg/L, 0.1 mL of the solution was used for the quantification of Cr(VI).

The amount of anion adsorbed at equilibrium conditions, q_e (g/kg), was calculated by

$$q_e = (C_o - C_e)V/W \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations (mmol/L), respectively, and V and W are the liquid volume (L) and the weight of adsorbent applied (kg), respectively.

Effect of pH on anion adsorption

In order to assess the effect of pH on anion adsorption, 0.2 g of chitosan-montmorillonite was weighed in 60 mL-centrifuge tubes containing 30 mL of a solution with an initial concentration of 2 mmol/L Cr(VI) and 1 mmol/L As(V), respectively. Subsequently, the suspension was adjusted with 0.1 M HCl or 0.1 M NaOH to pH 3, 3.5, 4, 4.5, 5, 6, 7, or 9, respectively. The suspensions were shaken for 24 h at room temperature. The suspensions were centrifuged and the supernatants were passed through a 0.45 μm acetate membrane filter and used for analysis of anions.

Competitive adsorption of anions

The competitive adsorption of anions on chitosan-montmorillonite was determined in batch mode. Solutions containing varying combinations of the competitive anions Cl^- and SO_4^{2-} (in concentrations of 0.42, 0.83, 1.25, 1.75, or 2.16 mmol/L) and Cr(VI) and As(V) (in concentrations of 0.08, 0.42, 0.83, or 1.25 mmol/L) were prepared as a 30 mL volume and transferred to centrifuge tubes, then 0.2 g of chitosan-montmorillonite was added and the pH adjusted to 4.5.

The concentrations of Cr(VI) and As(V) in two sample series were kept constant at 2 mmol/L Cr(VI) and 1 mmol/L As(V). The suspensions were shaken for 24 h at room temperature, centrifuged, the supernatant filtered, and the solutions used for analysis of anions. The concentrations of SO_4^{2-} and Cl^- were analyzed by anion chromatography (DIONEX ICS-90). The amount of anions adsorbed was calculated using equation 5. To describe competitive adsorption, the selectivity (S) of anion A for another anion, B, for an adsorbent was defined by the ratio of q_A/q_B in a binary system (Inglezakis *et al.*, 2003; Lv *et al.*, 2005).

$$S = q_A/q_B \quad (2)$$

where q_A and q_B are the amounts of anions A and B adsorbed, with stronger and weaker affinities, respectively, to an adsorbent at defined conditions.

Modeling of the adsorption process

To describe the adsorption properties of anions on chitosan-montmorillonite, the Langmuir and the Dubinin-Radushkevich (D-R) isotherms were used.

The Langmuir equation has the following form:

$$1/q_e = 1/q_{\text{max}} + 1/(q_{\text{max}}K_L C_e) \quad (3)$$

where q_e is the amount adsorbed (mol/kg); C_e , the equilibrium concentration (mmol/L); and q_{max} , the adsorption capacity (mol/kg). K_L is the Langmuir constant, which is related to the affinity of the binding sites for the adsorbate and is determined by the linear form of the Langmuir equation:

$$C_e/q_e = C_e/q_{\text{max}} + 1/(q_{\text{max}}*K_L) \quad (4)$$

Therefore, if the data obey the Langmuir equation, the plot of C_e/q_e vs. C_e will give a straight line with a slope of $1/q_{\text{max}}$ and an intercept from which K_L may be calculated.

According to Kundu and Gupta (2007) and Karahan and Yurdakoç (2006), the D-R isotherm has the form:

$$\ln q_e = \ln q_{\text{max}} - k\varepsilon^2 \quad (5)$$

where q_{max} is the theoretical adsorption capacity of the adsorbent (mol/g), and k is the constant related to the mean adsorption energy (mol²/kJ²).

ε is known as the Polanyi potential (equation 10).

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (6)$$

where R is the gas constant (8.31 J/mol K) and T the temperature (K).

If a linear relationship is obtained between $\ln q_e$ vs. ε^2 , the value of k and q_{max} can be determined. Then, the mean free energy of adsorption, E (mol/kJ), can be calculated from k with the following equation:

$$E = -(2k)^{-0.5} \quad (7)$$

The value of the energy is in the range 1–8 and 9–16 kJ/mol for physical and chemical adsorption, respectively (Saeed *et al.*, 2003).

RESULTS AND DISCUSSION

Adsorption sites of anions

Due to the modification of montmorillonite with chitosan, the surface charge changes from negative to positive values (Figure 1). If chitosan was applied in amounts corresponding to 60% of the CEC (Chi-60), the surface charge of the resulting chitosan-montmorillonite increased notably from -30.6 to 1.5 mmol_c/kg, but for larger amounts applied (up to 500% of the CEC), the

increase in surface charge is small (Chi-500: 8.1 mmol/kg). The neutralization of the surface charge is reached when an amount of chitosan equivalent to ~40% of the CEC is applied. The limited increase in surface charge indicates that chitosan is adsorbed not only on the external surfaces but also in the interlayer. This is evident from XRD and C content (Darder *et al.*, 2003).

At pH 4.5, where Cr(VI) is present as $\text{Cr}_2\text{O}_7^{2-}$ in solution, the amount adsorbed from Chi-0 to Chi-60 is relatively small (up to 9.7% relative adsorption). From Chi-100 to Chi-500 the amount adsorbed is increased notably (85% relative adsorption or 0.20 mol/kg for Chi-500), as Cr(VI) is also adsorbed in the interlayer of chitosan-montmorillonite. For Chi-200 and greater loadings, the bilayer arrangement can be detected by XRD. At greater loadings of chitosan on montmorillonite, the number of adsorption sites (free amine groups) is also increased. The course of surface charge (Figure 1) indicates also that the increase in Cr(VI) adsorption is due to the interlayer sites. Organic anions with large molecular weight such as tannic acid are typically adsorbed on the external surfaces of chitosan-montmorillonite. Here, the adsorption of tannic acid is correlated with surface charge (An and Dultz, 2007a).

Effect of the amount of the adsorbent

The amounts of Cr(VI) and As(V) adsorbed increased with increasing amounts of chitosan added to the montmorillonite (Figure 2). At 6.7 g/L of chitosan added, the amount of Cr(VI) and As(V) adsorbed was >90% and >80%, respectively. Chitosan loadings greater than 6.7 g/L yielded only a slight increase in metal adsorption.

Effect of pH on the adsorption of anions

The kind of multivalent chromate and arsenate anions in solution depends heavily on the pH (Seki *et al.*, 2005;

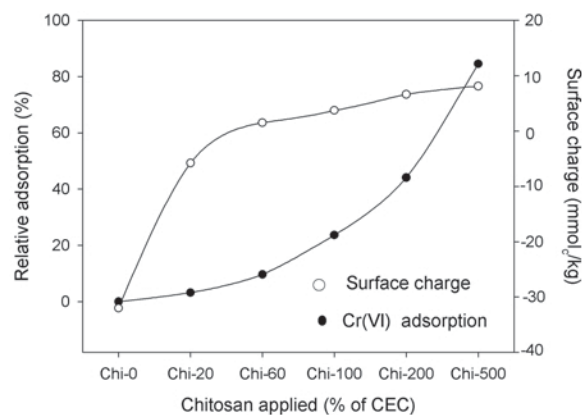
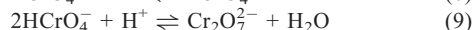
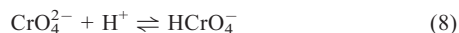


Figure 1. Surface charge for chitosan-montmorillonite (0–500% of the CEC applied) and corresponding amounts of adsorbed Cr(VI) at pH 4.5. Initial concentration C_0 : 2 mmol/L Cr(VI). Adsorbent concentration: 5 g/L.

Lin *et al.*, 2006). At pH >7 the bivalent anionic form of chromate CrO_4^{2-} is dominant in solution (Figure 3). At pH <7 down to pH 5.5, the weak decrease in pH following addition of acid reveals strong buffering of protons by the formation of monovalent HCrO_4^- . Down to pH 5.5 two chromate anions co-exist in solution (reaction 8). Due to further addition of acid, dichromate, $\text{Cr}_2\text{O}_7^{2-}$, is formed (reaction 9). The severe decrease in pH at pH <5.5 by the addition of acid indicates that no significant buffering occurs down to pH 3.8, where HCr_2O_7^- is formed.



As(V) is present as bivalent monohydroarsenate, HAsO_4^{2-} , at pH >7.5. At lower pH (7.5 to ~6.0), where the pH of the As(V) solution decreases only slightly through the addition of acid, the monovalent dihydroarsenate is formed (reaction 10). The severe decrease from pH 6.0 to ~3.8 reveals that H_2AsO_4^- is dominant in solution. At pH <3.8 the non-ionic form, H_3AsO_4 , is formed (reaction 11).



The amount of Cr(VI) adsorbed on chitosan-montmorillonite was >80% at pH <5.0, but with increasing pH it decreased considerably (Figure 4). At pH 7 it was only 9.4%. At pH <5.0 $\text{Cr}_2\text{O}_7^{2-}$ was adsorbed on the protonated amine groups of chitosan-montmorillonite. Here, the degree of protonation of the amine groups was >95% (Darder *et al.*, 2003). Note that at pH 5.0–7.0 several different ionic species of Cr(VI) are present in solution, namely, monovalent HCrO_4^- and divalent CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ (Figure 3). Moreover, the concentra-

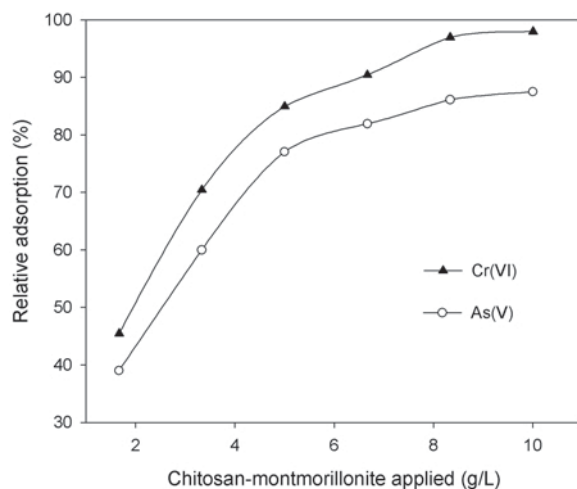


Figure 2. Influence of the concentration of chitosan-montmorillonite used in the adsorption of Cr(VI) and As(V) at pH 4.5. Initial adsorbate concentration C_0 : 2 mmol/L Cr(VI) and 1 mmol/L for As(V).

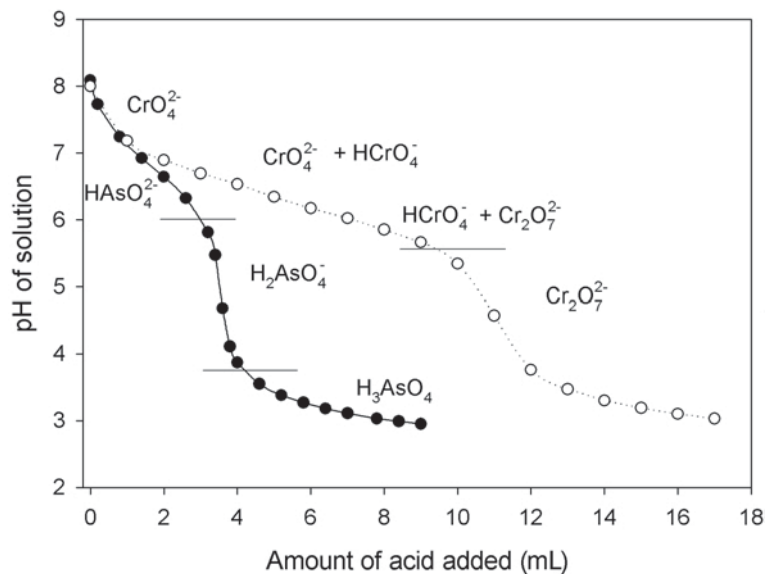


Figure 3. Relationship between pH and the speciation for the adsorbate oxyanions Cr(VI) and As(V).

tion of Cr(VI) anions increased in this pH range, due to the dissociation of dichromate to monochromate HCrO_4^- .

In order to explain the adsorption of chromate on kaolinite between pH 5.0 and 7.5, Zachara *et al.* (1988) assumed that chromate can form $\text{AlOH}_2^+-\text{CrO}_4^{2-}$ and $\text{AlOH}_2^+-\text{HCrO}_4^-$ complexes on the surface of the mineral, depending on pH. A similar assumption could be made in the case of the amount of Cr(VI) adsorbed on chitosan-montmorillonite, with the pH-dependent site being the degree of protonation of the amine groups. Many free amine groups were probably present on the external surface and also in the interlayer of chitosan-montmorillonite. Only protonated amine groups can act

as adsorption sites for anions. The degree of protonation is very dependent on the pH of the solution, as revealed by the extent of adsorption at different pH, i.e. >95% at pH <5.0 and ~15% at pH 7.0 (An and Dultz, 2007a). As a consequence, the amount of Cr(VI) adsorbed was almost zero at pH 9.0, where protonated adsorption sites on the adsorbent were absent.

The effects of pH on the adsorption tendency of As(V) differed from that of Cr(VI). The maximum, relative amount of As(V) adsorbed was >80%, observed between pH 4.0 and 5.0 (Figure 4). At pH >5.0, the amount adsorbed decreased for the same reason as it did for the adsorption of Cr(VI) on chitosan-montmorillonite. At pH <4.0, the amount of As(V) adsorbed decreased. Depending on pH, As(V) speciation in solution varies among monovalent H_2AsO_4^- , divalent HAsO_4^{2-} , and trivalent AsO_4^{3-} . Notice that the latter two are cations, whereas the first is an anion. The concentration of the anionic species, H_2AsO_4^- , at pH <4.0 decreased due to the formation of uncharged H_3AsO_3 . This explains the decrease in the adsorption of As(V) at pH <4.0.

The pH dependence of As(V) adsorption was also observed in other studies. For a methylated yeast biomass, the maximum amount of As(V) adsorbed was at pH 6.5 (Seki *et al.* 2005). This is also true for other phyllosilicates (Manning and Goldberg, 1996), in which the maximum adsorption appeared at ~pH 6.0 for montmorillonite and illite, at pH 5.0 for kaolinite, and in the pH range of 4.0–6.0 for fine-grained muscovite (Chakraborty *et al.*, 2007).

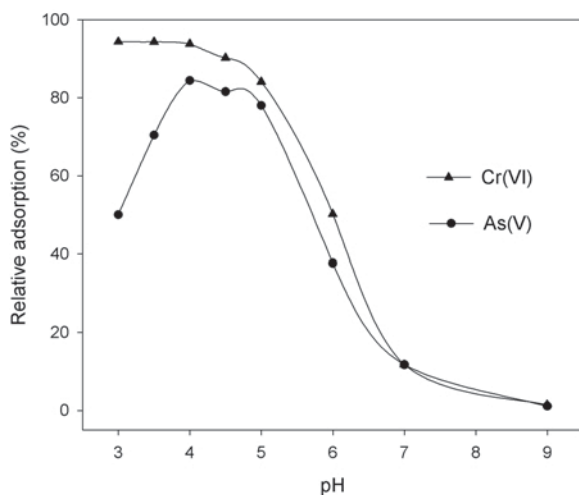


Figure 4. pH dependency of adsorption of Cr(VI) and As(V) anions on chitosan-montmorillonite. Initial concentration C_0 : 2 mmol/L Cr(VI) and 1 mmol/L As(V). Adsorbent concentration: 6.7 g/L.

Competitive adsorption of anions

The competitive adsorption of Cr(VI) studied in the presence of Cl^- and SO_4^{2-} shows that the amount of

Cr(VI) adsorbed is almost constant with increase in the Cl^- concentration in the binary system Cr(VI)- Cl^- (Figure 5a).

The amount of Cr(VI) adsorbed at a Cl^- concentration of 2 mmol/L was 0.26 mol/kg, which is only 3.7% less than it would be if Cl^- were absent (0.27 mol/kg). The opposite observations were made for SO_4^{2-} . Here, the amount of Cr(VI) adsorbed decreased significantly with increasing SO_4^{2-} concentration. Even in the case of As(V), the adsorption was almost unaffected by the Cl^- anion (Figure 5b). The amount adsorbed was very much decreased in the presence of SO_4^{2-} . At a SO_4^{2-} concentration of 1.2 mmol/L, it was 0.088 mol/kg, which is only 30% of the amount that would be adsorbed if SO_4^{2-} were absent (0.122 mol/kg). At an initial SO_4^{2-}

concentration of 0.7 mmol/L in the binary system of As(V)- SO_4^{2-} , the amount of SO_4^{2-} adsorbed was greater than that of As(V). A further increase was observed with increasing SO_4^{2-} concentrations in solution. In summary, Cl^- does not affect the adsorption of Cr(VI) and As(V), but the divalent SO_4^{2-} has a notable effect.

Evaluation of the selectivity for anions

The selectivity, S , of chitosan-montmorillonite for Cr(VI) and As(V), calculated using equation 5 from the competitive adsorption data for Cl^- and SO_4^{2-} , revealed that the selectivity of Cr(VI) over Cl^- is not only large (23.6) at small concentrations of Cl^- , but is large (14.8) at the greatest concentration ratio (Figure 6a). At small concentrations of the divalent competitive anion, SO_4^{2-} ,

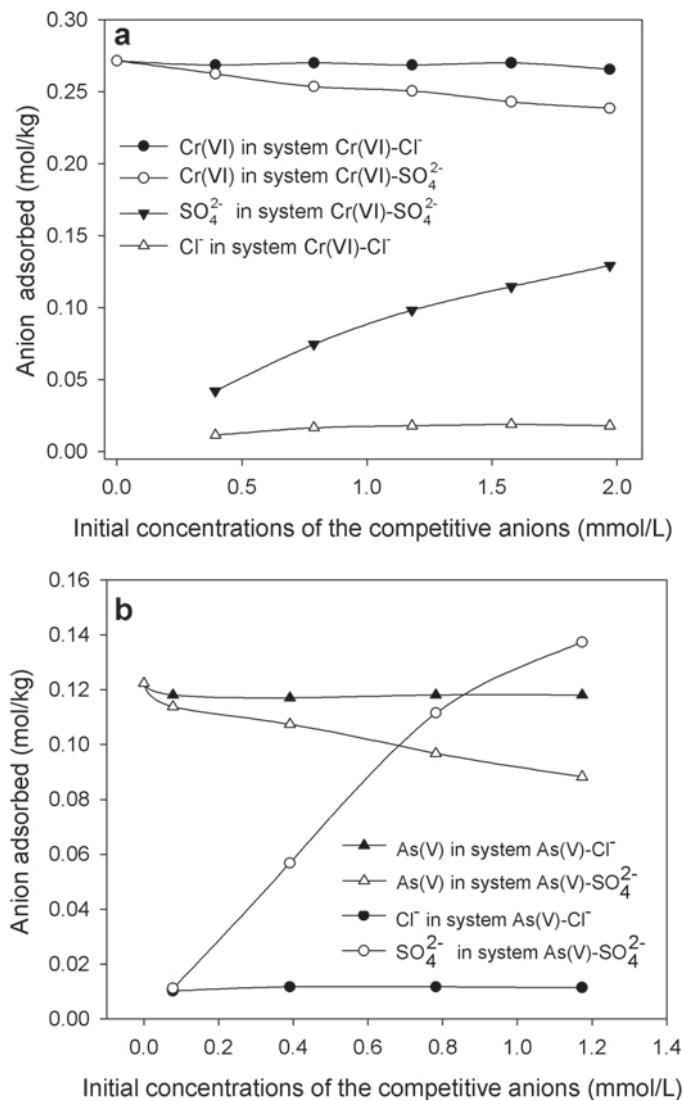


Figure 5. Effect of the competitive anions Cl^- and SO_4^{2-} on the adsorption of Cr(VI) (a) and As(V) (b) on chitosan-montmorillonite at pH 4.5. Initial adsorbate concentrations C_0 : 2 mmol/L Cr(VI), 1 mmol/L As(V); 0.42–2.16 mmol/L Cl^- and SO_4^{2-} . Adsorbent concentration: 6.7 g/L.

the selectivity is also relatively high (6.2), but decreases with increasing SO_4^{2-} concentrations. The selectivity is 1.9 at the initial concentration ratio of 0.75.

The selectivity of As(V) for Cl^- was found to be relatively large, even at high Cl^- concentrations, where the selectivity was 10.4, even at an initial concentration ratio of 1.2 (Figure 6b). The selectivity of As(V) over SO_4^{2-} was 10.3 at a concentration ratio of 0.09 of As(V) to SO_4^{2-} . By increasing the concentration ratio to 0.75, the selectivity decreased to 0.8. Consequently, the sequence of selectivity of chitosan-montmorillonite for the anions studied was $\text{Cr(VI)} > \text{SO}_4^{2-} > \text{As(V)} > \text{Cl}^-$.

Adsorption isotherms for Cr(VI) and As(V)

Adsorption isotherms for Cr(VI) and As(V) on chitosan-montmorillonite at pH 4.5 reveal that the slope of the curve is steepest for the adsorption of Cr(VI), indicating a greater selectivity for Cr(VI) than

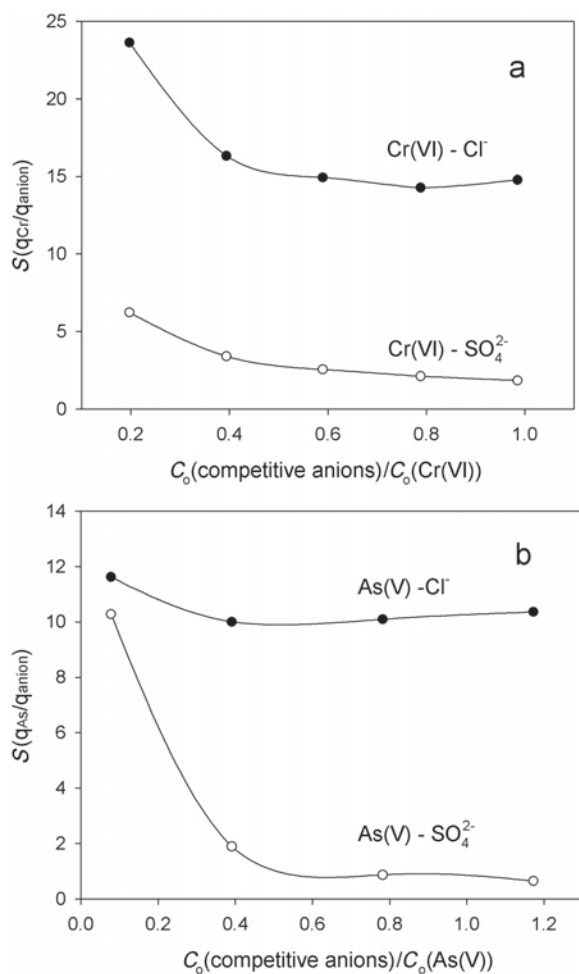


Figure 6. Effect of the concentration of the competitive anions Cl^- and SO_4^{2-} on the selectivity, S , of chitosan-montmorillonite for the adsorption of Cr(VI) (a) and As(V) (b) at pH 4.5. Initial adsorbate concentrations C_0 : 0.42–2.16 mmol/L for Cl^- and SO_4^{2-} ; 0.08–1.25 mmol/L for Cr(VI) and As(V).

for As(V) (Figure 7). The lesser adsorption of As(V) is in accordance with the smaller electronic attraction of As(V) to the adsorption sites of chitosan-montmorillonite. This was corroborated by fitting the data to the Langmuir (equation 4) and D-R (equation 5) adsorption equations, which yielded parameters related to adsorption capacity, degree of favored adsorption, and the nature of the adsorption (Table 1). The adsorption of both Cr(VI) and As(V) are well described by the Langmuir equation, giving $r^2 > 0.98$. The Langmuir constant, K_L , for Cr(VI) was much greater (56.2) than for As(V) (1.8). Therefore, the adsorption of Cr(VI) to chitosan-montmorillonite was very much favored over As(V). The anionic Cr(VI) species can probably be chelated by protonated amine groups and OH groups of the chitosan chain.

The adsorption capacity of chitosan-montmorillonite for Cr(VI) was 180 mmol/kg at pH 4.5, which is much greater than that of HDTMA-montmorillonite, where adsorption capacity for Cr(VI) was 53 mmol/kg, as reported by Li *et al.* (2003). For As(V), a lower affinity for chitosan-montmorillonite was observed; the adsorption capacity was also relatively large (120 mmol/kg). Until now, the adsorption of As(V) to organo-clay minerals has not been considered. For calcined bauxite treated with iron nitrate, As(V) adsorption was 21.01 mmol/kg (Bhakat *et al.*, 2006) and for original montmorillonite, 0.22 mmol/kg (Manning and Goldberg, 1996). The greatest values were reported for Fe-treated, activated carbon, where the adsorption capacity was ~470 mmol/kg (Payne and Abdel-Fattah, 2005).

Adsorption parameters were also obtained by fitting the data (Table 1) to the D-R equation (6). The constant, k , related to the mean adsorption energy, and the adsorption capacity, $\ln q_{\text{max}}$, for the adsorption of Cr(VI) and As(V) were determined from the plots of $\ln q_e$ vs. ε^2 (Figure 8). The adsorption energy, E , for Cr(VI) on chitosan-montmorillonite, calculated from the value

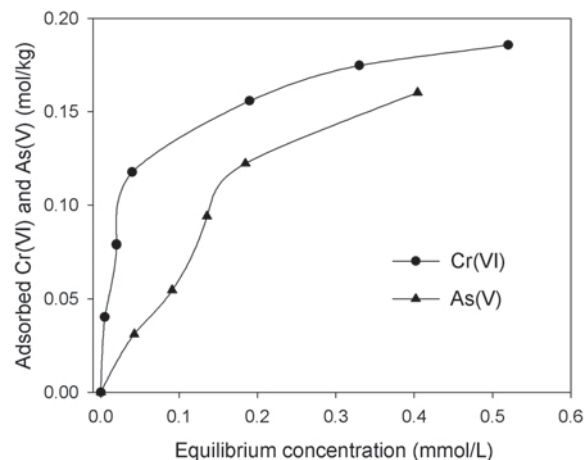


Figure 7. Adsorption isotherms of Cr(VI) and As(V) on chitosan-montmorillonite at pH 4.5.

Table 1. Langmuir constants and the corresponding adsorption energy, E , from fits according to the Langmuir and Dubinin-Radushkevich (D-R) equations for the adsorption of Cr(VI) and As(V) on chitosan-montmorillonite (Figure 7).

	Langmuir			Dubinin-Radushkevich (D-R)		
	K_L (L/mmol)	q_{max} (mol/kg)	r^2	k (mol ² /kJ ²)	E (kJ/mol)	r^2
Cr(VI)	56.5	0.18	0.98	0.0022	15.0	0.96
As(V)	1.8	0.12	0.99	0.0322	3.94	0.98

of k obtained by equation 6, was 15.08 kJ/mol (Table 1), indicating that Cr(VI) is chemically adsorbed due to electronic attraction of the adsorption sites of protonated amine groups.

For As(V) the adsorption energy was 3.94 kJ/mol, which is in the range 1–8 kJ/mol consistent with a physical adsorption process. For the adsorption of As(V) on modified calcined bauxite, the adsorption energy, E , was also found to be smaller (6.15 kJ/mol) than the limit (8 kJ/mol) for physical adsorption (Bhakat *et al.*, 2006). The difference in the adsorption behavior of Cr(VI) and As(V) on chitosan-montmorillonite is probably due to

differences in the chemistry of metal and non-metal oxyanions. Here, charge, ionic diameter, pK_a values, polarizabilities, *etc.* at a given solution pH have to be considered (Manning and Goldberg, 1996).

CONCLUSIONS

The adsorption of the inorganic anions Cr(VI) and As(V) on chitosan-montmorillonite was determined with the focus on the effect of solution pH and selectivity. Due to the adsorption in the interlayer, the amount of inorganic anions adsorbed on protonated amine groups was found to be much greater than that of organic anions with large molecular weights, *e.g.* tannic acid, which is adsorbed on the external surface alone (An and Dultz, 2007a).

Not only does the degree of protonation of the amine groups affect the amount of inorganic anions adsorbed, but the pH dependency of the kind of anionic species of Cr(VI) and As(V) also affects it. The best pH value for the most efficient retention of inorganic anionic pollutants in the water-purification process can be obtained from the results reported here. From the relatively large amount of Cr(VI) adsorbed and high selectivity of Cr(VI) in the presence of Cl^- and SO_4^{2-} , chitosan-montmorillonite may be an effective adsorbent in the treatment of Cr(VI)-contaminated waters. Despite the lower affinity of As(V) compared to Cr(VI), chitosan-montmorillonite may also be a useful adsorbent for As(V) due to the observed selectivity and relatively large amounts adsorbed. The reason for the less favored adsorption of the non-metal oxy-anions of As, in comparison to the metal oxy-anions of Cr, needs further clarification.

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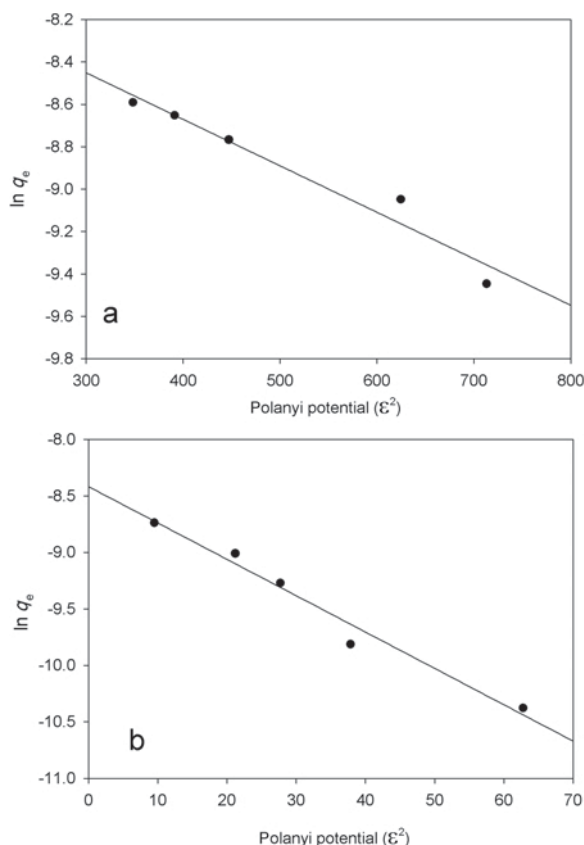


Figure 8. Determination of the nature of adsorption: quantification of adsorption energy from plots of $\ln q_e$ vs. ϵ^2 . Application of the Dubinin-Radushkevich (D-R) adsorption isotherms to determine the slope, k , and intercept, $\ln q_{max}$, for the adsorption of Cr(VI) (a) and As(V) (b).

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