

Adsorption Mechanism of Arsenic on Nanocrystalline Titanium Dioxide

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Arsenate [As(V)] and arsenite [As(III)] interactions at the solid–water interface of nanocrystalline TiO₂ were investigated using electrophoretic mobility (EM) measurements, Fourier transform infrared (FTIR) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, and surface complexation modeling. The adsorption of As(V) and As(III) decreased the point of zero charge of TiO₂ from 5.8 to 5.2, suggesting the formation of negatively charged inner-sphere surface complexes for both arsenic species. The EXAFS analyses indicate that both As(V) and As(III) form bidentate binuclear surface complexes as evidenced by an average Ti–As(V) bond distance of 3.30 Å and Ti–As(III) bond distance of 3.35 Å. The FTIR bands caused by vibrations of the adsorbed arsenic species remained at the same energy levels at different pH values. Consequently, the surface complexes on TiO₂ maintained the same nonprotonated speciation at pH values from 5 to 10, and the dominant surface species were (TiO)₂AsO₂[−] and (TiO)₂AsO[−] for As(V) and As(III), respectively. The surface configurations constrained with the spectroscopic results were formulated in the diffuse layer model to describe the adsorption behavior of As in the pH range between 4 and 12. The study suggests that TiO₂ is an effective adsorbent for As removal due to its high surface area and the presence of high affinity surface hydroxyl groups.

Introduction

Inorganic As(V) and As(III) species are commonly found in groundwater in many countries such as India, Bangladesh, Vietnam, and Chile (1). Arsenic contamination is believed to be geological, primarily due to the release of arsenic from arsenic-bearing sediments in groundwater aquifers. Numerous anthropogenic sources including mining, pesticide, fertilizer, and coal combustion also contribute to the As occurrence (2). Since arsenic is highly toxic and carcinogenic, the World Health Organization (WHO) has revised the guideline for arsenic in drinking water from 50 to 10 µg/L (3). The U.S. Environmental Protection Agency (EPA) has adopted an arsenic maximum contaminant level (MCL) of 10 µg/L, which will be enforceable as of January 23, 2006 (4).

The interactions of arsenic species with metal hydroxides and oxides are important mechanisms controlling the mobility of arsenic in the natural environment and for removal of arsenic using metal ion-based coagulants and adsorbents. As(V) is strongly adsorbed to the surface of several

common minerals such as goethite, ferrihydrite, and alumina in soils and sediments (1, 2). Activated alumina, granular ferric hydroxide, and ferric oxide adsorbents are widely used in the filtration treatment of arsenic (5–7). Recently, nanocrystalline titanium dioxide has been developed for effective removal of arsenic (8–10). Knowing the interactions between arsenic and metal (hydr)oxides will enable the accurate description of arsenic mobility in the environment and the prediction of adsorptive properties of the adsorbents.

Interactions of arsenic with TiO₂ in both the rutile and the anatase forms have been studied by many researchers. Most of the previous works were focused on the photocatalytic oxidation of As(III) using TiO₂ (11–14). Foster et al. used the extended X-ray absorption fine structure (EXAFS) to provide the direct evidence of As(III) oxidation in the presence of TiO₂ (15). Arsenic adsorption by TiO₂ was also investigated by some authors (9, 10, 16). It was observed that TiO₂ had a high adsorption capacity for As(V) at low pH values and had a maximum adsorption capacity for As(III) at about pH 9, which were similar to the adsorption behaviors of ferric (hydr)oxides; but the adsorption reactions and the species of the adsorbed As(V) and As(III) on TiO₂ are not well-established.

In the present study, the adsorption mechanisms of As(V) and As(III) on nanocrystalline TiO₂ were examined using a combination of macroscopic and microscopic techniques including EXAFS, FTIR, and electrophoretic mobility measurements. The configurations of the adsorbed arsenic species were further employed in formulating a surface complexation model to describe arsenic adsorption behavior. The use of these rigorous approaches enables the accurate determination of the adsorbed arsenic species.

Materials and Methods

Materials. All stock solutions were prepared using ACS grade chemicals and deionized water (DI). High purity nitrogen gas (purity 99.999%, AGL Welding Supply Co., Inc. Clifton, NJ) was used in batch tests. Stock solutions of arsenic were prepared by dissolving sodium arsenate heptahydrate (Na₂HAsO₄·7H₂O, Alfa Aesar) and sodium arsenite (NaAsO₂, Fisher) in distilled water. The TiO₂ used in this study was prepared by hydrolysis of titanium sulfate solution (8). The TiO₂ produced was in the anatase form with an average crystalline particle size of 6 nm. The BET surface area was 329 m²/g, and the surface site density was 6.0 mmol/g. The point of zero charge of TiO₂ was at pH 5.8 (17).

Batch Adsorption Experiments. Suspensions containing 0.04 M NaCl, 1.0 mg/L As(V) or As(III), and 0.2 g/L TiO₂ were prepared in a 1 L beaker. Then, 50 mL aliquots of the uniform suspension were transferred into 10 50 mL graduated polyethylene terephthalate (PETE) centrifuge tubes. The suspension pH was adjusted to desired levels in a range of 4–12 using dilute NaOH and HCl solutions. The centrifuge tubes were placed in a tumbler and mixed for 22 h to reach equilibrium (9). After mixing, the final pH of the suspension was measured as the equilibrium pH. The solid and solution were separated by centrifugation at 13 000 rpm for 35 min. The solution was then acidified using HNO₃, and the total soluble arsenic concentrations were determined using a furnace atomic absorption spectrometer (FAAS) (Varian Spectra AA-400) with a method detection limit (MDL) of 0.7 µg/L. Duplicate adsorption experiments were performed, and averaged results were reported.

Electrophoretic Mobility (EM) Measurements. The EM was determined using a ZetaSizer 3000 (Malvern Instrument). All EM experiments were done under N₂ atmosphere to

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eliminate CO₂ from the system. The pH of the suspension containing 0.01 g/L TiO₂ in 0.04 M NaCl was adjusted to between 3 and 11 using dilute NaOH and HCl solutions. Suspensions with or without 50 or 100 µg/L As (V) or As (III) were placed on a rotating shaker for 22 h. The final pH and the EM of the mixed samples were measured.

FTIR Spectroscopic Study. Infrared spectra of aqueous solutions of Na₂HAsO₄·7H₂O and NaAsO₂ were collected using an attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometer (Thermo Nicolet Nexus 670). A ZnSe crystal with a 40° angle of incidence was employed in a horizontal ATR accessory. The ATR spectra of reference (0.01 M NaCl) and arsenic solutions were recorded after the ATR cell was filled with 1 mL of solution. Subtraction of the reference spectra from the sample spectra at the same pH produced the spectra of arsenic species in solution. The subtraction factor was always unified.

The adsorption samples for FTIR analysis were prepared by mixing 0.1 M As(III) or As(V) with 5.0 g of TiO₂ in 30 mL of a 0.04 M NaCl solution for 22 h. Then, the solid was separated from liquid by filtration through a 0.45 µm glass fiber. Infrared spectra of adsorbed species of As(III) on TiO₂ were obtained by measuring the wet paste and the corresponding filtrate as reference. The subtraction of reference spectra from wet paste spectra should yield the spectra of the adsorbed species of As(III) on TiO₂ surfaces. The As(V)-loaded TiO₂ solid samples were rinsed with 40 mL of DI water and freeze-dried in a Labconco 4.5 L Freeze-Dry System. The dry solids were ground to a very fine powder and then spread over KBr cuts. FTIR spectra of the dry samples were collected using the FTIR equipped with a Centaurus microscope. The spectra were collected in transmission mode at a resolution of 4 cm⁻¹, and 1000 scans were recorded in the 4000–700 cm⁻¹ range.

EXAFS Analysis. The XAS samples were prepared by mixing 0.04 M NaCl, 10 mg/L As(V) or As(III), and 2 g/L TiO₂ at pH 7 in a 1 L plastic bottle for As(V) and an amber glass bottle for As(III) suspensions. The As(III) suspension was purged with N₂ gas for 2 h while the pH of the suspension was maintained at 7. After the capped bottles were mixed in a rotary shaker for 22 h at ambient temperature, the samples were filtered through a 0.45 µm glass fiber filter. The wet paste was transferred to airtight, glass vials and stored for no longer than 24 h before analysis. Standard reference arsenic chemicals, NaAsO₂ and Na₂HAsO₄·7H₂O, were also analyzed. Elemental arsenic (As⁰) was used to calibrate the energy at 11 868 eV.

The spectra were collected at cryogenic temperature (70 K) on beamline X18B at the National Synchrotron Light Source (NSLS) in the Brookhaven National Laboratory. An energy range of –200–1000 eV from the K-edge of As (11 868 eV) was used to acquire the spectra. All spectra were collected in fluorescence mode using a 13-element energy dispersive Ge detector. An average of five scans was collected to achieve an adequate signal/noise ratio. The first and the last As(III) spectra were compared to confirm that no oxidation occurred during the sample analysis.

The EXAFS spectra were analyzed using the Athena and Artemis program in the IFEFFIT computer package (18). The general approach was the same as used in a previous study (19). Individual spectra were first averaged, and backgrounds were subtracted with a linear function through the preedge region. The averaged spectra were normalized to the atomic absorption, and the EXAFS signal was extracted from the spectra. Then, the data were converted from energy to photoelectron momentum (*k* space) and weighted by *k*³ to account for the dampening of oscillations with increasing *k*. Fourier transformation was then performed to obtain the radial structure functions (RSF) in *R*-space. Final fitting of the spectra was done on Fourier transformed *k*³ weighted

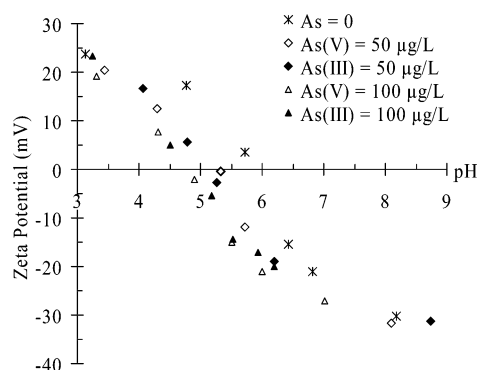


FIGURE 1. Zeta potential of 10 mg/L TiO₂ as a function of pH and total As concentration in 0.04 M NaCl solution.

spectra in *R*-space (Å). The experimental spectra were fitted with single-scattering theoretical phase-shift and amplitude functions calculated with the ab initio computer code FEFF6 (20) using hypothetical atomic clusters that were generated by replacing the Fe atom in scorodite (FeAsO₄·2H₂O) by Ti. The many-body amplitude reduction factor (*S*₀²) was fixed at 0.9. Each spectrum was fit by first isolating and fitting the first-shell As–O to estimate Δ*E*₀, the difference in threshold energy between theory and experiment, by fixing the Debye–Waller parameter (*σ*²) at 0 and coordination numbers (CN) at 4 and 3 for As(V) and As(III), respectively. Then, Δ*E*₀ was fixed to the best fit value from first-shell fitting. The CN of As–O and As–Ti was initially fixed to obtain estimated values for interatomic distances (*R*) and *σ*². Finally, the spectrum was fitted using estimated values for CN, *R*, and *σ*² as starting values.

Surface Complexation Modeling. The diffuse layer model (DLM) was used to describe the As(V) and As(III) adsorption behaviors on TiO₂ as a function of solution pH. The DLM has previously been employed to describe As adsorption on iron oxides (21). The specific surface area and surface site density for TiO₂ was determined to be 329 m²/g and 10.98 sites/nm², respectively (8). The equilibrium constants for protonation of the surface hydroxyl groups were taken from a previous study (22). The aqueous reactions were from the standard database of the chemical speciation program MINTQA2 (23). The As adsorption constants were obtained by fitting model-calculated values to the experimental data. The constants were varied systematically until the difference (Σ_{pH} (experimental adsorption – calculated adsorption)²) between the calculated and the observed adsorption values reached a minimum. The windows version of MINTQA2 was used to simulate adsorption and aqueous reactions with a fixed ionic strength at 0.04 M as NaCl.

Results and Discussion

Electrophoretic Mobility. Figure 1 shows the zeta potentials of TiO₂ in both the presence and the absence of 50 or 100 µg/L As(V) or As(III). The point of zero charge pH (pH_{pzc}) of the TiO₂ was 5.8 where the net surface charge was zero. The pH_{pzc} was derived by linear interpolation of the two points above and below the *x*-axis. The adsorption of either 50 µg/L As(V) or As(III) decreased the pH_{pzc} to approximately 5.2. In the presence of the higher As(V) or As(III) concentration, the PZC of TiO₂ was shifted to an even lower pH value. With increasing As concentrations, the pH_{pzc} of TiO₂ shifted from 5.8 to 5.2 and 4.8 in the presence of 50 and 100 µg/L As, respectively. The pH_{pzc} of metal oxides is determined by protonation and deprotonation of surface hydroxyl groups. The formation of outer-sphere surface complexes cannot shift the pH_{pzc} because there are no specific chemical reactions between the adsorbate and the surface that could change the surface charge (24). The shift of pH_{pzc} to a lower

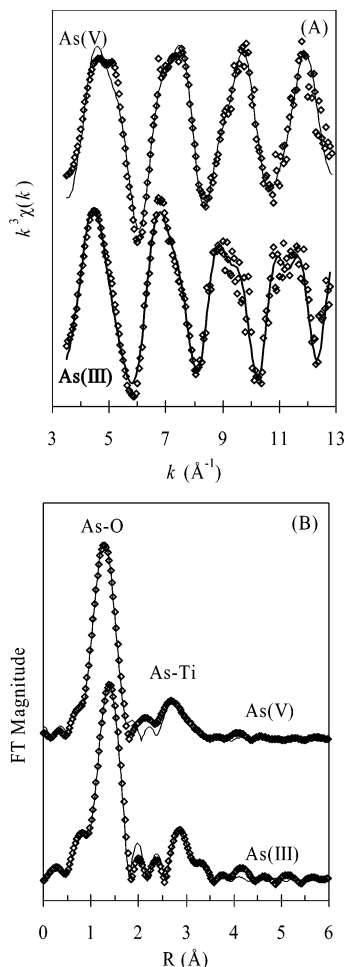


FIGURE 2. k^3 weighted observed (dotted line) and model calculated (solid line) As K-edge EXAFS spectra (A) and Fourier transform magnitude (B) resulting in a radial distance structure for the As(V) and As(III) adsorption on TiO_2 at pH 7. The peak positions are uncorrected for phase shift.

pH range is evidence of the formation of anionic negatively charged surface complexes (24). Therefore, the results of the EM measurements implied that both As(V) and As(III) formed negatively charged inner-sphere complexes on TiO_2 . The formation of negatively charged As(V) surface complexes was expected because anionic H_2AsO_4^- and HASO_4^{2-} are the predominant As(V) species in the pH range between 3 and 11. However, the formation of negatively charged As(III) surface species was not expected because the predominant aqueous As(III) species is neutral H_3AsO_3 at pH < 9. It could be possible that the adsorption reaction enhanced the deprotonation of surface As(III).

Arsenic K-Edge EXAFS Analysis. Figure 2A shows the k^3 weighted As K-edge EXAFS spectra obtained for As(V) and As(III) sorption on TiO_2 . Figure 2B shows the corresponding radial structure functions (RSF) as Fourier transform (FT) versus radial distance. The structural parameters obtained by fitting the theoretical paths to the experimental spectra are shown in the Supporting Information. The FT of the EXAFS spectra isolates the contributions of different coordination shells, in which the peak positions correspond to the interatomic distances. However, these peak positions in Figure 2B are uncorrected for the phase shift, so they deviate from the true distance by 0.3–0.5 Å.

The first peak in the FT was the result of backscattering from the nearest neighbor As–O shell. The average As–O distance was 1.69 and 1.77 Å for As(V) and As(III) samples, respectively, which is in agreement with previous publications

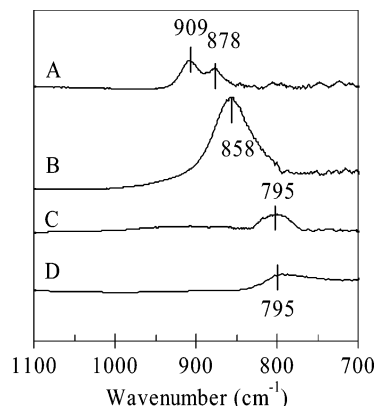


FIGURE 3. ATR-FTIR spectra of 0.1 M As(V) and As(III) solutions at different pH values. A: pH 5, H_2AsO_4^- ; B: pH 9, HASO_4^{2-} ; C: pH 12.5, AsO_4^{3-} ; and D: pH 10.5, H_2AsO_3^- .

(19, 25–30). The average coordination number (CN) of oxygen was calculated to be 3.8 and 3.0 for As(V) and As(III), respectively. EXAFS data analysis confirmed that the geometry of As(V) and As(III) was not changed by the formation of TiO_2 surface complexes. The As–O interatomic distance and CN obtained for the As(III) sample suggest that oxidation to As(V) had not occurred. In addition, the first and final X-ray scans of As(III) sample were identical, indicating that no As(III) oxidation occurred during exposure to X-rays. The second peak in the FT was attributed to As–Ti bonding with interatomic distances of 3.30 and 3.35 Å for As(V) and As(III) samples, respectively. Fitting the As–Ti peak was completed in both k -space and R -space using a single As–Ti shell, resulting in a CN of 2.5 and 1.7 for the As(V) and As(III) samples, respectively.

The EXAFS results show that As(V) formed bidentate binuclear inner-sphere complexes on the surfaces of TiO_2 , which is consistent with previous reports of the association of As(V) with anatase (19) and other mineral surfaces (25–28). On the basis of EXAFS analysis, the As(III) formed inner-sphere complexes on TiO_2 , as noted by the As(III)–Ti shell distance of 3.35 Å. With the distance and the average CN of 1.7 Ti atoms, the most likely configuration of the As(III)– TiO_2 surface species is a bidentate, binuclear complex. The As(III) surface configuration is in agreement with previous EXAFS studies of As(III) adsorption on iron and aluminum oxides (29–30).

FTIR Study of Dissolved As Species. The coordination chemistry of dissolved and adsorbed As species was studied using ATR-FTIR. The spectra of As(V) and As(III) species at different pH values are shown in Figure 3. The observed band positions as compared to literature values along with band assignments are listed in the Supporting Information. The stretching vibrations were the focus of this study. On the basis of a previous discussion on nomenclature, ν_s and ν_{as} were used to represent symmetric stretching and asymmetric stretching vibrations, respectively (31).

AsO_4^{3-} is the primary As(V) species at pH 12.5 (32) and belongs to the high symmetry point group T_d . Only one peak was observed for AsO_4^{3-} at ca. 795 cm^{-1} corresponding to $\nu_{as}(\text{As–O})$ (Figure 3C). The symmetry of AsO_4^{3-} is lowered from T_d to C_{3v} , C_{2v} , and C_{3v} due to protonation to form HASO_4^{2-} , H_2AsO_4^- , and H_3AsO_4 , respectively (31). Figure 3B shows the band at 858 cm^{-1} for HASO_4^{2-} at pH 9.0 that was assigned as $\nu_{as}(\text{As–O})$. Peaks at 878 and 909 cm^{-1} were observed in the spectrum of H_2AsO_4^- at pH 5.0 (Figure 3A). These bands were assigned to $\nu_s(\text{As–O})$ and $\nu_{as}(\text{As–O})$, respectively. The observed As(V) IR bands and assignments at various pH are in agreement with previous reports (33–37). The peak position is strongly affected by changes in pH. The $\nu_{as}(\text{As–O})$ band position increased from 795 cm^{-1} in

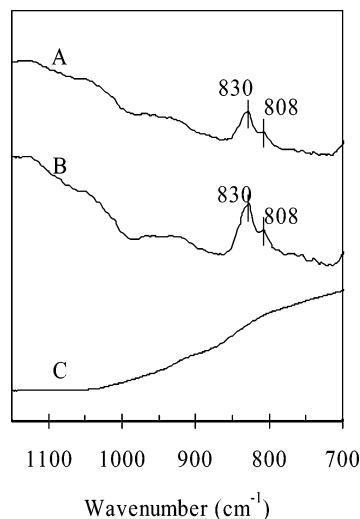


FIGURE 4. FTIR spectra of As(V) adsorbed on TiO₂. A: TiO₂ with adsorbed As(V) at pH 9; B: TiO₂ with adsorbed As(V) at pH 5.5; and C: TiO₂ at pH 5.5.

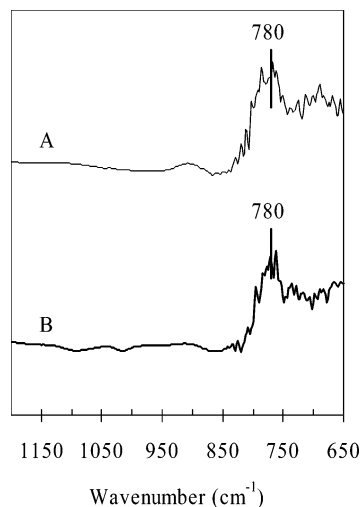


FIGURE 5. FTIR spectra of As(III) adsorbed on TiO₂. A: TiO₂ with adsorbed As (III) at pH 10.5 and B: TiO₂ with adsorbed As (III) at pH 8.

AsO₄³⁻ to 909 cm⁻¹ in H₂AsO₄⁻ when the pH was decreased from 12.5 to 5.0. Myneni et al. reported that $\nu_s(\text{As}-\text{OH})$ shifts to higher wavenumbers with increasing protonation of the As(V) complex, from 720 cm⁻¹ for HAsO₄²⁻ to 790 cm⁻¹ for H₃AsO₄ (38).

No IR peak was detected for H₃AsO₃ above 650 cm⁻¹, which is the threshold of the ZnSe crystal. Figure 3D shows the spectrum of H₂AsO₃⁻ at pH 10.5, which has C_s symmetry and exhibited $\nu_s(\text{As}-\text{O})$ at 795 cm⁻¹. The observations are supported by previous reported values (35, 37).

FTIR Study of Adsorbed As Species. The symmetry was lowered when As was adsorbed onto TiO₂ by forming inner-sphere complexes, leading to peak splitting or shifting. Figures 4 and 5 show the spectra of As(V) and As(III) adsorbed onto TiO₂ at various pH values, respectively. The band position and assignment along with comparable published data are summarized in the Supporting Information.

The peak positions of the adsorbed samples, however, were significantly different from those of the dissolved As species (Figures 3 and 4). The difference was due to symmetry reduction as a result of inner-sphere complex formation. If the symmetry reduction were caused by protonation, as would be the case for outer-sphere adsorption, the bands

should exhibit the similar positions with regard to the corresponding dissolved As species in the pH range. Therefore, the symmetry reduction and band shift indicated the formation of inner-sphere complexes, which is in agreement with EM measurement and EXAFS analysis. Contrary to the IR spectra for dissolved As species, a shift in band position was not observed in As(V) and As(III) adsorbed spectra with changing pH (Figures 4 and 5). The lack of change in band position at various pH values suggests that As formed the same inner-sphere surface complexes on TiO₂.

The adsorbed As(V) spectra exhibited two bands at 808 and 830 cm⁻¹ corresponding to $\nu(\text{As}-\text{OTi})$ and $\nu(\text{As}-\text{O})$, respectively (Figure 4). No peak was detected in the TiO₂ sample in the wavenumber range between 700 and 1000 cm⁻¹. With the similarities of phosphate and arsenate, the band assignment of adsorbed As(V) spectra was comparable to that of (MO)₂PO₂ surface complexes having C_{2v} symmetry (39–40). Because metal ions are not as strongly coordinated to oxygen ions as protons are (31, 39–40), the As–OTi bond should be stronger than As–OH, and the As–O bond in (TiO)₂AsO₂ should be weaker than that in (HO)₂AsO₂⁻. Therefore, the higher wavenumber at 830 cm⁻¹, due to the stretching of the uncomplexed As–O bond, was detected below 878 cm⁻¹, the $\nu(\text{As}-\text{O})$ in (HO)₂AsO₂⁻ (Figure 3). The lower wavenumber at 808 cm⁻¹, due to the stretching of the As–OTi bond, was observed above 765 cm⁻¹, the $\nu(\text{As}-\text{OH})$ in (HO)₂AsO₂⁻ (31, 37, 41). In addition, the positions of 808 and 830 cm⁻¹ are too high in frequency to be assigned to an $\nu(\text{As}-\text{OH})$ vibration (37). The results are in agreement with previous studies (31, 37–38). In a study of As(V) adsorption on iron oxide, Goldberg and Johnston (37) detected two peaks and assigned the 817–824 and 854–861 cm⁻¹ band to the stretching of As–OFe and As–O bonds, respectively. The absence of the As–OH vibration and the presence of As–O and As–OTi bands detected at 830 and 808 cm⁻¹, respectively, indicate that the adsorbed As(V) was nonprotonated.

The ATR-FTIR spectra of the adsorbed As(III) in Figure 5 exhibited a peak at 780 cm⁻¹ due to the stretching vibration of an uncomplexed As–O bond. Because the As–O vibration in (TiO)₂AsO₂⁻ is weaker than that in the (HO)₂AsO₂⁻, the band position shifted from 795 to 780 cm⁻¹ (Figures 3 and 5). This observation is in agreement with previous FTIR studies of As(III) adsorption on iron oxides (36–37). The observation of an uncomplexed As–O band suggest that the As(III) surface complex was nonprotonated.

It is worth noting that FTIR and EXAFS were performed at selected pH values in this study. The results obtained over a full range of experimental conditions would have been interesting to better corroborate the proposed adsorption mechanisms.

Surface Complexation Modeling. The spectroscopic results indicated that the adsorbed As(V) and As(III) species had three characteristics: (a) they were negatively charged; (b) they had only one species at different pH values; and (c) they had a bidentate binuclear nonprotonated configuration. Under these constraints, only Ti₂AsO₄⁻ and Ti₂AsO₃⁻ could be formed as As(V) and As(III) surface complexes, respectively. The diffuse double layer surface complexation model was used to describe As(V) and As(III) adsorption on the TiO₂ surface. Thermodynamic calculations were performed using the Windows version of the computer program MINTQA2 (23). More details about surface parameters, aqueous and surface reactions, and equilibrium constants used in the model calculations are provided as Supporting Information.

The results of batch adsorption tests and DLM model calculations are shown in Figure 6. The experimental observations showed that greater than 98% of the As(V) was removed by TiO₂ in the pH range from 4 to 9.5. The As(V) adsorption decreased significantly to about 10% as the pH increased to 11.8. Contrary to As(V) adsorption, As(III)

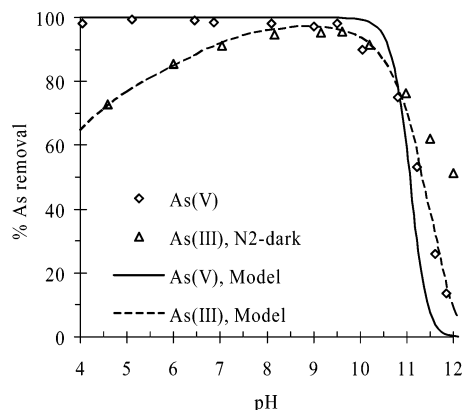


FIGURE 6. Experimental and DLM calculations of As(V) and As(III) adsorption edges on 0.2 g/L TiO₂ in 0.04 M NaCl. Total As(V) and As(III) concentration is 1.0 mg/L.

removal increased from 72 to 95% when the pH was increased from 4.5 to 9.5. The maximum uptake of As(III) occurred at approximately pH 9.5. The maximum adsorption pH value was coincident with the first dissociation constant of H₃AsO₃ (pK₁ = 9.2). Similar adsorption behaviors have been reported for As on iron (hydr)oxides surfaces (32, 42) and often have been observed for anions of weak acids (43). The solid and dashed lines in Figure 6 were model calculations for As(V) and As(III) adsorption behaviors, respectively. The DLM described the observed As(V) and As(III) adsorption data well at pH < 11. It underestimated the removal of the arsenic species at pH > 11. The modeling results demonstrated that As surface complex configurations constrained with the results of microscopic measurements could be employed in the adsorption modeling to describe the macroscopic behaviors. A more extensive data set including various adsorption densities and anion competition such as phosphate and silicate at different ionic strengths would be beneficial to constrain the model.

Acknowledgments

We acknowledge the staff of Beamline X18B at the National Synchrotron Light Source (NSLS) for their assistance with EXAFS analysis.

Supporting Information Available

Four tables showing the results of EXAFS analysis, FTIR band position and assignment for dissolved and adsorbed species, and DLM model parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review October 15, 2005. Revised manuscript received December 15, 2005. Accepted December 19, 2005.

ES052040E