Molecular Insights into Ternary Surface Complexation of Arsenite and Cadmium on TiO₂

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S Supporting Information

ABSTRACT: Insights from molecular-level mechanisms of arsenite [As(III)] and cadmium (Cd) co-adsorption on TiO₂ can further our understanding of their synergistic removal in industrial wastewaters. The motivation for our study is to explore the interfacial interactions of neutrally charged As(III) and cationic Cd²⁺ on nanocrystalline TiO₂ using multiple complementary techniques. The results of adsorption edge, ζ potential, and surface complexation modeling suggest that coexistence of As(III) and Cd²⁺ enhanced their synergistic adsorption on TiO₂ and, consequently, resulted in the formation of a ternary surface complex. This ternary surface complex, in turn, inhibited the metal release into the aqueous phase and, therefore, facilitated the immobilization of the heavy metals. Our *in situ* flow-cell attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy evidence showed that, regardless of the order of contact, As(III) was preferentially adsorbed on TiO₂ rather than Cd. In agreement with our spectroscopic analysis, quantum chemistry calculations also illustrated that the Cd–As(III)–TiO₂ ternary surface complex should be formed with the adsorbed As(III) as the bridging molecule. At high As(III) concentrations, the formation of the Cd–As(III)–TiO₂ complex is responsible for the Cd removal. The simultaneous removal mechanisms will further our understanding of the removal of multiple pollutants in industrial wastewaters.

INTRODUCTION

Coexistence of arsenic (As) and cadmium (Cd) with extremely high concentrations in mining and smelting wastewaters presents a major challenge to the environment.^{1,2} Arsenate [As(V)] is the primary As species in oxic environments, whereas under reducing conditions and especially in industrial wastewaters, the more toxic and mobile arsenite [As(III)] is predominant.^{3–5} Simultaneous adsorptive removal of As(III) and Cd can be successfully achieved using regenerable TiO₂.⁶ However, the molecular-level interactions between cationic Cd and neutrally charged As(III) on the TiO₂ surface are poorly understood.

The rapid increase in industrial mineral exploration and extraction over the past 2 decades⁷ has motivated extensive studies on the interactions of metals and oxyanions on solids.^{8–10} The synergistic uptake of cationic metals and anionic ligands on metal oxide surfaces is generally attributed to the electrostatic effect, formation of ternary surface complexes, and surface and bulk precipitation, as evidenced by spectroscopic analysis.^{11–14} However, no clear boundaries exist distinguishing ternary surface complexes and surface precipitation, and these two terms sometimes are even used interchangeably.¹² For example, surface precipitation was used

to describe elevated As(V) removal in the presence of Zn¹¹ and Cu¹⁵ on goethite. On the other hand, more recent reports use ternary surface complexation to describe the co-adsorption of cations and anions on a surface where the newly formed cation–anion solid phase does not grow beyond monolayer coverage. For instance, formation of a ternary surface complex enhanced Cd adsorption in the presence of PO₄ and SO₄ on goethite^{9,16} and ferrihydrite.¹⁷ In addition, SO₄ anions could form ternary surface complexes with Pb, Cu, and Zn on goethite,^{9,14} ferrihydrite, and schwertmannite.¹⁸ Although metal–As(V) ternary complexes on surfaces are well-known,^{11,15,19} limited reports are available on metal–As(III) mutual effects on surfaces.¹⁹

The objective of this study was to explore the molecular-scale interactions of As(III) and Cd on TiO₂ surfaces. To investigate the hypothesis that As(III) and Cd form a ternary surface complex on TiO₂, multiple complementary techniques were used, including macroscopic adsorption/extraction experi-

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Figure 1. Experimental pH adsorption edges (symbols) and CD-MUSIC calculations (lines) of (i) Cd and (ii) As(III) in the simulated wastewater [molar ratio of As(III)/Cd, $R = 2$; As(III) = 5.26 mM] and copper-smelting wastewater [$R = 10.4$; As(III) = 51.52 mM]. The wastewater sample with the highest Cd concentration (4.96 mM) was used to test the adsorption capacities under the worst scenarios.

ments, extended X-ray absorption fine structure (EXAFS) spectroscopy and *in situ* flow-cell attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy analysis. The insights gained from this study should improve our knowledge in predicting the fate of neutral and cationic heavy metals.

MATERIALS AND METHODS

Materials. A wastewater sample containing an average concentration of 51.87 mM (3890 mg/L) As(III), 3.28 mM (369 mg/L) Cd, 0.38 mM (24 mg/L) Cu, and 0.02 mM (5 mg/L) Pb was obtained from a copper-smelting company in China.⁶ The As(III) concentration ranged from 50.93 to 52.41 mM, and the Cd concentration varied from 2.48 to 4.96 mM. The average molar ratio of As(III)/Cd, R , was 15.8 for the copper-smelting wastewater. The stock solutions of 13.35 mM (1000 mg/L) As(III) and 8.90 mM (1000 mg/L) Cd were prepared by dissolving NaAsO₂ and Cd(NO₃)₂ in deionized (DI) water, respectively. To prevent As(III) oxidation and to remove CO₂, DI water was purged with nitrogen for at least 1 h. The nano-TiO₂ was prepared by hydrolysis of titanyl sulfate, as described in our previous report.⁶ The Brunauer-Emmett-Teller (BET) surface area was 196 m²/g; the site density was 6 mmol/g; and the point of zero charge was 5.3.

Batch Experiments. Adsorption envelope experiments were performed to determine the adsorption edge, which is the amount of As(III) or Cd adsorbed as a function of the final solution pH. Suspension samples containing As(III), Cd, and 1 g/L TiO₂ were adjusted to desired pH values in the range of 3–9 with NaOH and HClO₄. The initial Cd and As(III) concentrations in the binary and ternary adsorption systems were 2.63 and 5.26 mM, respectively, resulting in $R = 2.0$. In a wastewater sample, the initial Cd and As(III) concentrations were 4.96 and 51.52 mM, respectively, leading to $R = 10.4$. The highest Cd concentration (4.96 mM) was selected to test the adsorption capacities under the worst scenarios. After the samples were mixed on a rotating shaker for 24 h in the dark, the final pH was measured and the suspension was passed through a 0.45 μm membrane filter for measurements of soluble metals.

Analysis. The concentration of dissolved Cd was measured using a furnace atomic absorption spectrometer (FAAS) (AAS-800, PerkinElmer, Waltham, MA). The As concentration and speciation were determined by a high-performance liquid chromatography atomic fluorescence spectrometry system (HPLC-AFS, Jitian, China) as detailed in our previous

report.²⁰ The As speciation results confirm that no As(III) oxidation occurred during the experiments. Details of As speciation analysis, ζ potential measurement, surface-enhanced Raman scattering (SERS), EXAFS, ATR-FTIR, X-ray diffraction (XRD), scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDXS), surface complexation modeling, and quantum chemical calculations are reported in the Supporting Information.

RESULTS AND DISCUSSION

pH Dependence of Cd and As(III) Co-adsorption on TiO₂. To investigate the Cd and As(III) removal under different As(III)/Cd molar ratios (R), the pH-dependent adsorption behaviors were studied in simulated wastewater ($R = 2$) and copper-smelting wastewater ($R = 10.4$). The presence of As(III) (Figure 1i) substantially enhanced the Cd adsorption, and the Cd adsorption edges shifted to lower pH ranges with increasing R . The highest enhancement in Cd adsorption occurred in the copper-smelting wastewater with 51.52 mM As(III) and 4.96 mM Cd (Figure 1i) at pH 9.

At pH 5–9, the Cd adsorption increased from 4.0 to 13.4 μmol/m² in the Cd–TiO₂ binary system to 9.7–15.2 and 17.1–25.2 μmol/m² in the Cd–As(III)–TiO₂ ternary system for simulated and smelting wastewater, respectively (Figure 1i). The site density of TiO₂ is 6 mmol/g,⁶ corresponding to a theoretical site concentration of 30.6 μmol/m² in our system. This total available site, however, is not sufficient for Cd uptake (17.1–25.2 μmol/m²) from the wastewater if adsorption is the only removal mechanism, because one Cd atom should occupy two sites, as evidenced by our EXAFS study detailed in the following section. Therefore, other mechanisms besides adsorption must contribute to the Cd removal, such as the formation of surface precipitates or ternary surface complexes. In line with our results, elevated Cd adsorption in the presence of As(V) is observed and explained by electrostatic effects and the formation of a ternary Cd–As(V)–goethite complex.²¹ Meanwhile, a ternary surface complex of Zn and As on magnetite is also inferred as a possible mechanism for the enhanced adsorption of As and Zn.¹⁹

Similar to Cd adsorption, considerable enhancement in As(III) adsorption was observed in the presence of 2.63 and 4.96 mM Cd (Figure 1ii). For example, As(III) adsorption increased from 1.6 μmol/m² in the As(III)–TiO₂ binary system to 4.6 μmol/m² in the Cd–As(III)–TiO₂ ternary system. Nevertheless, As(III) removal exhibited no significant difference ($p = 0.052$) when R increased from 2 to 10.4. The

Figure 2. Experimental and CD-MUSIC simulations of ζ potential of 0.2 g/L TiO_2 as the blank (black), 0.03 mM As(III) or Cd (red), and 0.03 mM As(III) in the presence of Cd (blue) adsorbed TiO_2 as a function of pH in 0.04 M NaClO_4 solution. Error bars in (i) Cd and (ii) As(III) pre-adsorption systems represent the standard deviation ($n = 3$).

maximum adsorption of As(III) occurred at approximately pH 9, corresponding to the first dissociation constant of H_3AsO_3 ($\text{p}K_1 = 9.3$).²² In fact, this maximum As(III) adsorption ($4.6 \mu\text{mol}/\text{m}^2$) was substantially less than the theoretical site concentration of TiO_2 ($30.6 \mu\text{mol}/\text{m}^2$).

The shift in the point of zero charge (PZC) of TiO_2 (Figure 2) corresponded to the change in the adsorption curve. The PZC shifted from 5.3 for pristine TiO_2 to approximately 5.7 upon Cd adsorption (Figure 2i), indicating the formation of positively charged inner-sphere complexes on TiO_2 .²³ After the addition of As(III) to the Cd– TiO_2 system, the PZC moved to 4.4, suggesting that the As(III) uptake reduced the charge of the surface complex. Although soluble As(III) exists in the form of neutral H_3AsO_3 species below pH 9.3, the adsorption reaction may facilitate the deprotonation of the surface As(III) complex.²³ A similar trend in the PZC shift was also observed in the As(III) pre-adsorption system (Figure 2ii): the PZC shifted first to 4.6 because of As(III) adsorption and then moved to 5.2 with the addition of Cd. This charge neutralization signals the formation of the ternary surface complex.¹²

One possibility for ternary surface complex formation is that the Cd–As(III) aqueous complex may initially form in solution and then adsorb on the TiO_2 surface as an assembly. To test such a premise, we used surface-enhanced Raman scattering (SERS) analysis because it provides an ultrasensitive probe of molecular structure. The lack of change in the As(III) characteristic peak at 726 cm^{-1} in the presence of Cd suggests that no Cd–As(III) complex was formed under the experimental conditions (see Figure S1 of the Supporting Information). Had aqueous Cd–As(III) complexes formed, the As(III) symmetry and the As–O bond energy would be changed accordingly, which should result in a peak shift or split.²⁴

Arsenic K-Edge EXAFS Analysis. EXAFS spectroscopy was employed to determine the As local coordination environment on TiO_2 in the presence of Cd. Figure 3 presents the k^3 -weighted As K-edge EXAFS spectra and corresponding Fourier transforms (FT) for the Cd–As(III) precipitate, As(III)– TiO_2 binary, and Cd–As(III)– TiO_2 ternary adsorption samples, and their fitting parameters are shown in Table S3 of the Supporting Information. The strong FT signal at $1.79 \text{ \AA}$ was resolved corresponding to three As–O single scattering (SS) paths in the first shell for all samples.

A multiple scattering (MS) contribution corresponding to the As–O–O paths within the AsO_3 pyramid was also

Figure 3. Observed (red circles) and fitted (black lines) (i) k^3 -weighted As K-edge EXAFS spectra and their corresponding (ii) FT magnitudes and (iii) real parts. The precipitation sample was prepared by reacting 20 mM As(III) and 30 mM Cd at pH 5 in 0.04 M NaClO_4 . The fitting parameters are shown in Table S3 of the Supporting Information, and the F -test results are shown in Table S4 of the Supporting Information. The binary As(III)– TiO_2 sample was prepared by mixing 2.0 mM As(III) with 1 g/L TiO_2 at pH 5.0 in 0.04 M NaClO_4 . Spectra $R = 0.5$ – 15.8 represent As(III) and Cd co-adsorption on TiO_2 at the As(III)/Cd ratios of 0.5, 1.0, 2.0, 5.0, and 15.8. The Cd concentration was 3.11 mM.

considered in the EXAFS fitting. Implementation of MS improved the fitting quality without adding extra variables because the MS parameters were constrained with the corresponding values of the As–O SS path.

In the Cd–As(III) precipitate sample (Figure 3), the second peak in the FT was attributed to an As–Cd SS path with a distance of $3.51 \text{ \AA}$. Fitting this As–Cd peak was completed in both k space and R space using a single As–Cd shell, resulting in a coordination number (CN) of 0.9. Low CN less than unity has been reported in several studies^{25–28} and may be attributable to a monodentate mononuclear As complex with hydrogen bonding to an adjacent singly coordinated OH group.²⁵ For example, 0.3 Fe atoms at $2.94 \text{ \AA}$ and 0.9 Fe atoms at $3.37 \text{ \AA}$ have been detected in a Fe(III)–As(III) precipitate.²⁶

In the binary As(III)– TiO_2 adsorption sample, the second FT peak was ascribed to As–Ti bonding at $3.35 \text{ \AA}$ with 1.8 Ti atoms. The As–Ti distance and CN indicate the formation of a bidentate binuclear corner-sharing As complex on the TiO_2 surface.²³

In the ternary Cd–As(III)– TiO_2 adsorption samples, only SS paths, such as As–Ti (see Figure S2 and Table S1 of the

Supporting Information) and As–Cd (see Figure S3 and Table S2 of the Supporting Information) were initially attempted to fit the second shell. However, these approaches resulted in unsatisfactory *R* factors (0.019–0.046). Then, mixed As–Ti and As–Cd paths were considered in the fit, and the model resolved 1.3–1.7 Ti atoms at the distance of 3.34–3.66 Å and 0.4–1.4 Cd atoms at the distance of 3.48–3.62 Å in the second shell (see Table S3 of the Supporting Information). Furthermore, the significance of adding an additional As–Cd path in ternary samples was justified using the *F* test.^{29,30} The *F*-test results show that the confidence level with the inclusion of the As–Cd SS path was 86.4–98.2% (see Tables S4, S6, and S8 of the Supporting Information), significantly higher than the required value at 67%,³⁰ confirming the appropriateness of adding this As–Cd with the As–Ti path. Thus, the existence of an As–Cd bond suggests the formation of a ternary surface complex in the Cd–As(III)–TiO₂ system. This ternary surface complex, corroborated by our density functional theory (DFT)-optimized surface configuration (see Figure S18 and Table S15 of the Supporting Information), is proposed to explain the synergistic enhanced removal of Cd and As(III) from the smelting wastewater (Figure 1).

Cadmium K-Edge EXAFS Analysis. The *k*³-weighted Cd K-edge EXAFS spectra and their FT as a function of the As(III) concentration are shown in Figure 4 and Table S9 of the

Figure 4. Observed (red circles) and fitted (black lines) (i) *k*³-weighted Cd K-edge EXAFS spectra for binary Cd–TiO₂ and ternary Cd–As(III)–TiO₂ systems and their corresponding (ii) FT magnitudes and (iii) real parts. The fitting parameters are shown in Table S9 of the Supporting Information, and the *F*-test results are shown in Table S10 of the Supporting Information. The Cd(OH)₂ sample was prepared by reacting 31 mM Cd in 0.04 M NaClO₄ solution at pH 12. The precipitation sample was prepared by reacting 20 mM As(III) and 30 mM Cd in 0.04 M NaClO₄ at pH 5. The binary Cd–TiO₂ sample was prepared by reacting 3.11 mM Cd(NO₃)₂ with 1 g/L TiO₂ at pH 5.0 in 0.04 M NaClO₄. Spectra *R* = 0.5 and 15.8 represent ternary Cd–As(III)–TiO₂ adsorption samples with the As(III)/Cd molar ratio of 0.5 and 15.8, respectively. The Cd concentration was 3.11 mM.

Supporting Information. The spectra of Cd(OH)₂ precipitation, Cd–As(III) precipitation, and binary Cd–TiO₂ adsorption samples were also collected as controls. In these samples, the first and strongest peak in the FT curve was contributed by six oxygen atoms at distances of 2.26–2.29 Å (Figure 4 and Table S9 of the Supporting Information). This Cd–O octahedral structure is in line with published results.^{31,32} In the precipitate samples, Cd–Cd paths were observed at the distance of 3.54 Å with 8.8 Cd atoms for Cd(OH)₂ and 3.61 Å

with 1.1 Cd atoms for Cd–As(III) precipitates, which were comparable with previous studies.^{33,34}

In the Cd–As(III)–TiO₂ samples, no Cd–Cd paths were detected, indicating that no Cd(OH)₂ or Cd–As(III) precipitates existed (Table S9 of the Supporting Information).³² When the As(III) concentration was low (*R* = 0.5), Cd bonded with 0.6 Ti and 0.5 As atoms, while in the presence of elevated concentrations of As(III) (*R* = 15.8), only 0.6 As atoms were resolved in the second shell around each Cd atom. The confidence levels for the existence of a Cd–Ti SS path in low As(III) concentration samples were 93.4–99.3%, as determined with the *F* test, whereas in the high As(III) concentration samples, the addition of a Cd–Ti SS path led to unacceptable *R* factors (see Table S10 of the Supporting Information). The absence of Ti in the second shell indicated that Cd could not be directly attached to TiO₂ at high As(III) levels. Thus, in comparison to As(III), Cd had a lower affinity for TiO₂ surfaces. The synergistic removal of Cd, therefore, could be mainly ascribed to the formation of a Cd–As(III)–TiO₂ ternary surface complex.

To investigate the effect of contact sequence on the surface configuration, As(III) (or Cd) was pre-adsorbed on TiO₂ before contact with Cd [or As(III)]. The EXAFS results in Figures S4–S6 and Tables S5–S12 of the Supporting Information show that, regardless of the adsorption sequence, As(III) had a higher priority for adsorption on TiO₂ than Cd. These contact sequence results and Cd K-edge EXAFS analysis consistently suggest that As(III) has a higher affinity for TiO₂, and the Cd–As(III)–TiO₂ ternary surface complex should be formed with the adsorbed As(III) as the bridging molecule.

The DFT-optimized clusters of Ti₂AsO₁₅H₁₉ and Ti₂AsO₁₆CdH₁₉ (see Figure S18 of the Supporting Information) were in agreement with the EXAFS results, as evidenced by their similar As–O, As–Ti, and As–Cd interatomic distances (see Table S15 of the Supporting Information). In accordance with our EXAFS results, the DFT-calculated configuration of the As(III) surface complex remained unchanged during the formation of the ternary surface complex.

Surface Complexation and Precipitation. The XRD analysis shows that a Cd–As(III) surface precipitate may form at high Cd and As(III) concentrations at elevated pH (see Figure S7–S11 of the Supporting Information). However, the surface precipitation may not be the primary mechanism for As(III) and Cd removal from wastewater. The SEM–EDXS analysis showed that the atomic As/Cd ratio (7.36) in the wastewater adsorption sample was much higher than that in the Cd–As(III) precipitate, which is about 1 (see Figures S12 and S13 and Table S13 of the Supporting Information). If surface precipitation was the dominate mechanism in As(III) and Cd removal from wastewater samples, the atomic As/Cd ratio should be close to the Cd–As precipitate. In the wastewater sample, the high atomic As/Cd ratio may be ascribed to the high As(III) adsorption density on TiO₂. The results indicate that adsorption and ternary surface complexation could be the major process for As(III) and Cd removal.

The formation of a surface ternary complex might be a prerequisite and starting point for the nucleation process of surface precipitation.³⁵ Thus, the Cd–As(III) surface complex and then precipitate could be formed on TiO₂, even with concentrations of Cd and As(III) appreciably lower than their supersaturation condition. The presence of TiO₂ greatly enhanced Cd and As(III) removal compared to precipitation

samples, especially at pH < 7 (see Figure S14 of the Supporting Information).

ATR–FTIR Study. *In situ* flow-cell ATR–FTIR was used to probe the surface reactions of As(III) and Cd on TiO₂. The FTIR spectra of As(III) and Cd pre-adsorption as a function of As(III)/Cd molar ratio (*R*) are shown for *R* = 0.5–15.8 in Figure 5, and the corresponding FTIR spectra in time series are

Figure 5. FTIR spectra of (i) As(III) and (ii) Cd pre-adsorbed TiO₂ film at pH 5.0 in 0.04 M NaCl solution. For As(III) pre-adsorption, the solution consisted of the As(III) concentration (0.67 mM) and various Cd concentrations (0.34–10.59 mM; *R* = 0.5–15.8). For Cd pre-adsorption, the solution consisted of the Cd concentration (0.44 mM) and various As(III) concentrations (0.22–6.95 mM; *R* = 0.5–15.8). The spectrum was equilibrated on TiO₂ film for 3 h, and the blank was taken after the 0.04 M NaCl solution flowed over the TiO₂ film for 3 h.

shown in Figure S15 of the Supporting Information. The details of peak assignments are shown in Figures S16 and S17 and Table S14 of the Supporting Information. The initial concentration of As(III) was 0.67 mM because the As(III) peak could not be detected below this concentration.

Two groups of peaks were detected in the range of 1200–900 and 900–750 cm^{−1} (Figure 5). The first group consisted of three peaks that are not directly associated with As–O vibrations: the mixed OH vibrations of TiOOH^{36,37} and AsOH (see Table S14 of the Supporting Information) at 1124 cm^{−1}, the Ti–O vibration at 947 cm^{−1},³⁷ and the unidentate carbonate vibration at 1072 cm^{−1}.^{38,39} CO₂ can be adsorbed on TiO₂ during drying in preparation of the film, and its surface structure changed from bidentate to unidentate upon As(III) adsorption. This structural change was evidenced by the negative peaks at 1685 and 1570 cm^{−1} because of the loss of bidentate carbonate^{38,39} and the positive peak at 1072 cm^{−1} from unidentate carbonate adsorption (see Figure S17 of the Supporting Information). Moreover, the intensity of this group of peaks increased as a function of the reaction time (see Figure S15 of the Supporting Information), confirming that these peaks were induced by As(III) adsorption.

The second group of peaks in the range of 900–750 cm^{−1} was directly associated with As–O vibrations. When As(III) was pre-adsorbed on TiO₂, a peak at 798 cm^{−1} and a shoulder at 770 cm^{−1} were observed because of the Ti–O–As stretching vibration (Figure 5i), which agrees well with previous

studies.^{40–42} In addition, a shoulder at 816 cm^{−1} was exhibited because of the asymmetric stretching of As(III)–OH.⁴³ In line with our FTIR results, our DFT calculations resolved the Ti–O–As stretching vibrations at 773 and 816 cm^{−1} and the uncomplexed As(III)–OH stretching vibration at 827 cm^{−1} (see Table S16 of the Supporting Information).

With the Cd solution flowed through over this As pre-adsorbed TiO₂ film, the intensity of the As(III)–OH peak at 816 cm^{−1} decreased and became imperceptible at high Cd concentrations (Figure 5i). At low Cd concentrations, i.e., *R* = 15.8–5.0, only part of the surface Ti–O–As complexes were associated with Cd, resulting in some dangling As(III)–OH bonds. With a further increase in the Cd concentration, i.e., *R* = 2.0–0.5, Cd may occupy almost all of the Ti–O–As complex sites, leading to the disappearance of the uncomplexed As(III)–OH vibration at 816 cm^{−1} (Figure 5i). This extinction of the As(III)–OH peak indicates that the initially formed As(III) bidentate binuclear surface complex changes its C_s symmetry²³ when transforming into the Ti–O–As–O–Cd ternary complex.^{13,14} Similar results have been reported when a ternary Ca and phosphate complex formed on TiO₂: the phosphate adsorption peak at about 1100 cm^{−1} disappeared with the addition of Ca, implying that the adsorbed phosphate symmetry changed from C_{2v} to C_{3v}.⁴⁴ In agreement with our FTIR results, our DFT calculations also justified the ternary complex formation with two notable observations. First, the As(III)–OH vibration at 816 cm^{−1} in the binary As(III)–TiO₂ cluster was not resolved in the Ti–O–As–O–Cd ternary complex (see Figure S18 and Table S16 of the Supporting Information). Second, two peaks at 773 and 790 cm^{−1}, corresponding to the experimental observations of bands at 770 and 798 cm^{−1} because of Ti–O–As vibrations, were resolved in the ternary complex (see Figure S18 and Table S16 of the Supporting Information). Moreover, the peak intensities at 770 and 798 cm^{−1} increased as a function of the Cd concentration (Figure 5i), which is in line with the enhanced As(III) adsorption in the presence of Cd (Figure 1ii). Increased inner-sphere adsorption peak intensities have been observed when SO₄/PO₄ and Cd ternary surface complexes formed on iron oxides.^{13,16}

When Cd was pre-adsorbed on TiO₂, a broad peak in the range of 750–1100 cm^{−1} was detected (Figure 5ii). With the introduction of As(III), vibrations of Ti–O–As (770 and 798 cm^{−1}) and As(III)–OH (816 cm^{−1}) were detected at *R* = 0.5–2.0, which agrees with As(III) pre-adsorption samples (Figure 5i). Interestingly, the broad peak because of Cd adsorption disappeared upon the uptake of As(III), indicating the desorption of Cd. With the further increase in the As(III) concentration, i.e., *R* = 5.0–15.8, the peak at 816 cm^{−1} because of As(III)–OH vibration was indiscernible, implying that this dangling bond was complexed with Cd to form the Ti–O–As–O–Cd ternary complex.

In combination with the EXAFS results, our FTIR and DFT results show that As(III) may be preferentially adsorbed on TiO₂ rather than Cd. At low As(III) concentrations, Cd–O–Ti and Cd–O–As bonds were formed, indicating that both binary and ternary surface complexes exist on the TiO₂ surface. Conversely, at high As(III) concentrations, only a Cd–O–As bond was detected by EXAFS and the As(III)–OH vibration disappeared, suggesting the formation of the ternary surface complex. This ternary surface complex could form over a wide As(III) and Cd concentration range to achieve their synergistic removal.

Surface Complexation Modeling and Ternary Surface Complex. The charge distribution multi-site complexation (CD-MUSIC) modeling is a powerful tool to interpret macroscopic observations under the constraint of molecular-level spectroscopic results. Thus, on the basis of our EXAFS and FTIR results, the bidentate binuclear complexes $\text{Ti}_2\text{O}_2\text{AsO}^{-5/3}$ and $\text{Ti}_2\text{O}_2\text{Cd}(\text{H}_2\text{O})_4^{-2/3}$ were used in CD-MUSIC to simulate binary As– TiO_2 and Cd– TiO_2 adsorption systems, respectively. In addition, a ternary surface complex, $\text{Ti}_2\text{O}_2\text{AsOCd}^{1/3}$, was included in CD-MUSIC for the ternary Cd–As(III)– TiO_2 system, as evidenced by the spectroscopic analysis (see Table S17 of the Supporting Information). With the inclusion of these surface species, our CD-MUSIC modeling results agreed well with the experimental adsorption edge curves and ζ potential shift (Figures 1 and 2) and confirmed that the synergistic uptake of Cd and As(III) was mainly due to the formation of the ternary surface complex. In agreement with our present study, ternary surface complexes have been successfully used to simulate the co-adsorption of Cu, Zn, Pb, and Cd with SO_4 on ferrihydrite, schwertmannite, and goethite.^{9,18}

Release of As and Cd from Binary and Ternary Surface Complexation Samples. The potentially different impacts of binary and ternary surface complexes on the mobility of Cd and As(III) motivated our further study using extraction experiments. The release of Cd and As(III) followed the pseudo-second-order kinetics model (see Figures S19 and S20 and Table S18 and S19 of the Supporting Information). The leaching results show that 0.2–5.5% Cd and 3.2–20.1% As(III) were released in the ternary Cd–As(III)– TiO_2 system, appreciably less than that in binary adsorption systems (2.3–15.5% Cd and 7.6–46.3% As; see Figure S19 of the Supporting Information). In the pH range of 2–12, the Cd–As(III)– TiO_2 ternary complex was more stable than binary As(III)– TiO_2 and Cd– TiO_2 complexes, as evidenced by its lower desorption ratio (see Figure S21 of the Supporting Information).

The formation of the ternary surface complex significantly increased Cd and As(III) adsorption capacities on metal oxides. With the enrichment of Cd and As(III) on TiO_2 , surface precipitates might be subsequently formed and the occurrence of metal–As precipitates would generally lower their mobility and bioavailability. This hypothesis has been supported by the Zn–As(V) co-precipitation on goethite samples with reduced leachability.¹¹ Similarly, the adsorption and surface precipitation of As(III) with Fe(II, III) could dramatically reduce the solubility of As(III) under anoxic conditions.²⁶

■ ASSOCIATED CONTENT

■ Supporting Information

Details of As speciation analysis, ζ potential measurement, SERS, EXAFS, ATR–FTIR, XRD, SEM–EDXS, surface complexation modeling, and quantum chemical calculation results, with additional figures and tables. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/es5062903.

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Notes

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■ REFERENCES

- (1) Nakajima, K.; Takeda, O.; Miki, T.; Matsubae, K.; Nagasaka, T. Thermodynamic analysis for the controllability of elements in the recycling process of metals. *Environ. Sci. Technol.* **2011**, *45*, 4929–4936.
- (2) Bian, Z. F.; Miao, X. X.; Lei, S. G.; Chen, S. E.; Wang, W. F.; Struthers, S. The challenges of reusing mining and mineral-processing wastes. *Science* **2012**, *337*, 702–703.
- (3) Wang, S.; Xu, L.; Zhao, Z.; Wang, S.; Jia, Y.; Wang, H.; Wang, X. Arsenic retention and remobilization in muddy sediments with high iron and sulfur contents from a heavily contaminated estuary in China. *Chem. Geol.* **2012**, *314*, 57–65.
- (4) Kumar, P. S.; Onnby, L.; Kirsebom, H. Arsenite adsorption on cryogels embedded with iron–aluminium double hydrous oxides: Possible polishing step for smelting wastewater? *J. Hazard. Mater.* **2013**, *250*, 469–476.
- (5) Bednar, A. J.; Garbarino, J. R.; Ranville, J. F.; Wildeman, T. R. Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples. *Environ. Sci. Technol.* **2002**, *36*, 2213–2218.
- (6) Luo, T.; Cui, J.; Hu, S.; Huang, Y.; Jing, C. Arsenic removal and recovery from copper smelting wastewater using TiO_2 . *Environ. Sci. Technol.* **2010**, *44*, 9094–9098.
- (7) Erskine, P.; Van der Ent, A.; Fletcher, A. Sustaining metal-loving plants in mining regions. *Science* **2012**, *337*, 1172–1173.
- (8) Beattie, D. A.; Chapelet, J. K.; Grafe, M.; Skinner, W. M.; Smith, E. In situ ATR FTIR studies of SO_4 adsorption on goethite in the presence of copper ions. *Environ. Sci. Technol.* **2008**, *42*, 9191–9196.
- (9) Swedlund, P. J.; Webster, J. G.; Miskelly, G. M. Goethite adsorption of Cu(II), Pb(II), Cd(II), and Zn(II) in the presence of sulfate: Properties of the ternary complex. *Geochim. Cosmochim. Acta* **2009**, *73*, 1548–1562.
- (10) Collins, C. R.; Ragnarsdottir, K. V.; Sherman, D. M. Effect of inorganic and organic ligands on the mechanism of cadmium sorption to goethite. *Geochim. Cosmochim. Acta* **1999**, *63*, 2989–3002.
- (11) Grafe, M.; Nachtgaal, M.; Sparks, D. L. Formation of metal–arsenate precipitates at the goethite–water interface. *Environ. Sci. Technol.* **2004**, *38*, 6561–670.
- (12) Ler, A.; Stanforth, R. Evidence for surface precipitation of phosphate on goethite. *Environ. Sci. Technol.* **2003**, *37*, 2694–2700.
- (13) Elzinga, E. J.; Kretzschmar, R. In situ ATR–FTIR spectroscopic analysis of the co-adsorption of orthophosphate and Cd(II) onto hematite. *Geochim. Cosmochim. Acta* **2013**, *117*, 53–64.
- (14) Elzinga, E. J.; Peak, D.; Sparks, D. L. Spectroscopic studies of Pb(II)–sulfate interactions at the goethite–water interface. *Geochim. Cosmochim. Acta* **2001**, *65*, 2219–2230.
- (15) Grafe, M.; Beattie, D. A.; Smith, E.; Skinner, W. M.; Singh, B. Copper and arsenate co-sorption at the mineral–water interfaces of goethite and jarosite. *J. Colloid Interface Sci.* **2008**, *322*, 399–413.
- (16) Zhang, G. Y.; Peak, D. Studies of Cd(II)–sulfate interactions at the goethite–water interface by ATR–FTIR spectroscopy. *Geochim. Cosmochim. Acta* **2007**, *71*, 2158–2169.

- (17) Swedlund, P. J.; Webster, J. G.; Miskelly, G. M. The effect of SO_4 on the ferrihydrite adsorption of Co, Pb and Cd: Ternary complexes and site heterogeneity. *Appl. Geochem.* **2003**, *18*, 1671–1689.
- (18) Swedlund, P. J.; Webster, J. G. Cu and Zn ternary surface complex formation with SO_4 on ferrihydrite and schwertmannite. *Appl. Geochem.* **2001**, *16*, 503–511.
- (19) Yang, W. C.; Kan, A. T.; Chen, W.; Tomson, M. B. pH-dependent effect of zinc on arsenic adsorption to magnetite nanoparticles. *Water Res.* **2010**, *44*, 5693–5701.
- (20) Cui, J.; Shi, J.; Jiang, G.; Jing, C. Arsenic levels and speciation from ingestion exposures to biomarkers in Shanxi, China: Implications for human health. *Environ. Sci. Technol.* **2013**, *47*, 5419–5424.
- (21) Jiang, W.; Lv, J.; Luo, L.; Yang, K.; Lin, Y.; Hu, F.; Zhang, J.; Zhang, S. Arsenate and cadmium co-adsorption and co-precipitation on goethite. *J. Hazard. Mater.* **2013**, *262*, 55–63.
- (22) Meng, X.; Bang, S.; Korfiatis, G. P. Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. *Water Res.* **2000**, *34*, 1255–1261.
- (23) Pena, M.; Meng, X. G.; Korfiatis, G. P.; Jing, C. Y. Adsorption mechanism of arsenic on nanocrystalline titanium dioxide. *Environ. Sci. Technol.* **2006**, *40*, 1257–1262.
- (24) Du, J.; Cui, J.; Jing, C. Rapid *in situ* identification of arsenic species using a portable $\text{Fe}_3\text{O}_4/\text{Ag}$ SERS sensor. *Chem. Commun.* **2014**, *50*, 347–349.
- (25) Mikutta, C.; Kretzschmar, R. Spectroscopic evidence for ternary complex formation between arsenate and ferric iron complexes of humic substances. *Environ. Sci. Technol.* **2011**, *45*, 9550–9557.
- (26) Wang, Y.; Morin, G.; Ona-Nguema, G.; Menguy, N.; Juillot, F.; Aubry, E.; Guyot, F.; Calas, G.; Brown, G. E., Jr. Arsenite sorption at the magnetite–water interface during aqueous precipitation of magnetite: EXAFS evidence for a new arsenite surface complex. *Geochim. Cosmochim. Acta* **2008**, *72*, 2573–2586.
- (27) Ona-Nguema, G.; Morin, G.; Juillot, F.; Calas, G.; Brown, G. E. EXAFS analysis of arsenite adsorption onto two-line ferrihydrite, hematite, goethite, and lepidocrocite. *Environ. Sci. Technol.* **2005**, *39*, 9147–9155.
- (28) Morin, G.; Wang, Y.; Ona-Nguema, G.; Juillot, F.; Calas, G.; Menguy, N.; Aubry, E.; Bargar, J. R.; Brown, G. E., Jr. EXAFS and HRTEM evidence for As(III)-containing surface precipitates on nanocrystalline magnetite: Implications for As sequestration. *Langmuir* **2009**, *25*, 9119–9128.
- (29) Klementev, K. V. Statistical evaluations in fitting problems. *J. Synchrotron Radiat.* **2001**, *8*, 270–272.
- (30) Downward, L.; Booth, C. H.; Lukens, W. W.; Bridges, F. A variation of the F-test for determining statistical relevance of particular parameters in EXAFS fits. In *X-Ray Absorption Fine Structure—XAFS13: 13th International Conference: Stanford, California, USA, 9–14 July, 2006*; Hedman, B., Painetta, P., Eds.; American Institute of Physics: College Park, MD, 2007; Vol. 882, pp 129–131.
- (31) Ramstedt, M.; Norgren, C.; Shchukarev, A.; Sjöberg, S.; Persson, P. Co-adsorption of cadmium(II) and glyphosate at the water–manganite ($\gamma\text{-MnOOH}$) interface. *J. Colloid Interface Sci.* **2005**, *285*, 493–501.
- (32) Vasconcelos, I. F.; Haack, E. A.; Maurice, P. A.; Bunker, B. A. EXAFS analysis of cadmium(II) adsorption to kaolinite. *Chem. Geol.* **2008**, *249*, 237–249.
- (33) Randall, S. R.; Sherman, D. M.; Ragnarsdottir, K. V.; Collins, C. R. The mechanism of cadmium surface complexation on iron oxyhydroxide minerals. *Geochim. Cosmochim. Acta* **1999**, *63*, 2971–2987.
- (34) Bochatay, L.; Persson, P.; Sjöberg, S. Metal ion coordination at the water–manganite ($\gamma\text{-MnOOH}$) interface I. An EXAFS study of cadmium(II). *J. Colloid Interface Sci.* **2000**, *229*, 584–592.
- (35) Stumm, W. *Chemistry of the Solid–Water Interface*; Wiley-Interscience: New York, 1999.
- (36) Nakamura, R.; Imanishi, A.; Murakoshi, K.; Nakato, Y. In situ FTIR studies of primary intermediates of photocatalytic reactions on nanocrystalline TiO_2 films in contact with aqueous solutions. *J. Am. Chem. Soc.* **2003**, *125*, 7443–7450.
- (37) Roddick-Lanzilotta, A. D.; Connor, P. A.; McQuillan, A. J. An in situ infrared spectroscopic study of the adsorption of lysine to TiO_2 from an aqueous solution. *Langmuir* **1998**, *14*, 6479–6484.
- (38) Liao, L. F.; Lien, C. F.; Shieh, D. L.; Chen, M. T.; Lin, J. L. FTIR study of adsorption and photoassisted oxygen isotopic exchange of carbon monoxide, carbon dioxide, carbonate, and formate on TiO_2 . *J. Phys. Chem. B* **2002**, *106*, 11240–11245.
- (39) Wijnja, H.; Schulthess, C. P. Carbonate adsorption mechanism on goethite studied with ATR–FTIR, DRIFT, and proton coadsorption measurements. *Soil Sci. Soc. Am. J.* **2001**, *65*, 324–330.
- (40) Parikh, S. J.; Lafferty, B. J.; Sparks, D. L. An ATR–FTIR spectroscopic approach for measuring rapid kinetics at the mineral/water interface. *J. Colloid Interface Sci.* **2008**, *320*, 177–185.
- (41) Voegelin, A.; Hug, S. J. Catalyzed oxidation of arsenic(III) by hydrogen peroxide on the surface of ferrihydrite: An in situ ATR–FTIR study. *Environ. Sci. Technol.* **2003**, *37*, 972–978.
- (42) Bhandari, N.; Reeder, R. J.; Strongin, D. R. Photoinduced oxidation of arsenite to arsenate on ferrihydrite. *Environ. Sci. Technol.* **2011**, *45*, 2783–2789.
- (43) Zheng, Y.-M.; Yu, L.; Wu, D.; Chen, J. P. Removal of arsenite from aqueous solution by a zirconia nanoparticle. *Chem. Eng. J.* **2012**, *188*, 15–22.
- (44) Ronson, T. K.; McQuillan, A. J. Infrared spectroscopic study of calcium and phosphate ion coadsorption and of brushite crystallization on TiO_2 . *Langmuir* **2002**, *18*, 5019–5022.