Arsenic Adsorption on Lanthanum-Impregnated Activated Alumina: Spectroscopic and DFT Study

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ABSTRACT: Rare earth-modified adsorbents (REMAs) have been widely used to remove oxyanion pollutants from water, including arsenic (As). However, the molecular-level structural information and reactions at the liquid/solid interface are still murky, which limits the design of applicable REMAs. Herein, a lanthanum-impregnated activated alumina (LAA) was synthesized as a representative REMA, and its As uptake mechanisms were explored using multiple complementary characterization techniques. Our adsorption experiments showed that LAA exhibited 2–3 times higher As adsorption capacity than AA. In contrast to the bidentate configuration formed on most metal oxide surfaces, our EXAFS and DFT results suggest that As(III) and As(V) form monodentate surface complexes on LAA through As-O-La coordinative bonding. In situ flow cell ATR-FTIR observed a strong dependence of As-O peak positions on pH, which could be interpreted as the change in the fractions of As(V) surface complexes with zero- to double-protonation on LAA, AA, and LaOOH. As(V) on LAA existed as singly and doubly protonated surface species, and the pH of transition from double to single protonation (∼5.8) was lower than that for its soluble counterpart (6.97). The surface reaction and structural configuration were incorporated in a CD-MUSIC model to satisfactorily predict macroscopic As adsorption behaviors. The insights gained from the molecular-level reactions shed light on the design and application of REMAs in environmental remediation for As and its structural analogues.

KEYWORDS: adsorption, arsenic, coordination modes, surface chemistry, lanthanum

INTRODUCTION

Adsorption using hybrid materials has been demonstrated to be an effective technique to remove hazardous materials from water due to its easy operation, low cost, and high efficiency.1−3 Recent advances in hybrid materials highlight the fact that rare earth-modified adsorbents (REMAs) may substantially enhance the removal of oxyanions, including arsenic (As), phosphate, selenite, and chromate (Table S1).1−3 Although their promising performance has been reported in many publications, the mechanism of oxyanion adsorption on REMAs is generalized as ligand exchange based on infrared (IR) and X-ray photoelectron spectroscopy (XPS) studies.4−7 This simplified model lacks molecular-level structural information on the coordination geometry and protonation of the surface species, which is fundamental to be able to design and fabricate REMAs and predict their performance.

For exploration of the molecular-level surface reaction mechanisms, multiple complementary spectroscopic techniques should be employed. For example, extended X-ray adsorption fine structure (EXAFS) and Fourier transform infrared (FTIR) spectroscopies have been used to explain why As(V) adsorption could be enhanced on an iron−cerium (Fe−Ce) bimetal oxide REMA.8,9 Their results show that As(V) is covalently bonded with Fe instead of Ce on REMA.8 The addition of Ce in iron oxides, alternatively, contributes to the destruction of the magnetite crystal phase and the formation of an amorphous Fe−Ce structure.6 However, this explanation had difficulty interpreting the enhanced As removal efficacy of REMAs without iron oxides.7,10−12

Lanthanum (La)-impregnated activated alumina (LAA), an example of a REMA, has demonstrated advantages over activated alumina (AA) in F adsorption efficiency, applicable pH range, and Al leachability.13 Meanwhile, a simple physical mixing of lanthanum oxide with AA was found to substantially enhance the As adsorption capacity.14 These observations promote the hypothesis that the rare earth elements in REMAs, such as La in LAA, may provide additional adsorption sites with different adsorption mechanisms from those of its supporting materials.

The purpose of this study was to investigate the molecular-level adsorption structure and reaction mechanism of As on LAA. Density function theory (DFT) calculations, EXAFS, and in situ flow cell attenuated total reflectance (ATR) FTIR spectroscopy were used. The surface reactions were incorpo-
rated in the charge distribution multisite surface complexation (CD-MUSIC) model to simulate the As adsorption behaviors. The results of our work shed new light on the interaction mechanisms of As and its structural analogues with REMAs, which is fundamental to be able to design and implement REMAs for environmental remediation.

■ MATERIALS AND METHOD

Materials. Stock solutions of 1,000 mg/L As(III) and As(V) were prepared by dissolving 1.733 g of NaAsO₂ and 3.653 g of Na₃AsO₄·12H₂O in 1 L of deionized (DI) water (18.2 MΩ, Milli-Q), respectively. The La stock solution was prepared by dissolving 19.485 g of analytical grade La(NO₃)₃·6H₂O in 50 mL of DI water, and the pH was adjusted to 6.0 using NH₃·H₂O. All regents were purchased from Sinopharm, China. Granular activated alumina (AA) was used, and the infrared spectra were collected using 256 scans per ATR crystal with 45° beveled faces (infrared angle of incidence, θ) was 45°. The EXAFS data analysis was performed using the ATHENA and ARTEMIS programs in the Demeter computer package. The analysis procedure was similar to our previous studies and is detailed in the Supporting Information.

Preparation of LAA and LaOOH. LAA and lanthanum oxyhydroxide (LaOOH) were prepared using the method described in our previous report. Briefly, to impregnate La on AA, a mixture of 10 mL of La stock solution and 14.5 g of AA was sonicated for 4 h. The solid was separated, dried at 328 K, and then calcined at 573 K for 4 h. The obtained material was cooled, it was washed with DI water until the conductivity of the wash water was below 100 μS/cm. The impregnation process was repeated five times. LaOOH was synthesized using the same process in the absence of AA.

Adsorption Experiments. Batch adsorption experiments were conducted to compare the efficiency of the adsorbents. In a typical experiment, 0.1 g samples of adsorbents were mixed with 100 mL of As solution at desired pH values. The samples were mixed on a rotary shaker at 200 rpm for 298 K for 24 h and then centrifuged and filtered through a 0.45 μm membrane filter for analysis. A background electrolyte of 0.01 mol/L NaCl was used in the experiment. HCl and NaOH were used to adjust the pH.

The As(III) and As(V) adsorption isotherms on AA and LAA were investigated at pH 7. The adsorbent concentration was fixed at 1 g/L, and the As(III) and As(V) concentrations were increased to 100 and 300 mg/L, respectively. The adsorption kinetics on AA and LAA were also studied at pH 7 in 1 L of 0.01 mol/L NaCl solution with 10 mg/L of As(V) or 5 mg/L of As(III). The As concentration and speciation were determined by high performance liquid chromatography atomic fluorescence spectrometry (HPLC-AFS, Jitian, China).

Zeta (ζ) Potential Measurements. The ζ potential was measured using a Zetasizer Nano ZS (Malvern Instrument Ltd., UK). All experiments were performed under N₂ atmosphere to eliminate CO₂ from the system. The pH of the suspension containing 0.1 g/L of adsorbent in 0.01 mol/L NaCl was adjusted from 6.5 to 12.0 using 0.1 mol/L NaOH and HCl solutions. Suspension samples were placed on a rotating shaker for 24 h, and the final pH was measured. The reported ζ potential values were the average of three measurements and are shown in Figure S1. The results showed that the points of the zero charge (PZC) for AA, LAA, and LaOOH were 7.9, 8.9, and 9.1, respectively.

XAS Analysis. The EXAFS samples were prepared using batch adsorption experiments with 100 mg/L of As(III) or 300 mg/L of As(V) in the presence of 1 g/L of AA, LAA, or LaOOH in 0.01 mol/L NaCl solution at pH 7. The As K-edge spectra were collected at beamline 01C1 at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. An energy range of −200 to 1000 eV from the K-edge was used to acquire the spectra with a standard Lytle detector at cryogenic temperatures (<20 K) using a helium cryostat to prevent beam-induced oxidation. Three to six scans were collected from each sample, inspected for overall quality, and averaged to improve the signal/noise ratio. The EXAFS data analysis was performed using the ATHENA and ARTEMIS programs in the Demeter computer package. The analysis procedure was similar to our previous studies and is detailed in the Supporting Information.

In Situ Flow Cell ATR-FTIR Study. The in situ flow cell ATR-FTIR measurements were performed using a Thermo-Nicolet Nexus 6700 FTIR spectrometer equipped with a horizontal attenuated total reflectance (HATR) cell (PIKE Tech) and a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector. A multibounce ZnSe ATR crystal with 45° beveled faces (infrared angle of incidence, θ) was used, and the infrared spectra were collected using 256 scans per spectrum at a resolution of 4 cm⁻¹.

The collection and treatment for the spectra of As(V) adsorption on AA, LAA, and LaOOH were similar to those described in our previous publications. Briefly, the adsorbent film was deposited on the ZnSe crystal by applying 500 μL of the adsorbent suspension (2.5 g/L) and drying at room temperature. Prior to use, the film was rinsed with DI water to remove loosely deposited particles. A 0.01 mol/L NaCl solution at a predetermined pH was passed through the flow cell at a
rate of 0.5 mL/min until there was no further change in the IR spectra. A background spectrum was collected that consisted of the absorbance of the ZnSe crystal and deposited adsorbents. Then, a 10 mg/L As(V) in 0.01 mol/L NaCl solution was passed through the flow cell at the designed pH values. Spectra were recorded as a function of time until the adsorption reached equilibrium (at least 4 h). All samples were purged with N₂ in the dark during the spectra collection. The second-order derivatives were used to locate the peak position in the curve fitting. The peak positions obtained from second derivatives and direct curve fitting were the same within a 5 cm⁻¹ difference.

**DFT Calculations.** The geometry optimization, IR frequency, and adsorption energy of the As surface complexes were calculated using the Gaussian 09 program with B3LYP hybrid density function theory (DFT). The 6-311+G (d, p) basis set for As, H, and O was used with a scale factor of 0.967, and the LanL2DZ basis set was employed for La with a scale factor of 0.961. An edge-sharing seven-coordinated hexagonal cluster was used to simulate neutral La₂(OH)₆(OH₂)₆·4(H₂O) and positively charged La₂(OH)₅(OH₂)₇·4(H₂O) surfaces. The solvation effect was considered by using an implicit continuum model (IEFPCM) combined with 8 H₂O molecules around As(V) and As(III) and 4 H₂O molecules around surface complexes.

**RESULTS AND DISCUSSION**

**Adsorption Kinetics and Isotherms.** The adsorption of As(III) and As(V) on AA and LAA followed pseudo-second order kinetics ($R^2 > 0.98$, Figure 1a, b), and the fitting parameters are shown in Figure S2 and Table S2. The adsorption isotherms conformed to the Langmuir model with parameters shown in the inset of Figure 1c and d. The material’s specific surface area was determined by the Brunauer–Emmett–Teller (BET) equation as described in our previous report. The results showed that the BET surface area of LAA (192 m²/g) is slightly smaller than that of AA (235 m²/g). Furthermore, LAA exhibited 2–3 times higher As adsorption capacity than AA (Figure 1). Thus, the specific adsorptions for As(V) and As(III) on LAA (0.137 and 0.048 mg/m², respectively) are higher than those on AA (0.039 and 0.021 mg/m², respectively). However, mechanistic information cannot be explicitly derived from the above macroscopic models. Therefore, spectroscopic techniques were used to decipher the molecular-level interaction mechanisms of As and LAA.

**EXAFS Characterization.** To explore the role of Al- and La-oxides in LAA for As removal, we employed EXAFS to characterize the local coordination environment of As(III) and As(V) adsorption on AA, LAA, and LaOOH. As shown in Figure 2 and Tables S3 and S4, the first FT peak in the As K-edge EXAFS spectra could be fitted with four O atoms at 1.69 Å for As(V) samples and three O atoms at 1.77 Å for As(III) samples, which agrees well with previous reports. The second FT peak for the As(V)-AA sample resulted from 1.5 Al atoms at 3.17 Å, and for the As(III)-AA sample, 1.4 Al atoms at 3.23 Å. This observation is in accordance with the reported bidentate binuclear configurations for As(III) and As(V) adsorption on AA. Though in a bidentate binuclear configuration, the fact that the coordination numbers for the As−Al shell were lower than two (1.4−1.5) could be attributed to the weak backscattering from the Al element. For the As-LaOOH samples, conversely, the second FT peak was ascribed to As−La...
bonding at 3.34 Å with 1.0 La atoms for As(V), and 3.39 Å with 0.9 La atoms around As(III), suggesting the formation of a monodentate surface complex. Furthermore, this monodentate configuration did not change in the pH range 5−9 (Figure S3, Table S5). Notably, the second FT peaks of the As-LAA samples were observed at the same position as those of As-LaOOH (ΔR ≈ 3.2 Å, Figure 2b). This match in terms of atomic distances implies that the second shell for As-LAA samples was La rather than Al. The As−La path was thus used to fit the second FT peak, and the results show that 0.7−1.0 La atoms existed at 3.34−3.42 Å in a monodentate surface configuration (Figure 2, Tables S3 and S4). For confirmation that Al would not contribute to the second FT peak, the significance of adding an additional As−Al path was evaluated using the F-test. The F-test results indicate that the confidence level with the inclusion of the As−Al path in As(V)-LAA (33.3%) and As(III)-LAA (48.7%) samples was lower than the required 67% (Figure S4, Tables S6 and S7), justifying the conclusion that Al does not exist in the second shell of As-LAA samples.

Figure 4. Observed (circles) and curve fitting results (lines) of in situ ATR-FTIR spectra for As(V) surface complexes on LAA (left column), LaOOH (middle), and AA (right column) as a function of pH. The panel in the bottom right shows the change of As(V) surface species on LAA with fitting results listed in Tables S8−S10. Band positions (cm⁻¹) are labeled in the same color as the corresponding lines. IR spectra of As(V) on AA at pH 9 are absent due to its low signal/noise ratio with low As(V) loads. As(V) concentration = 10 mg/L; ion strength = 0.01 mol/L NaCl; room temperature.
respectively (Table S8). These values are in reasonable agreement with our previous EXAFS characterization for the average La–La distance (3.92 Å) on LAA.\textsuperscript{13} The DFT-calculated interatomic distances of As(V)-O (1.72 Å), As(III)-O (1.82 Å), As(V)-La (3.39 Å), and As(III)-La (3.44 Å) were within 0.05 Å difference of those obtained from the EXAFS results (Tables S3, S4, and S8).

**In Situ ATR-FTIR.** A major limitation in the EXAFS analysis, however, is its inability to identify the protonation information on As surface complexes. In fact, this structural information is crucial to simulate and predict the As adsorption behaviors.\textsuperscript{37} For elucidation of the protonation of As(V) surface complexes, in situ flow-cell ATR-FTIR was employed to take advantage of its sensitive response to the change in interfacial configuration, especially for protonated oxyanions.\textsuperscript{8–40}

The ATR-FTIR spectra clearly resolved the characteristic peaks in the As-O fingerprint range (700–1000 cm\(^{-1}\)) upon As(V) adsorption on AA, LAA, and LaOOH at pH 5–9 (Figure 4 and Figure S5). In agreement with the pH dependence of the As(V) adsorption capacity,\textsuperscript{37} the peak intensity decreased with increasing pH. Furthermore, the peak intensity on LAA was appreciably higher than that on AA in accordance with our adsorption isotherm results (Figure 1c, d).

Significant peak shifts were observed on LAA and AA when the pH was increased from 5 to 9 (Figure 4 and Figure S5). For example, upon As(V) adsorption on LAA, the highest peak intensity As-O band shifted from 839 cm\(^{-1}\) at pH 5 to 831 cm\(^{-1}\) at pH 8 and further to 829 cm\(^{-1}\) at pH 9. Conversely, when As(V) was adsorbed on AA, with the increase in pH, the highest As-O peak at 842 cm\(^{-1}\) at pH 5 shifted to 860 cm\(^{-1}\) at pH 6, moved back to a low frequency (835 cm\(^{-1}\)) at pH 7, and was even lower at 792 cm\(^{-1}\) at pH 8.

Generally, the peak shifts of adsorbed oxyanions on metal oxides can be mainly attributed to two structural changes: denticity and protonation.\textsuperscript{30,41} The As denticity on La- and Al oxides was not changed, as evidenced by our EXAFS analysis (Figure S3, Table S5) and previous reports.\textsuperscript{35} Thus, the IR peak shift as a function of pH should be the result of variations in the protonation of As(V) surface complexes.

Interestingly, an IR peak shift, such as that observed in this and Persson’s study,\textsuperscript{30} could be interpreted as the change in relative intensity of each characteristic band. Each band in the As-O fingerprint range was resolved using curve fitting and DFT calculations. The curve fitting results using the second-order derivatives are shown in Figure 4 and Table S9–S11. The changes in protonation of As(V) surface complexes as a function of pH on LAA, LaOOH, and AA are discussed in detail in the following three sections.

**As(V) Protonation on LAA.** The curve fitting results show that four modes at 783, 801, 837, and 869 cm\(^{-1}\) were observed at pH 5–9 upon As(V) adsorption on LAA (Figure 4). To the best of our knowledge, no articles have reported the characteristic peak positions for As(V) adsorption on La-(hydro)oxides. Hence, to assign these modes, the IR frequencies of optimized As surface structures were further predicted with DFT calculations (Figure 3). The DFT calculated results agreed well with our experimental IR frequencies, which are presented in Table S9.

The DFT-calculated results showed that the modes at 783 and 837 cm\(^{-1}\) could be ascribed to the symmetric and asymmetric vibrations, respectively, of the uncomplexed As-O band in the singly protonated As(V) surface complex (Table S9). Conversely, for doubly protonated As(V) surface species, the symmetric (801 cm\(^{-1}\)) and asymmetric (869 cm\(^{-1}\)) vibrations exhibited a higher frequency than for the singly protonated ones. This observation is coincident with the change in As-O bond lengths from 1.68 to 1.69 to 1.66 Å as the protonation changed from double to single (Table S8). Such shortened bond lengths imply increased As-O bond strength, which increased the IR peak frequencies from 783 to 801 cm\(^{-1}\) and from 837 to 869 cm\(^{-1}\).

For quantitative analysis of the protonation of As(V) surface species on LAA, the ratio of each peak area to the total area within the fingerprint range (700–1000 cm\(^{-1}\)) is summarized in Table S9. Interestingly, the increase in singly protonated surface species with increasing pH was coincident with the change in the ionization fractions of dissolved HAsO\(_4^–\) species. Moreover, the pKa of the transition from doubly to singly protonated As(V) surface species (~5.8, Figure 4) was lower than for its soluble counterpart (pKa = 6.97). A similar trend as a function of pH has been reported for phosphate surface complexes.\textsuperscript{38} In addition, the DFT-calculated adsorption energy confirmed the preference for singly (~482.4 to ~233.1 kJ/mol) over doubly (32.3 to 36.9 kJ/mol) protonated surface species (Tables S12 and S13).

**As(V) Protonation on LaOOH.** As(V) protonation on LaOOH at pH 5–9 was the same as on LAA because they share the same surface configurations (Figures 3 and 4). Notably, an additional mode at 748 cm\(^{-1}\) was observed upon As(V) adsorption on LaOOH at pH 9. This mode could be attributed to the symmetric vibration of the La-complexed As-O band (As-OLa) upon HAsO\(_4^–\) adsorption, which was confirmed by DFT calculations (Tables S9 and S10). In contrast, this mode was not observed on LAA due to the low As load on LAA and the weaker strength of the metal-complexed As-O band than the uncomplexed one.\textsuperscript{38} In addition, the pKa for As surface complexes on LaOOH was lower than that on LAA because LaOOH, with more positive charge (Figure S1), favors the adsorption of negatively charged As species.

**As(V) Protonation on AA.** The FTIR spectra for As(V) adsorption on AA at pH 5–8 are shown in the right column of Figure 4. The bands at 877, 837, and 808 cm\(^{-1}\) were resolved at pH 5. With the increase in pH, the peak intensity at 808 cm\(^{-1}\) diminished and finally disappeared at pH 8. Instead, two new bands at 789 and 755 cm\(^{-1}\) appeared.

The assignments for As-O bands observed in our study are listed in Table S11. Asymmetric As-O stretching vibrations (837 cm\(^{-1}\)) exhibited a higher frequency than the symmetric As-O band (789 cm\(^{-1}\)). The band at 755 cm\(^{-1}\) was assigned to As-OAl stretching vibrations in unprotonated As(V) surface species, in agreement with previous reports (740–750 cm\(^{-1}\)).\textsuperscript{38,43} Furthermore, because a proton has a stronger interaction with the As-O bond than a metal, the As-O atomic distance in As-OH is generally longer than in As-OAl. Consequently, the As-OAl band in doubly protonated As surface species (808 cm\(^{-1}\)) resulted in a higher frequency than As-OH (<770 cm\(^{-1}\)).\textsuperscript{38,43} In concordance with our results, the symmetric As-OFe band has been reported at 802 cm\(^{-1}\) in a previous study.\textsuperscript{43} Notably, the As-OAl with double protonation (808 cm\(^{-1}\)) exhibited a higher frequency than that for unprotonation (755 cm\(^{-1}\)). The two protons interact strongly with oxygen as evidenced by a longer As-O atomic distance in As-OH (1.75–1.77 Å) than in As-O (1.66 Å, Table S8). Such an interaction, in turn, could move the As atom in the H\(_2\)O\(_2\)-As-O\(_2\)Al\(_2\) surface complex closer to the oxygen atoms bound to Al, and result in a higher frequency band at 808 cm\(^{-1}\).
Analysis of the change in ratios of each band (Table S11) illustrated three distinct patterns as the pH increased from 5 to 8: (1) an increase of bands at 837, 789, and 755 cm$^{-1}$ due to unprotonated surface species, (2) a decreased band at 808 cm$^{-1}$ due to doubly protonated surface species, and (3) the band at 877 cm$^{-1}$ due to singly protonated surface species increased its ratio from pH 5 to 6 and then decreased from pH 6 to 8.

The As-O band of singly protonated As(V) surface species showed a higher frequency (877 cm$^{-1}$) than that of un- (837 cm$^{-1}$) and doubly protonated (808 cm$^{-1}$) As(V) surface species. When unprotonated species change to single-protonation, one of the two uncomplexed As-O bonds becomes As-OH. The addition of a proton moves more electron density to the other As-O bond and thus enhances the As-O bond strength.$^{35,36}$ Conversely, as the surface As(V) species changes to the other As-O bond and thus enhances the As-O bond species. When unprotonated species change to single-protonation, no uncomplexed As-O bond exists. Under this condition, protonated or metal-complexed As-O bonds (As-OM) would be predominant, resulting in a lower band position than As-O.$^{38,43}$ Thus, the As-O band for doubly protonated As(V) showed a lower frequency than those of un- and singly protonated As(V) surface complexes (Figure 4).

The bidendate binuclear As(V) surface complexes occurred with no, single, and double protonation on AA. Table S10 summarizes the pK$_a$ for these surface complexes. Interestingly, these pK$_a$ values were much lower than those of their dissolved As(V) counterparts (Figure S6). In a comparison of the pK$_a$ values on different surfaces, we found that complexes on AA with a bidentate configuration resulted in a lower value (<5) than that on LAA with a monodentate structure (~8.8). The observation suggests that deprotonation may readily occur upon the formation of bidentate complexes.

Predicting Macroscopic Adsorption Behaviors under Microscopic Constraints. The adsorption configurations and reactions derived from our spectroscopic and DFT studies were incorporated in surface complexation modeling to predict the macroscopic adsorption behaviors of As on REMAs. The As(V) and As(III) adsorption isotherms on LAA and AA could be well-predicted with the CD-MUSIC model (Figure S7, Table S14 and S15). The CD-MUSIC fitting results showed that the logK for HAsO$_4^{2-}$ adsorption on LAA (26.4, Table S14) was higher than that for H$_2$AsO$_4^{2-}$ (24.3) at pH 7, indicating preferential HAsO$_4^{2-}$ adsorption over H$_2$AsO$_4^{2-}$ in agreement with our IR and DFT results.

CONCLUSIONS

In conclusion, multiple complementary spectroscopic techniques and DFT calculations provide evidence for monodentate As surface complexes on LAA, a rare earth-modified adsorbent (REMA). The monodentate configurations may result in a higher site density on REMA surfaces than on bidentate structures for anion adsorption and thus could increase the anion removal capacity. On REMA surfaces, As preferentially adsorbs on rare earth metal oxides rather than the supporting metal oxides. In particular, As(V) on REMAs exhibits singly or doubly protonated configurations. The molecular-level mechanisms should be incorporated to model and predict the adsorption behaviors of oxyanions on REMAs, which is essential in the design and application of these materials.

REFERENCES
