Influence of pH on Initial Concentration Effect of Arsenate Adsorption on TiO₂ Surfaces: Thermodynamic, DFT, and EXAFS Interpretations

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Under the same thermodynamic condition where the total mass of arsenate was fixed, when the initial arsenate was added to TiO₂ suspension by multiple batches, adsorption isotherms declined as the multi-batch increased, which was termed initial concentration (C_0) effect. The extent of C_0 effect decreased gradually as pH decreased from 7.0 to 5.5. Extended X-ray absorption fine structure analysis of 1-batch and 3-batch isotherm samples showed that the relative proportion of bidentate binuclear (BB) and monodentate mononuclear (MM) complex was rarely affected by pH change from 5.5 to 7.0, indicating that the dependence of C_0 effect on pH was not due to inner-sphere chemisorption. The influence of pH on adsorption was simulated by density functional theory through changing the number of H⁺ in model clusters. Calculation of adsorption energy showed that BB surface complex was the most thermodynamically favorable mode (-244.5 kJ mol⁻¹) at low pH, but MM surface complex was the most thermodynamically favorable mode (-135.6 to 27.5 kJ mol⁻¹) at intermediate and high pH, which indicated the influence of surface functional groups ($-H_2O$ and $-OH$) on adsorption reaction pathways. As pH decreased, C_0 effect weakened gradually because outer-sphere H-bond adsorption became thermodynamically favorable (-203.1 kJ/mol). The dependence of C_0 effect on pH showed that traditional equilibrium adsorption constants could not accurately describe the real adsorption equilibrium at solid–liquid interface, because real equilibrium adsorption state is generally a mixture of various outer-sphere and inner-sphere metastable–equilibrium states.

1. Introduction

Oxyanions adsorption on metal-(hydr)oxides are significantly affected by pH, hydration state, and mineral surface charge.¹ pH is one of the most crucial parameters governing the adsorption–desorption of metal ions between mineral surface and aqueous solution.² The surface protonation–deprotonation process controlled by pH modifies the charge density and redox properties of mineral surface, and changes its reactivity and adsorption capacity.^{1,2}

Studies of sulfate at Al- and Fe-(hydr)oxide–H₂O interface showed that the thermodynamic favorability of surface complexation was directly related to surface pH condition (surface proton density).^{1,3} The dependence of oxyanions adsorption on pH created a complicated network of potential reaction pathways. However, the species (i.e., protonated or deprotonated states) of oxyanions in adsorption process at solid–liquid interface is still controversial.^{4,5} Little is known on the interaction between inner-sphere and outer-sphere complexes and the influence of adjacent surface functional group ($-H_2O$ or $-OH$) on adsorption reaction pathways.

So far, the most commonly reported adsorption geometry of oxyanions on metal-(hydr)oxide surfaces was bidentate binuclear (BB) surface complex.^{1,3–8} However, two crucial issues are neglected. First, the influence of adjacent surface functional group ($-H_2O$ and $-OH$) on adsorption reaction pathways and the stability of surface complex were not considered. Second, most geometric results were obtained from extended X-ray

absorption fine structure (EXAFS) spectra, but EXAFS spectra cannot accurately measure the structure of outer-sphere complexes because it does not give the information of long-range structure.⁹

In a related study, a clear initial concentration effect (i.e., C_0 effect) was observed in arsenate–TiO₂ adsorption system under pH 7.0, where under the same thermodynamic condition, when a series of fixed total mass of arsenate was added by multi-batch, adsorption isotherms, and real equilibrium adsorption constants declined as the number of multi-batch increased.¹⁰ This new thermodynamic phenomenon could not be interpreted by traditional thermodynamic adsorption theories but was successfully explained by metastable equilibrium adsorption (MEA) theory.^{10,11} The existence of C_0 effect implied that real equilibrium constants, when defined by macroscopic parameters of concentration and adsorption density, was affected by not only thermodynamic condition but also adsorption kinetics. Experimentally measured equilibrium adsorption constants therefore bear the property of inconstancy in nature.^{10,12} However, C_0 effect under different pH conditions has not been studied. The influence of pH on adsorption reaction and C_0 effect needs to be further elucidated.

Here, the dominant inner-sphere adsorption complexes of arsenate on TiO₂ surfaces in multi-batch isotherm samples under pH from 5.5 to 7.0 were analyzed by EXAFS spectroscopy. Density functional theory simulation was used to explore how the adsorption reaction pathways were affected by surface functional groups ($-H_2O$ and $-OH$) and pH. According to calculated adsorption energies, we were able to obtain the thermodynamic favorability sequence of inner-sphere and outer-

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sphere adsorption reaction pathways under a certain pH range and explain the change of C_0 effect under different pH conditions.

2. Theoretical and Experimental Methods

2.1. Theoretical Section. 2.1.1. DFT Calculation. Low-spin and restricted closed-shell DFT-B3LYP calculation formula^{13,14} and fully optimized calculation strategy were employed to study the adsorption behavior of arsenate on various protonated Ti-(hydr)oxide surfaces. To eliminate boundary effect and reduce charge of the clusters, the hanging bonds of O atoms were saturated with H atoms.^{5,15,16} Geometries were predicted using 6-31+G(d) basis set for O, H, 6-311+G(d) basis set for As, and LANL2DZ relativistic effective core potential (RECP) basis set for Ti atoms.^{14,15}

It was reported that the surface of anatase TiO₂ particle predominantly consisted of (101), (100), and (001) crystal plane,^{17,18} and the exposition of crystal plane depended on the synthetic technique.^{19,20} Because of the high computational cost of electronic structure methods,^{5,15,21} a Ti₂O₈ cluster of (100) surface was used for DFT calculation. This fragment was reasonably large to describe the typical adsorption sites for arsenate on Ti-(hydr)oxides.^{1,3,5,21,22} The good agreement of calculated As–O and As–Ti distances with experimental EXAFS results implied that (100) surface was dominant in the TiO₂ powder used in this adsorption experiment.^{10,14} There were two different oxygen atoms O(2) and O(3) in anatase TiO₂, which were bonded by two and three titanium atoms, respectively.²⁰ The 8 boundary oxygen in Ti₂O₈ model cluster were saturated with 12 H atoms to ensure the bonding numbers of O(2) and O(3) were the same as that of anatase bulk structure. This method avoided the over-relaxation of model clusters.^{5,14,15} Therefore, a [Ti₂(OH)₄(H₂O)₄]⁴⁺ cluster of TiO₂ was used to simulate pH effect and determine the geometry of Ti–AsO₄ surface complexes. In addition, we also investigated cluster size effects by using a larger [Ti₄O₂(OH)₈(H₂O)₆]⁴⁺ cluster model of TiO₂ (Figure S4 in Supporting Information). The result indicated that the smaller cluster models used here are reliable for studying the adsorption of arsenate on TiO₂ surfaces (discussed in Supporting Information).

It was reported that an accurate single point energy calculation using a large basis set on the geometry calculated using a small basis set gave results comparable to performing all calculations using a larger basis set.¹⁵ Therefore, to improve the estimation of adsorption reaction energies, single point energy calculations were subsequently performed on each optimized gas-phase geometry using 6-311++G (2df, p) basis set for O, H, As, LANL2DZ relativistic effective core potential (RECP) basis set for Ti atoms in combination with the integral equation formalism polarized continuum model (IEFPCM). IEFPCM calculation has been applied to simulate the effect of water molecules on outer coordination sphere (i.e., long-range solvent effect) and estimate the total free energy in solution (including nonelectrostatic terms) for each optimized species.^{1,13} The single point energies in solution were estimated by UFF (Universal Force Field) atom radii. The DFT calculation was performed using Gaussian03.¹³

2.1.2. Adsorption Energy and Equilibrium Constant Calculation. The adsorption reaction Gibbs free energy ΔG_{ads} ^{1,20} of arsenate on TiO₂ surfaces was calculated as $\Delta G_{\text{ads}} = G_{\text{tot}}(\text{Ti-AsO}_4) - [G_{\text{tot}}(\text{arsenate}) + G_{\text{tot}}(\text{TiO}_2)]$ (1), where $G_{\text{tot}}(\text{Ti-AsO}_4)$ is the total Gibbs free energy of Ti–AsO₄ adsorption complex, $G_{\text{tot}}(\text{arsenate})$ and $G_{\text{tot}}(\text{TiO}_2)$ are the total Gibbs free energy of arsenate molecule and TiO₂ cluster, respectively. The theoretical equilibrium adsorption constant K was calculated by equation

$\Delta G_{\text{ads}} = -RT \ln K$ (2), where R is the universal gas constant (8.314×10^{-3} kJ/mol·K) and T is Kelvin temperature.

2.2. Experimental Section. 2.2.1. Materials and Chemicals.

All solutions were prepared in ultrapure water (resistivity 18 MΩ) obtained with a Liyuan UPW-10N ultrapure water system. Arsenate stock solution was prepared from sodium arsenate (Na₂HAsO₄·7H₂O, ACS, 98.0–102.0%, Alfa Aesar China) and stored at 4 °C.

Anatase TiO₂ (Beijing chemical reagents company, China) was used as the adsorbent. BET surface area analysis indicated a surface area of 201.3 m²/g (ASAP-2010, Micromeritics). The particle size distribution, measured with a Mastersizer 2000 analyzer (Malvern, UK), ranged from 0.3 to 2.5 μm. The average particle size was 0.95 μm.

2.2.2. Multibatch Isotherm Experiments under Different pH.

Adsorption isotherms of As(V) on anatase TiO₂ were conducted in a series of polypropylene tubes under pH 5.5, 6.2, and 7.0, respectively. Under a series of fixed total mass of arsenate, initial arsenate was added by different modes (i.e., 1-batch and 3-batch) to the suspension of TiO₂ (1.0 g/L, 30 mL). Details about experiments can be found in a related study.¹⁰ Briefly, in 3-batch isotherm experiment, we divided a series of total arsenate into three equal parts and then added them into TiO₂ suspension by 3 times at 0, 4, and 8 h. All adsorption experiments were conducted in 0.01 M NaNO₃ solution at 25 °C. The pH of the reaction system was constantly monitored and adjusted to the desired value (5.5, 6.2, 7.0) with 0.1 mol/L NaOH or 0.1 mol/L HNO₃. The tubes were capped and shaken for 24 h. Kinetic experiments indicated that adsorption reached an apparent equilibrium within 4 h (see Figure 2 in ref 10). After 24 h of equilibration, suspensions of 1-batch and 3-batch adsorption experiments were centrifuged and filtered through 0.25 μm nominal pore-size membrane filters prior to analysis. Arsenate concentration was analyzed by hydride generation atomic fluorescence spectrometry (AFS 610, Ruili Beijing). Adsorption density was calculated from the difference between initial and final concentrations of arsenate. The moist solids of adsorption samples were mounted in a 2 mm thick cell and sealed with adhesive PVC tape for EXAFS measurements. The preparation of materials and the specific operation of 1-batch and 3-batch isotherm experiment were specially introduced in a related study.¹⁰ All reagents used in this study were analytical grade and labware was acid-washed.

2.2.3. EXAFS Sample Preparation and Data Collection. To study the influence of pH on C_0 effect, six comparable adsorption samples under pH 5.5, 6.2, and 7.0 from 1-batch and 3-batch isotherms of As(V) adsorption on anatase TiO₂ were prepared for EXAFS measurement. The six samples were generated from the same initial condition (0.80 mmol/L total arsenate and 1.0 g/L TiO₂ particle) but different addition modes of arsenate (1-batch and 3-batch).

The samples were sealed between two layers of adhesive PVC tape to prevent moisture loss and stored at 4 °C before EXAFS measurement. EXAFS data were collected on beamline 4W1B at Beijing Synchrotron Radiation Facility (BSRF), China. An energy range of –200–1000 eV from the K -absorption edge of As (11868 eV) was used to collect the spectral data under ambient conditions. Si(111) monochromator double crystals (energy resolution 0.5 eV) were utilized to minimize the high harmonics in the incident beam. The spectra of solid-phase samples were collected in fluorescence mode using a Lytle detector because As(V) concentration was low in adsorption samples, and the standard reference As(V) aqueous solutions (Na₂AsO₄·7H₂O) was measured in transmission mode. The

Figure 1. Adsorption isotherms of As(V) on TiO₂ in 0.01 mol/L NaNO₃ solution at 25 °C under different pH. TiO₂ particle concentration is 1 g/L. 1-batch stands for a series of total arsenate being added to TiO₂ suspension in one time, and 3-batch stands for the total arsenate being added averagely to TiO₂ suspension in 3 times every 4 h. EXAFS samples were marked by ellipse, in which the initial total As(V) concentration is 0.80 mmol/L.

fluorescence signal was filtered by a Ge foil to remove the elastically scattered radiation. An average of three scans was performed to achieve an adequate signal/noise ratio.

2.2.4. EXAFS Data Analysis. EXAFS data were analyzed with the Winxas 3.1 program.²³ The spectral data were processed by removing the background absorption, normalization, k -space conversion, Fourier transformation and then extracting the EXAFS structural information using WinXAS 3.1 software package. To remove the background absorption, spectra were background-corrected using a two-polynomial fit. Following the background correction, spectra were normalized. Normalized spectra were then converted to frequency (k) space, weighted by k^3 , and generating $k^3\chi(k)$ spectra. $k^3\chi(k)$ in k -space ($\text{\AA}^{-1}$) from 2.0 to 12.0 $\text{\AA}^{-1}$ was Fourier transformed (FT) using Bessel window function to produce the radial structure function (RSF) in R -space ($\text{\AA}$). The coordination numbers (CN) and interatomic distances (R) were then determined by a fitting procedure between the theoretical and the experimental curves.²⁴

The spectra were fitted with theoretical phase shift and amplitude functions of As–O, As–Ti and multiple scattering As–O–O–As paths calculated by ab initio FEFF 8.2 code²⁵ using the cluster of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) with the Fe atom replaced by Ti atom. This method has been widely used in the study of arsenate adsorption on Ti- and Al-(hydr)oxide

surfaces.^{4,10,26} Noncollinear As–O–O–As multiple scattering (MS) contributions to the EXAFS spectrum were fitted to all spectra by correlating the mean-square disorder of the radial distance (σ^2) of the As–O single scattering path to σ^2 of the MS As–O–O–As path.^{27,28} Therefore, the multiple scattering effect from AsO₄ tetrahedron was included in EXAFS data fitting. The many body amplitude reduction factor (S_0^2) was fixed to 0.9.^{29,30} More details on the EXAFS analysis were presented in Supporting Information.

3. Results and Discussion

3.1. Adsorption Isotherms under Different pH. Initial concentration effect (i.e., C_0 effect) refers to the phenomenon that, under the same thermodynamic condition, adsorption isotherms and real equilibrium adsorption constants are affected by reaction kinetic pathways such as the addition modes of arsenate (i.e., 1-batch or multi-batch). The existence of C_0 effect implies that real equilibrium adsorption constant, when defined by macroscopic parameters of concentration and adsorption density, bears the property of inconstancy in nature.¹⁰ 1-batch and 3-batch adsorption isotherms of arsenate on anatase TiO₂ at different pH were presented in Figure 1. The adsorption isotherms were empirically well described with Freundlich equations ($R^2 > 0.99$).

As shown in Figure 1, arsenate adsorption density increased as pH decreased from 7.0 to 5.5. 3-batch adsorption isotherm was significantly lower than 1-batch adsorption isotherm at pH 7.0. The gap of 1-batch and 3-batch isotherms reduced at pH 6.2. As pH decreased to 5.5, there was almost no difference between 1-batch and 3-batch isotherms. The C_0 effect weakened gradually and even disappeared with the decrease of pH from 7.0 to 5.5 (Figure 1), indicating the existence of notable C_0 effect at high pH and the dependence of C_0 effect on pH in As (V)-TiO₂ adsorption system. This result showed that the influence of multi-batch (3-batch) addition mode on adsorption isotherm and equilibrium adsorption constant varied with pH. To study the influence of pH on C_0 effect, six comparable adsorption samples were chosen for EXAFS measurement to detect the microstructure of adsorbed arsenate under different pH conditions. These six EXAFS samples were denoted by ellipse on isotherms (Figure 1), which had a same initial As(V) concentration (0.80 mmol/L) but under different reaction addition modes of total arsenate (1-batch and 3-batch).

3.2. Microscopic Structure of Adsorbed Arsenate. **3.2.1. EXAFS Analysis of Inner-Sphere Complexes.** Fourier transform spectra of As(V) K-edge EXAFS for dissolved and adsorbed

Figure 2. (a) Arsenic RSFs (radial structural functions) for 1-batch and 3-batch adsorption samples at different pH. (b) Arsenic RSFs for As(V) aqueous solutions and correlative adsorption samples at different pH. The small peak after the largest peak is the contribution from As–O–O–As multiple scattering (MS). The peak positions are uncorrected for phase shift.

TABLE 1: Summary of As(V) K-edge EXAFS Results for 1-Batch and 3-Batch Adsorption Samples at pH 5.5, 6.2, and 7.0^a

sample	As-Ti									Res.	CN ₁ /CN ₂
	As-O			BB			MM				
	CN	<i>R</i> (Å)	<i>σ</i> ²	CN ₁	<i>R</i> ₁ (Å)	<i>σ</i> ²	CN ₂	<i>R</i> ₂ (Å)	<i>σ</i> ²		
1-batch pH 5.5	3.9	1.68	0.002	1.9	3.17	0.008	1.1	3.60	0.01	8.6	1.8
3-batch pH 5.5	4.0	1.68	0.002	2.2	3.26	0.01	0.9	3.61	0.008	14.2	2.4
1-batch pH 6.2	4.0	1.68	0.002	1.8	3.16	0.007	1.0	3.59	0.006	11.0	1.7
3-batch pH 6.2	3.9	1.68	0.002	2.1	3.19	0.008	0.8	3.59	0.01	9.0	2.5
1-batch pH 7.0	4.1	1.69	0.002	1.8	3.17	0.007	1.1	3.59	0.001	13.2	1.6
3-batch pH 7.0	4.1	1.68	0.002	2.2	3.22	0.004	1.0	3.60	0.001	10.9	2.2
As(V)-pH 5.5	4.1	1.68	0.004							6.7	
As(V)-pH 7.0	4.1	1.69	0.003							5.3	
calculated values	4.0	1.70		2.0	3.25		1.0	3.52			

^a The amplitude reduction factor (S_0^2) was fixed to 0.9 in fitting process..^{4,9}

arsenate at pH 5.5–7.0 were given in Figure 2. EXAFS measured structural parameters were presented in Table 1. EXAFS results showed that the first coordination shell of As (V) consisted of four oxygen atoms at distance of 1.69 ± 0.01 Å. The second coordination shell of Ti-AsO₄ surface complexes at pH 5.5 to 7.0 contained two titanium subshells at As–Ti distances of 3.20 ± 0.05 and 3.60 ± 0.02 Å (Table 1). The small peak after the largest As–O peak in Fourier transform was observed in not only adsorption samples but also arsenate solution sample (Figure 2b), so they were obviously not from Ti backscatter but from As–O–O–As multiple scattering that was a common phenomenon for the structure with low Z (<10) nearest scatterers such as oxygen.^{9,31}

In a related study,¹⁴ DFT calculation indicated that single edge linkage would yield an As–Ti distance near 2.76 Å (structures not shown here) that was much smaller than the distance obtained from EXAFS analysis (3.20 ± 0.05 and 3.60 ± 0.02 Å). Single edge linkage mode was therefore excluded in the adsorption of arsenate on TiO₂. The two experimental As–Ti distances (3.20 ± 0.05 and 3.60 ± 0.02 Å) were close to DFT calculated values of BB (3.25 Å) and MM (3.50 and 3.53 Å) complexes (Figure 3a–c). Calculated As–O distance (1.70 Å) agreed well with EXAFS values (1.69 ± 0.01 Å). The comparison of EXAFS measured and DFT calculated structural parameters indicated that arsenate mainly formed inner-sphere BB and MM surface complexes on TiO₂ over the pH range between 5.5 and 7.0.

EXAFS coordination number (CN) was a little different from theoretical values (Table 1). Since the EXAFS coordination number of CN₁ and CN₂ represented statistically the average number of nearest Ti atoms around the As atom corresponding to a specific interatomic distance,^{10,24,32,33} the CN₁/CN₂ ratio can qualitatively reflect the relative population of BB and MM complexes. In a related study, we have used the coordination number ratio of CN₁/CN₂ to describe the relative proportion of BB mode to MM mode in adsorption samples and successfully explained the C₀ effect under pH 7.0.¹⁰

Table 1 showed that CN₁/CN₂ was 1.6 and 2.2 for 1-batch and 3-batch adsorption samples at pH 7.0, respectively, indicating that 3-batch adsorption samples contained more BB adsorbed arsenate than that of 1-batch adsorption samples. BB complex occupies two active sites on adsorbent surface whereas MM occupies only one. For monolayer chemiadsorption, a unit surface area of a given adsorbent can contain more arsenate molecules adsorbed in MM mode than that in BB mode. Therefore, the increase of the proportion of BB complex from 1-batch to 3-batch addition mode was shown as the decrease of adsorption density in 3-batch isotherm (Figure 1).

The increase of CN₁/CN₂ from 1-batch to 3-batch adsorption sample was similarly observed at pH 5.5 and 6.2. CN₁/CN₂ increased from 1.8 (1-batch) to 2.4 (3-batch) at pH 5.5, and from 1.7 (1-batch) to 2.5 (3-batch) at pH 6.2 (Table 1). The CN₁/CN₂ results indicated that the change of the proportion between BB and MM from 1-batch to 3-batch little affected by pH change from 5.5 to 7.0. Thus, the dependence of C₀ effect on pH (i.e., C₀ effect weakened and gradually disappeared as pH decreased from 7.0 to 5.5) could not be attributed to inner-sphere chemiadsorption.

3.2.2. DFT Calculation of H-bonded Complex. Because EXAFS spectrum could not give long-range information,⁹ EXAFS technique could not accurately measure the structure of outer-sphere Ti-AsO₄ complexes in which As–Ti distances would be more than 5 Å (Figure 3d). Therefore, DFT calculation played a unique role in structure analysis of H-bonded complex. Compared to inner-sphere complexes, H-bonded structure was difficult to be simulated because it had more translational and rotational freedom than inner-sphere complexes.¹

It was shown that outer-sphere arsenate adsorption was an electrostatic attraction between positively charged surface site(s) and negatively charged arsenate without release of surface functional groups (Figure 3d). Arsenate and –H₂O surface functional groups formed two H–O hydrogen bonds in H-bonded complex, where, H₁–O₃ (H₂–O₄) distance decreased to 1.00 Å and the two opposite O–H bonds of hydrated surface groups were lengthened to 1.79 Å, indicating the break of H₁–O₁ (H₂–O₂) bond and the partial formation of H₁–O₃ (H₂–O₄) bond. The strong H-bonded interaction occurred after the two O–H–O bond angles (O₁–H₁–O₃ and O₂–H₂–O₄) increasing to 176.8 and 176.5°. NBO (natural bond orbital) analysis showed that the interaction between O₁ (O₂) lone pair (LP) and $\sigma_{\text{H}_1-\text{O}_3}^*$ ($\sigma_{\text{H}_2-\text{O}_4}^*$) antibond NBO gave a stabilization energy of 11.00 (11.10) kcal/mol, which led to the donation from the O₁ (O₂) lone pair to the $\sigma_{\text{H}_1-\text{O}_3}^*$ ($\sigma_{\text{H}_2-\text{O}_4}^*$) antibond NBO. DFT calculation indicated that arsenate can also be H-bonded to hydrated TiO₂ surfaces to form stable outer-sphere complex. In addition, we also investigated the effect of explicit H₂O molecules on H-bonded complex with four H₂O molecules (Figure S5b in Supporting Information). We found that the explicit H₂O molecules have little influence on the geometry of H-bond adsorption complex. The result indicated the validity of the calculated H-bonded complex without explicit H₂O molecules (discussed in Supporting Information).

3.3. DFT Calculation of Adsorption Reaction Energies under Different pH. **3.3.1. Simulation of pH Effect.** For arsenate, H₂AsO₄[−] is the dominant species in experimental pH range from 5.5 to 7.0 ($\text{p}K_{\text{a}1} = 2.2$, $\text{p}K_{\text{a}2} = 7.0$).^{4,5,34} Thus,

Figure 3. DFT calculated structure of inner-sphere and H-bond adsorption products of arsenate on TiO₂: (a) monodentate mononuclear arsenate H-bonded to a H₂O surface functional group occupying the adjacent surface site (MM₁); (b) monodentate mononuclear arsenate H-bonded to a -OH surface functional group occupying the adjacent surface site (MM₂); (c) bidentate binuclear (BB) complex; (d) H-bonded complex. Red, big gray, small gray, and purple circles denote O, Ti, H, and As atoms, respectively. Distances are shown in angstroms.

Figure 4. Schematic diagram of surface protonation-deprotonation processes controlled by pH conditions.

H₂AsO₄⁻ species was used in DFT calculation. For TiO₂ surfaces ($pK_{a1} = 3.8$, $pK_{a2} = 7.8$),⁴ pH effect on adsorption reaction was simulated by adjusting the ratio of surface -OH/-H₂O functional groups (Figure 4). =TiOH and =TiOH₂⁺ surfaces were calculated by changing the number of H⁺ in TiO₂ cluster surfaces. =TiO⁻ surface type can hardly adsorb arsenate due to the strong electrostatic repulsion,^{1,4} so it was omitted in the simulated pH range. Therefore, the effect of pH on adsorption reaction was involved in the calculated TiO₂ surface conditions. In a related study,¹⁴ the chemical reactivity analysis of arsenate (H₂AsO₄⁻) and TiO₂ showed that inner-sphere complexation occurred via ligand exchange of the two unprotonated oxygen atoms on arsenate with TiO₂ surface functional groups (-H₂O for low pH and -OH for high pH). On the basis of this reaction mechanism, a series of stoichiometrically balanced equations (Table 3) were calculated to estimate the relative Gibbs free energies for arsenate adsorption on TiO₂ surfaces under different pH conditions.

3.3.2. Calculated Adsorption Reaction on pH-dependent TiO₂ Surfaces. The reactants and products used to calculate the adsorption reaction Gibbs free energies (ΔG_{ads}) of arsenate on various protonated Ti-(hydr)oxide surfaces were given in Table 2. pH-dependent TiO₂ surfaces were simulated by changing the number of H⁺ in model clusters. The calculated results of adsorption reaction energies were presented in Table 3.

Bidentate binuclear (BB) adsorption was predicted to be exergonic (-244.5 kJ/mol) on simulated low pH condition, but endergonic (+13.1 to +211.5 kJ/mol) on intermediate and high pH conditions (Table 3). The DFT calculated results indicated that arsenate reacted with a labile group (H₂O, low pH condition) was much easier than with a stable group (OH⁻, high pH condition). For monodentate mononuclear (MM) complex, to study the influence of adjacent surface site (i.e., the type of surface functional group) on adsorption reaction, four adsorption processes were calculated for two MM (MM₁ and MM₂) complexes (Table 3), where the adjacent surface site was occupied by either a H₂O (for MM₁ complex) or a OH⁻ (for MM₂ complex) functional group. Calculated adsorption energies showed that, in the TiO₂ surfaces where H₂O and OH⁻ surface functional groups were coexistent on the two adjacent sites (e.g., intermediate pH condition), arsenate preferred to react with the adjacent labile H₂O surface group to form MM₂ complex (-135.6 kJ/mol), but not to react with the stable OH⁻ surface

TABLE 2: Reactant and Product Energies of Arsenate Adsorption on Various Protonated Ti-(hydr)oxides^a

reaction species	E_{gas}	E_{IEFPCM}	G_{IEFPCM}
Free Species			
$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12}$	-3455.3525	-3456.0308	-3455.9820
$12\text{H}_2\text{O}$	-917.26105	-917.7175	-917.6832
$\text{OH}^-(\text{H}_2\text{O})_{11}$	-916.7387	-917.2475	-917.2116
$(\text{OH}^-)_2(\text{H}_2\text{O})_{10}$	-916.0962	-916.7630	-916.7264
Surface Clusters			
$[\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6]^{4+}$	-876.7841	-878.1081	-878.0713
$[\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_5]^{3+}$	-876.8320	-877.7307	-877.6978
$[\text{Ti}_2(\text{OH})_6(\text{H}_2\text{O})_4]^{2+}$	-876.7263	-877.3219	-877.2882
Bidentate Binuclear Complex			
$[\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_4\text{AsO}_2(\text{OH})_2]^{3+}(\text{H}_2\text{O})_2$	-3415.4960	-3416.5111	-3416.4632
Monodentate Mononuclear Complexes			
$[\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_5\text{AsO}_2(\text{OH})_2]^{3+} \text{H}_2\text{O}$	-3415.4837	-3416.5035	-3416.4560
$[\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_4\text{AsO}_2(\text{OH})_2]^{2+} \text{H}_2\text{O}$	-3415.3434	-3416.0917	-3416.0482
H-Bonded Complex			
$[\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6\text{AsO}_2(\text{OH})_2]^{3+}$	-3415.4752	-3416.4947	-3416.4475

^a Energies are listed in Hartrees/molecule. E_{gas} : gas-phase electronic energy of geometry optimized species (B3LYP, 6-31+G(d) basis set on O, H, 6-311+G(d) basis set on As, LANL2DZ basis set on Ti). E_{IEFPCM} : electronic energy in solution of single-point energy calculation (B3LYP, 6-311++G (2df, p) basis set on O, H, As, LANL2DZ basis set on Ti) from the gas-phase optimized geometries. G_{IEFPCM} : total Gibbs free energy in solution with nonelectrostatic terms from single-point energy calculation (B3LYP, 6-311++G (2df, p) basis set on O, H, As, LANL2DZ basis set on Ti).

TABLE 3: Calculated ΔG_{ads} (kJ/mol) and Equilibrium Adsorption Constant K at 25 °C of Arsenate on Various Protonated Ti-(hydr)oxide Surfaces

HO/AsO ₄	adsorption reaction equations	ΔG	K
Bidentate Binuclear Complexes			
0	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6]^{4+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_4\text{AsO}_2(\text{OH})_2]^{3+}(\text{H}_2\text{O})_2 + 12\text{H}_2\text{O}$	-244.5	6.80×10^{42}
1	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_5]^{3+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_4\text{AsO}_2(\text{OH})_2]^{3+}(\text{H}_2\text{O})_2 + \text{OH}^-(\text{H}_2\text{O})_{11}$	13.1	5.15×10^{-3}
2	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_6(\text{H}_2\text{O})_4]^{2+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_4\text{AsO}_2(\text{OH})_2]^{3+}(\text{H}_2\text{O})_2 + 2\text{OH}^-(\text{H}_2\text{O})_{10}$	211.5	8.72×10^{-38}
Monodentate Mononuclear Complexes			
0	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6]^{4+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_5\text{AsO}_2(\text{OH})_2]^{3+}\text{H}_2\text{O} + 12\text{H}_2\text{O}$	-225.4	3.13×10^{39}
1-1	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_5]^{3+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_5\text{AsO}_2(\text{OH})_2]^{3+}\text{H}_2\text{O} + \text{OH}^-(\text{H}_2\text{O})_{11}$	32.1	2.37×10^{-6}
1-2	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_5]^{3+} \rightarrow [\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_4\text{AsO}_2(\text{OH})_2]^{2+}\text{H}_2\text{O} + 12\text{H}_2\text{O}$	-135.6	5.72×10^{23}
2	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_6(\text{H}_2\text{O})_4]^{2+} \rightarrow [\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_4\text{AsO}_2(\text{OH})_2]^{2+}\text{H}_2\text{O} + \text{OH}^-(\text{H}_2\text{O})_{11}$	27.5	1.54×10^{-5}
H-Bond Complexes			
0	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6]^{4+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6\text{AsO}_2(\text{OH})_2]^{3+} + 12\text{H}_2\text{O}$	-203.1	3.91×10^{35}
1	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_5(\text{H}_2\text{O})_5]^{3+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6\text{AsO}_2(\text{OH})_2]^{3+} + \text{OH}^-(\text{H}_2\text{O})_{11}$	54.4	2.96×10^{-10}
2	$\text{H}_2\text{AsO}_4^-(\text{H}_2\text{O})_{12} + [\text{Ti}_2(\text{OH})_6(\text{H}_2\text{O})_4]^{2+} \rightarrow [\text{Ti}_2(\text{OH})_4(\text{H}_2\text{O})_6\text{AsO}_2(\text{OH})_2]^{3+} + 2\text{OH}^-(\text{H}_2\text{O})_{10}$	252.9	5.01×10^{-45}

Figure 5. Relative Gibbs free energies of arsenate adsorption on various protonated Ti-(hydr)oxide surfaces. The horizontal coordinate represents the ratio of surface $\text{-H}_2\text{O}$ group to arsenate. MM₁ and MM₂ correspond to the MM complex where the adjacent surface site occupied by a H_2O or OH^- functional group, respectively.

group to form MM₁ complex (+32.1 kJ/mol). The DFT calculated results of MM adsorption indicated that there was an obvious influence of the adjacent surface functional group on adsorption reaction pathways.

The adsorption energy curves showed that the thermodynamic favorability of inner-sphere and outer-sphere adsorption was directly related to pH (Figure 5). Both the inner-sphere and outer-sphere adsorption were predicted to be energetically favorable (ranging from -203.1 to -244.5 kJ/mol) at low pH, but moderately unfavorable to highly unfavorable (ranging from $+13.1$ to $+252.9$ kJ/mol) at intermediate and high pH. As pH decreased, the thermodynamic favorability of inner-sphere and outer-sphere arsenate adsorption on Ti-(hydr)oxides increased. This DFT result explained why the adsorption densities of arsenate (Figure 1) and equilibrium adsorption constants (Table 3) increased with the decrease of pH.

The most thermodynamically favorable surface complex was BB complex (-244.5 kJ/mol) at low pH but MM complex (-135.6 to 27.5 kJ/mol) at intermediate and high pH, which indicated that only when MM arsenate overcame a high energy barrier can it exchange with a stable group (OH^-) to form BB complex under high pH condition. EXAFS analysis showed that the relative proportion of BB and MM complexes were little affected by pH change from 5.5 to 7.0. This EXAFS results indicated that, even at relatively high pH (e.g., pH = 7.0), MM adsorbed arsenate could further form a BB complex when the adjacent surface site was not occupied but needed to overcome a higher energy barrier than that at low pH. The transformation from MM to BB complex at pH 7.0 was also confirmed by XANES fingerprinting analysis in a related study.¹² The forming processes of H-bonded complex were the most thermodynamically unfavorable under intermediate and high pH ($+54.4$ and $+252.9$ kJ/mol), indicating that H-bonded adsorption hardly occurred at high pH.

Theoretical equilibrium adsorption constants (K) of calculated surface complexes (BB, MM and H-bonded complexes in this adsorption system) were significantly different in the order of magnitude under the same thermodynamic conditions (Table 3). The theoretical K were in the order of BB (6.80×10^{42}) > MM (3.13×10^{39}) > H-bonded complex (3.91×10^{35}) under low pH condition, and in the order of MM (1.54×10^{-5}) > BB (8.72×10^{-38}) > H-bonded complex (5.01×10^{-45}) under high pH condition. Therefore, even under the same thermodynamic conditions, the real equilibrium adsorption constant would vary

with the change of the proportion of different surface complexes in real equilibrium adsorption.

3.4. Microscopic Explanation for pH Dependence of C_0 Effect. EXAFS and XANES analysis indicated that the notable C_0 effect at pH 7.0 was caused by the increase of the proportion of BB complex from 1-batch to 3-batch addition mode.^{10,12,22} However, the relative proportion of BB and MM complexes were little affected by pH change from 5.5 to 7.0. Therefore, the dependence of C_0 effect on pH was not due to inner-sphere chemisorption. It can be expected that TiOH_2^+ , TiOH , and TiO^- surface group are coexistent in the actual infinite TiO₂ surfaces. The pH controls the relative proportion between them. We simulated the ΔG_{ads} variation of inner-sphere and outer-sphere adsorption with pH (Figure 5) using the three kinds of surface (Figure 4), which were achievable in DFT calculation. On the basis of the acid dissociation constants of TiO₂ surfaces ($\text{p}K_{\text{a}1} = 3.8$, $\text{p}K_{\text{a}2} = 7.8$), the adsorption reaction energy (thermodynamic favorability) of arsenate under low pH conditions (5.5 and 6.2) were expected in the region A in Figure 5. DFT results showed that H-bond adsorption became thermodynamically favorable (-203.1 kJ/mol) as pH decreased. Thus, the TiOH_2^+ surface group and hence the H-bond adsorption complex would exist under the experimental pH conditions (especially under pH 5.5). H-bond adsorption is essentially an outer-sphere electrostatic attraction (Figure 3d), so it was hardly influenced by the addition mode of arsenate (1-batch and 3-batch). Therefore, as the proportion of outer-sphere adsorption complex increased under low pH condition, the C_0 effect would weaken and even disappear (Figure 1).

The coexistence and interaction of outer-sphere and inner-sphere adsorptions caused the extreme complicity of real adsorption processes at solid–liquid interface, which was not taken into account in traditional thermodynamic adsorption theories. Metastable equilibrium adsorption (MEA) theory pointed out that adsorbate would exist on solid surfaces in different forms^{11,22} (i.e., MEA states) and recognized the influence of adsorption reaction kinetics on the final MEA states (e.g., MM, BB, and H-bonded complexes in this study) that construct real adsorption equilibrium state.^{10,12,14} Therefore, traditional thermodynamic adsorption theories need to be further developed by taking metastable equilibrium adsorption into account in order to accurately describe real equilibrium properties of surface adsorption.

4. Conclusion

The influence of pH on initial concentration (C_0) effect of As(V) on TiO₂ surfaces was studied by EXAFS spectra and DFT calculation. EXAFS results indicated that the relative proportion of BB and MM complexes were little affected by pH change from 5.5 to 7.0, and hence the dependence of C_0 effect on pH was not due to inner-sphere chemisorption. The study of the influence of pH on C_0 effect motivated the investigation of outer-sphere adsorption by DFT calculation. DFT results indicated that the adsorption of As(V) on TiO₂ surfaces involved not only chemical bond but also H-bond, especially at low pH. On the basis of the DFT results, it was suggested that the coexistence of outer-sphere and inner-sphere adsorption weakened the C_0 effect under low pH condition.

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Supporting Information Available: Details on EXAFS analysis and the discussion on cluster size effects. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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