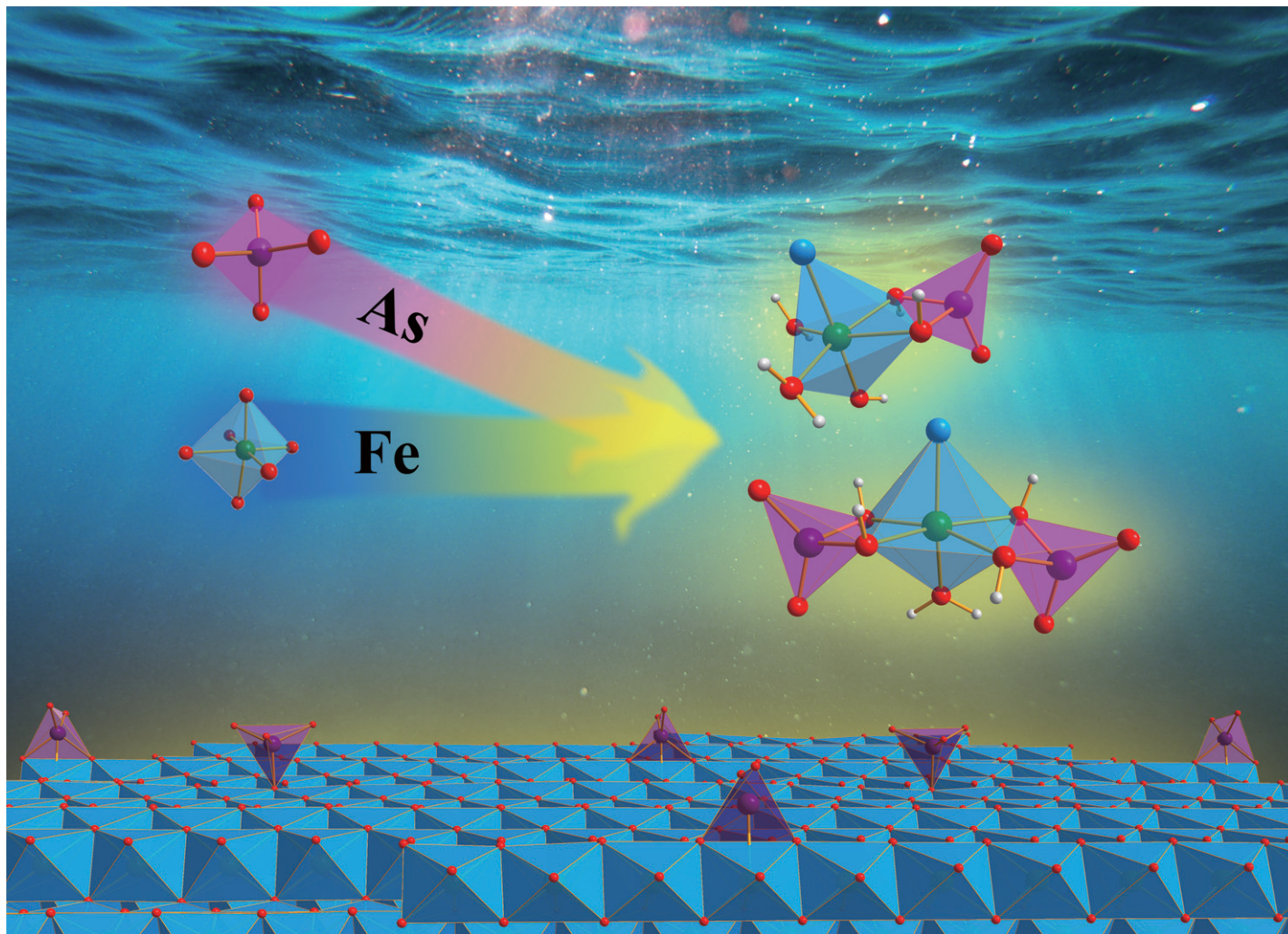




Featuring work from Prof. Xiaoguang Meng and Dr. Qiantao Shi at the Center for Environmental Systems, Stevens Institute of Technology.

Formation of Fe(III)-As(V) complexes: effect on the solubility of ferric hydroxide precipitates and molecular structural identification

A soluble Fe(III)-As(V) complex was discovered and its molecular structure was determined. The presence of this complex increases the solubility of iron hydroxides and may result in the release of As(V) from iron hydroxide sludge.

As featured in:



See Xiaoguang Meng *et al.*,
Environ. Sci.: Nano, 2020, **7**, 1388.

PAPER



Cite this: *Environ. Sci.: Nano*, 2020, 7, 1388

Formation of Fe(III)–As(v) complexes: effect on the solubility of ferric hydroxide precipitates and molecular structural identification†

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Ferric iron (Fe(III)) and arsenate (As(v)) generally co-exist in natural waters. Also, Fe(III) chemicals are widely used for treatment of As(v) in water. This paper reported the existence of Fe(III)–As(v) complexes, which are molecular clusters containing only one iron atom with sizes of less than 1 nm, typically considered as soluble species. The formation of Fe(III)–As(v) complexes varies with the change of pH. Specifically, the soluble Fe(III)–As(v) complex formed at acidic conditions (pH < 2) with a Fe : As mole ratio of 1 : 1. When the pH increased to 2–5, Fe(III) and As(v) formed precipitate rather than a soluble complex, which led to a reduced solubility of Fe(III) at pH 2–5. The soluble Fe(III)–As(v) complex again appeared at pH > 5 with the Fe : As mole ratio of 1 : 2. DFT calculation identified that these soluble Fe(III)–As(v) complexes were in a monodentate configuration. The chloride was found to be coordinated with the Fe(III)–As(v) complexes, which improved their thermodynamic stability. The existence of these soluble complexes promoted the solubility of Fe(III) at neutral pH (*i.e.*, total soluble Fe(III) increased to 0.73 mM (~41 mg L^{−1}) with an initial 0.1 M Fe(III)). The findings in this study shed new light on the understanding of the transport and fate of Fe(III) and As(v) in natural water systems, as well as the As(v) leaching from the sludge produced in the Fe(III)-based As(v) removal techniques.

Received 7th January 2020,
Accepted 21st April 2020

DOI: 10.1039/d0en00024h

rsc.li/es-nano

Environmental significance

This study reports the existence of soluble ferric-arsenate (Fe(III)–As(v)) complexes at both acidic and neutral pH, which are molecular clusters containing only one iron atom and show sizes of less than 1 nm. The formation of the soluble Fe(III)–As(v) complexes has a significant impact on the transport behaviors of both Fe(III) and As(v) in natural systems. Specifically, these complexes significantly affect the solubility of ferric oxide particles in water systems, particularly when As(v) is involved. In addition, because the Fe(III)–As(v) complex is soluble at neutral pH, it is essential to consider this complex in future studies on As(v) treatment by Fe(III)-based nanotechnology, as well as the possible leaching of As(v) from treated sludges.

1. Introduction

Ferric iron (Fe(III)) plays a critical role in arsenic (As) mobility in the natural soil and water systems due to the high affinity of ferric (hydr)oxides for As adsorption. Moreover, numerous As removal techniques using Fe(III)-based chemicals have been reported, such as coagulation^{1–3} and adsorption.^{4–6}

Therefore, it is of great importance to understand the interaction between As and ferric, which has already attracted much interest and has been the subject of extensive studies in the past several decades.

The theory that the mobility of As was controlled by ferric oxides has been well developed by numerous studies, which was attributed to the formation of surface complexes on iron (hydr)oxides or the formation of co-precipitates. Furthermore, the solubility of ferric-arsenate (Fe(III)–As(v)) precipitate and its natural mineral form (scorodite, FeAsO₄·2H₂O) has been studied since the 1970s.^{7–11} Various solubility constants under different conditions have been reported in those studies. However, an interesting phenomenon has not been well understood yet. The solubility of pure ferric oxides ranges from 10^{−10.9} to 10^{−3.1} μM (less than 1 μg L^{−1}) Fe at neutral pH,¹² while increases to 0.1–73 mg L^{−1} in the presence of As(v).¹³ Moreover, increasing the As/Fe ratio tends

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† Electronic supplementary information (ESI) available: The ESI includes the kinetic study of soluble Fe concentration, soluble As in solution as a function of pH, particle size analysis, linear regression of soluble Fe vs. total Fe and As concentration, daughter scan of ESI-MS, FTIR spectra, XAS spectra collection and analysis procedure, details of the binding energy calculation, and estimation of reaction constant. See DOI:10.1039/d0en00024h

to enhance the Fe solubility of Fe–As precipitate.¹³ These phenomena suggest the possible formation of aqueous Fe(III)–As(V) complexes in water, which could significantly affect the mobility of As due to the changes in the geometric structure and the strength of ionic charge.

The complexation of the metal ions could significantly change its precipitation and mobility in solution. For example, the metallic complexes of EDTA usually mobilize the metal ions in solution.^{14,15} Iron has been known to bond to natural organic materials as soluble complexes, which affects the iron solubility and hydrolysis.¹⁶ Moreover, it was reported that arsenic, Fe, and organic matter (OM) formed soluble ternary complexes in water,^{17–19} influencing the mobility and toxicity of As.

The possible direct complexation between As(V) and cations was suggested for the first time in 1977 by Lowenthal *et al.*,²⁰ who observed that the dissociation constant of arsenic acid varies in different artificial seawaters. The existence of FeAsO_4^0 , FeHAsO_4^+ , and $\text{FeH}_2\text{AsO}_4^{2+}$ and the related stability constants were then reported in the studies by Marini *et al.* and Robins *et al.*^{21,22} Recently, the molecular structure of Fe(III)–As(V) complex in acidic HClO_4 and H_2SO_4 solutions was identified by Chai *et al.* and Yang *et al.*^{23,24} However, the possible existence of soluble Fe(III)–As(V) complex at neutral pH was not studied. Moreover, the effect of chloride (Cl) ion was not considered in their system, which could complex with the Fe atom in solution^{25,26} and affect the polymerization of Fe(III).²⁷

The physiochemical properties of the arsenic species generally depend on the molecular structure. Therefore, multiple spectroscopic methods have been used to acquire the molecular structure of arsenic complexes in previous studies. The complexation of metal ions leads to a change in the local coordination environment of the metal atom, which could be measured by Fourier transform infrared (FTIR) and extended X-ray absorption fine structure (EXAFS) analyses. In a previous study,¹⁹ the complexation of As(V) and Fe(III)–OM resulted in the shift of an IR peak from 1585 to 1630 cm^{-1} . In another study regarding As(V)/As(III)–Fe(III)–OM complexes, the As and Fe K-edges EXAFS analysis provided direct evidence for the complexation between As(V)/As(III) and Fe(III)–OM colloid/complex.^{17,18} Moreover, the chemical formula of soluble metal complexes could be identified by electrospray ionization mass spectrometry (ESI-MS), *e.g.*, the detection of the formation of $\text{As}(\text{OH})_2\text{CO}_3^-$ using ESI-MS by Han *et al.*²⁸ In addition, the possible structures are usually further confirmed by quantum chemical calculations. For example, the possible uranyl arsenate complexes derived from EXAFS analysis were further confirmed using density functional theory (DFT) calculations.²⁹

In this study, the existence of the aqueous Fe–As complexes was investigated by a combination of spectroscopic analyses and computational techniques. The effect of As on iron solubility over a broad pH range from 0 to 12 was investigated in batch tests. To investigate the molecular structure of the complex, single and binary Fe(III)

and As(V) solutions were characterized using ESI-MS, attenuated total reflectance (ATR)-FTIR, and EXAFS. The possible structures derived from experimental spectroscopic studies were further verified by DFT calculations. Although the relation between Fe(III) and As(V) has been known for several decades, no study regarding the aqueous Fe(III)–As(V) complex has been reported. This study confirms the formation of Fe(III)–As(V) complexes and further identifies the molecular structures of the complexes, which is of great importance in understanding the transport of As(V) and Fe(III) in water.

2. Materials and methods

2.1 Materials

The solutions of 1 M Fe(III) and As(V) were prepared directly by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ into 4% HCl solutions. The other solutions containing Fe(III) and As(V) were diluted from the solutions mentioned above. All chemicals were reagent grade, and were purchased from Fisher (United States) or Sigma (United States).

2.2 Batch experiments

2.2.1 Effect of pH. The Fe(III) and As(V) stock solutions were added into 12 centrifuge tubes with 50 mL 0.01 M NaCl solutions to reach a concentration of 2 mM Fe(III) and 2 mM As(V). The pH was adjusted to 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, and 12 by adding HCl or NaOH. In another control test, only Fe(III) stock solution was added into another 12 tubes with 50 mL 0.01 M NaCl solutions to reach the same concentration. The pH values of solutions were measured after 1, 7, and 180 days of mixing. The experiments were conducted in closed centrifuge tubes without the sunlight or UV radiation.

The definition of “soluble” in this study followed the study by Wu *et al.*,³⁰ in which the species after filtration using a 0.02 μm pore size filter was considered as soluble species. Therefore, 5 mL suspension was collected and filtered through a 0.02 μm syringe filter, for which the 0.2 μm filter was used as a prefilter. The filtered solutions were then added to 75 μL HCl for measuring the As and Fe concentrations by inductively coupled plasma optical emission spectrometry (Agilent ICP-OES 5100, United States).

2.2.2 Effect of initial As and Fe concentrations. In another batch test, solutions containing 0.4, 10, and 100 mM Fe(III) and As(V) were also prepared at pH 7, and the soluble Fe was also measured after 180 days mixing. Triplicate samples were conducted in this test.

2.3 Particle size analysis

To investigate if the syringe filter (0.02 μm) could effectively separate the iron oxides nanoparticles, the filtered solutions was characterized by particle size analysis. Specifically, about 0.75 mL of sample was collected from the filtered (by 0.02 μm syringe filter) 100 mM Fe(III) and As(V) solutions (pH 7) and injected into a clear disposable zeta cell (DTS-1060C,

Malvern Instrument, UK) for measurement. The particle size measurements were performed at 25 ± 0.1 °C using dynamic light scattering (DLS) by Zetasizer Nano ZS (Malvern Instrument, UK), equipped with an avalanche photodiode (APD) detector and a 4 mW He–Ne laser ($\lambda = 633$ nm). The particle size analysis of the filtered solution (Fig. S1 in (ESI†)) at pH 7 showed that the size of particles in solution was around 1 nm. Such a size is much smaller than the smallest ferrihydrite nanoparticles (3 nm),³¹ indicating that ferrihydrite nanoparticles barely existed in the filtered solutions. To conclude, the soluble Fe species after filtration using the 0.02 μm filter is in a size of less than 1–3 nm, in agreement with previous studies by Liao *et al.*,^{32,33} in which the Fe species with a size less than 1–3 nm was considered as truly dissolved species.

2.4 Quadrupole-time-of-flight mass spectroscopy

The solutions containing 0.4 mM Fe(III) in the absence and presence of 0.4 mM As(V) in 4% HCl were characterized by ESI-MS using a Waters quadrupole-time-of-flight (Q-ToF) instrument equipped with an electrospray ion source. Samples were filtered using a 0.02 μm filter and introduced to the source at a flow rate of 15 $\mu\text{L min}^{-1}$. The source temperature was held at 135 °C, with capillary voltage of 2950 V, cone voltage of 30 V and ToF voltage of 9.1 kV. The desolvation gas flow rate was set at 440 L h^{-1} .

2.5 Attenuated total reflectance Fourier transform infrared spectroscopy

Solutions of 10 mM Fe(III) in the absence and presence of 10 mM As(V) in 4% HCl solution were characterized using ATR-FTIR. The measurements were performed using a spectrometer (Thermo-Nicolet Nexus IS50, United States) equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. An additional horizontal attenuated total reflectance (HATR) cell (PIKE Tech, United States) with a multibounce Ge crystal with 45° beveled faces (infrared angle of incidence, θ) was used, and the infrared spectra were collected using 1024 scans per spectrum at a resolution of 4 cm^{-1} . Fe(III) solutions with or without As(V) was dropped into the cell with a volume of 1.0 mL for spectra collection. The background spectrum of the absorbance of the Ge crystal with 1.0 mL 4% HCl solution was collected.

2.6 X-ray absorption spectroscopy

Solutions of 20 mM Fe(III) in the absence and presence of 20 mM As(V) in 4% HCl solution were analyzed by Fe K-edge (7112 eV) EXAFS. The solutions containing As(V) (10 mM) in the absence and presence of Fe(III) (20 mM) in 4% HCl solution were analyzed by As K-edge (11867 eV) EXAFS. The XAS spectra for those solutions were collected at beamline 9-BM at the Advanced Photon Source (APS, Argonne National Laboratory, United States). Meanwhile, the filtered solution from 100 mM As(V) and Fe(III) at pH 7 was characterized using Fe K-edge at beamline 6-BM at the National Synchrotron

Light Sources II (NSLS-II, Brookhaven National Laboratory, United States), where the detector could reach a detection limit of 1 mg L^{-1} . An energy range of –200 to 1000 eV relative to the Fe and As K-edges was used to acquire spectra with a 4-element Vortex silicon drift detector (SDD). Five to ten 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.^{34,35} The procedure for the analysis of the measurements is similar to that used in our previous works^{36–38} and is detailed in the ESI.†

2.7 Computational methods

The *ab initio* DFT calculations were performed by the Vienna *ab initio* simulation package (VASP)³⁹ using a hybrid function of B3LYP^{40,41} with an optimized cutoff energy of 450 eV. Similar to the previous calculations for molecular clusters,^{42,43} the molecules were put into a cubic box with a $20 \times 20 \times 20$ Å size. Only the gamma point in the Brillouin zone was sampled. All structures were optimized without any symmetry restriction, and a spin-unrestricted self-consistent field was employed during calculation. The effect of the solvation was considered by an implicit solvent model using VASPsol,^{44,45} while the long-range dispersion correction was considered by adding the Becke–Johnson (BJ) damped atom-pair wise potential (D3BJ).^{46,47} For the geometry optimization, the stopping criteria of the self-consistent calculations was 10^{-5} eV per atom and remaining forces acting on all the atoms were less than 0.01 eV Å^{−1}.

The binding energy (BE) was calculated based on the following equation:

$$\text{BE} = E_{\text{products}} - E_{\text{reactants}} \quad (1)$$

where E_{products} and $E_{\text{reactants}}$ are the sum of total energy of products and reactants in the chemical reactions in Table S4,† respectively. Negative values of binding energy suggested that the formation of the complex is thermodynamically favorable.

3. Results and discussion

3.1 Effect of As(V) on soluble Fe concentration

In order to investigate the possible interaction between As(V) and Fe(III) ions, the soluble Fe concentrations in FeCl₃ solutions at different pH were measured in the absence and presence of As(V) (Fig. 1a). In agreement with previous studies,^{31,48,49} the soluble Fe decreased significantly at pH >1.5 because of the formation of the iron oxides. Interestingly, in the presence of As(V), the soluble Fe significantly decreased at pH 2–5 and increased at pH >5.

At pH 2–5, the soluble Fe in the presence of As(V) rapidly decreased to 0.35–11 mg L^{-1} at pH 2–5 after 1 day mixing (Fig. S2†) and remained similar concentrations after 180 days mixing. On the other hand, the soluble Fe in the absence of

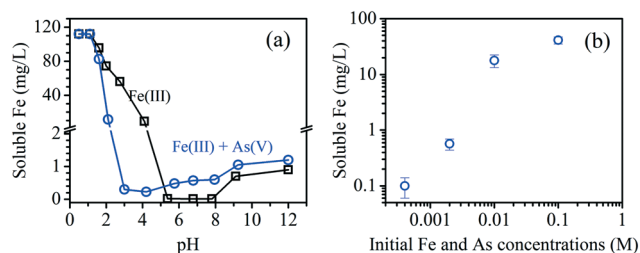


Fig. 1 Soluble Fe concentration in 2 mM Fe(III) solutions without (black square) and with (blue circle) 2 mM As(V) after 180 days of mixing as a function of equilibrium pH (a), and in the solutions with different initial Fe(III) and As(V) concentrations (b) at pH 7 (ionic strength = 0.01 M NaCl, room temperature).

As(V) was 28.9–97.6 mg L⁻¹ after 1 day mixing, and still as high as 9.2–74.3 mg L⁻¹ after 180 days mixing. This significant difference suggests that the presence of As(V) facilitated precipitation from soluble Fe. Moreover, a different kinetic behavior might result from the rapid formation of solid ferric arsenate (FeAsO₄·2H₂O) at acidic conditions (pH < 5)⁵⁰ and the slow formation of hematite.^{48,51} The formation of ferric arsenate was also evidenced by the significant decrease of the soluble As(V) concentration at pH > 2 (Fig. S3†).

Fig. 1-a also shows that the soluble Fe in the absence of As(V) increased above pH 8, owing to the formation of Fe(III)–OH complex.⁴⁸ On the other hand, the presence of As(V) dramatically improved the soluble Fe, suggesting the formation of the soluble Fe(III)–As(V) species.

Similar to our study, Virčíková *et al.*¹³ found that the increase in As/Fe ratio of amorphous Fe–As precipitates led to an increase in the soluble Fe concentration. In another study, the addition of As(V) into ferric oxides suspension also resulted in an increase of soluble Fe concentration.⁴² These results suggest that the presence of As(V) might result in the formation of Fe(III)–As(V) complex, which is similar to the formation of Fe(III)–OH complex at high pH,⁴⁸ and consequently increased the soluble Fe concentration.

To confirm the formation of Fe(III)–As(V) complex, the soluble Fe concentration in the solutions containing different initial Fe(III) and As(V) concentrations was measured (Fig. 1b). The results clearly showed that the soluble Fe concentration increased from 0.1 mg L⁻¹ (1.8 μM) to 41 mg L⁻¹ (0.73 mM), when the initial Fe(III) and As(V) concentrations increased from 0.4 to 100 mM, respectively. The linear fitting in Fig. S4† further provides evidence that the soluble Fe concentration is significantly dependent on the initial Fe(III) and As(V) concentrations ($R^2 = 0.84$, $p < 0.05$). Therefore, the promotion of soluble Fe concentration in the presence of As(V) was due to the formation of Fe(III)–As complexes. Otherwise, the soluble Fe concentration should be controlled by the solubility product constant (K_{sp}) of ferric precipitates, which is independent of the initial Fe(III) and As(V) concentrations at fixed pH and ionic strength.

Overall, the batch experimental results suggest that Fe(III) and As(V) might form soluble complexes in solutions at pH

> 5. The formation of the soluble Fe(III)–As(V) complex promoted the soluble Fe concentration at neutral pH. At pH 2–5, Fe(III) and As(V) form precipitate rather than a soluble complex. At pH < 2, Fe exists as aqueous ion, which was complexed with As(V) ion. The precipitation of ferric arsenate at pH 2–5 has already been reported in previous study.⁵⁰ The formation of the Fe(III)–As(V) complex at pH < 2 has been reported in previous study,²³ but in H₂SO₄ solution without the presence of the Cl⁻. However, the formation of Fe(III)–As(V) in the solution containing chloride, which has a high affinity towards Fe(III) and exists in all natural waters, has not been investigated. Therefore, the molecular structure of soluble Fe(III)–As(V) complex in the chloride system needs to be further explored.

In the following sections, we firstly characterized the soluble Fe(III)–As(V) complexes in NaCl solution at both acidic (4% HCl solution, section 3.2) and neutral conditions (pH 6–8, section 3.4). Then, possible molecular structures derived from experimental characterizations were verified by the DFT calculation (section 3.3 and 3.5). The neutral pH (6–8) was selected rather than alkaline pH (9–12), because the formation of Fe(III)–OH complex (0.7–0.9 mg L⁻¹) occupied a high proportion of total soluble Fe(III) (1.1–1.2 mg L⁻¹) at pH 9–12.

3.2 Characterization of Fe(III)–As(V) complexes under acidic condition

To confirm the formation of the soluble Fe(III)–As(V) complex, ESI-MS was employed to characterize single and binary Fe(III) and As(V) solutions (Fig. 2). The MS peaks at mass-charge-ratio (m/z) 123 and 141 in Fig. 2-a identify the molecules of As(V) with a charge of -1, corresponding to AsO₃⁻ and H₂AsO₄⁻, respectively. Meanwhile, in agreement with a previous study,⁵² MS peaks at m/z 159–165 and 194–202 in Fig. 2-b are signals for Fe^{II}Cl₃ and Fe^{III}Cl₄, respectively. The presence of As(V) in FeCl₃ solution resulted in new peaks centered at m/z 266 and 268, indicating the formation of the soluble Fe(III)–As(V) complex (Fig. 2-e).

To further confirm these chemical formulas, MS/MS was conducted for species at m/z 266 (Fig. S5-a†) and 268 (Fig. S5-b†). The major daughter ions of species at 266 are [AsO₃]⁻ (m/z 123), [FeH₃AsO₆]⁻ and [FeAsO₄Cl]⁽³⁵⁾⁻ (m/z 230), and [FeH₂AsO₅Cl]⁽³⁵⁾⁻ (m/z 248). The daughter scan of MS peak at m/z 268 showed ions of [AsO₃]⁻ (m/z 123), [FeH₃AsO₆]⁻ (m/z 230), [FeAsO₄Cl]⁽³⁷⁾⁻ (m/z 232), and [FeH₂AsO₅Cl]⁽³⁷⁾⁻ (m/z 250). Based on these results, the chemical formulas of the compounds at m/z 266 and 268 might be [FeH₄AsO₆Cl]⁽³⁵⁾⁻ and [FeH₄AsO₆Cl]⁽³⁷⁾⁻, respectively.

The high magnification of ESI-MS spectra (ranged from m/z 250–350, Fig. 2-b, d, and f) indicates the existence of [FeH₄AsO₆Cl]⁽³⁵⁾⁻·H₂O, [FeH₄AsO₆Cl]⁽³⁷⁾⁻·H₂O, [FeH₄AsO₆Cl]⁽³⁵⁾⁻·(H₂O)₂, and [FeH₄AsO₆Cl]⁽³⁷⁾⁻·(H₂O)₂, at m/z 284, 286, 302, and 304, respectively. These results suggest that the water molecules in Fe(III)–As(V) complexes were dissociated from the Fe–As complex during the electrospray process, such as the

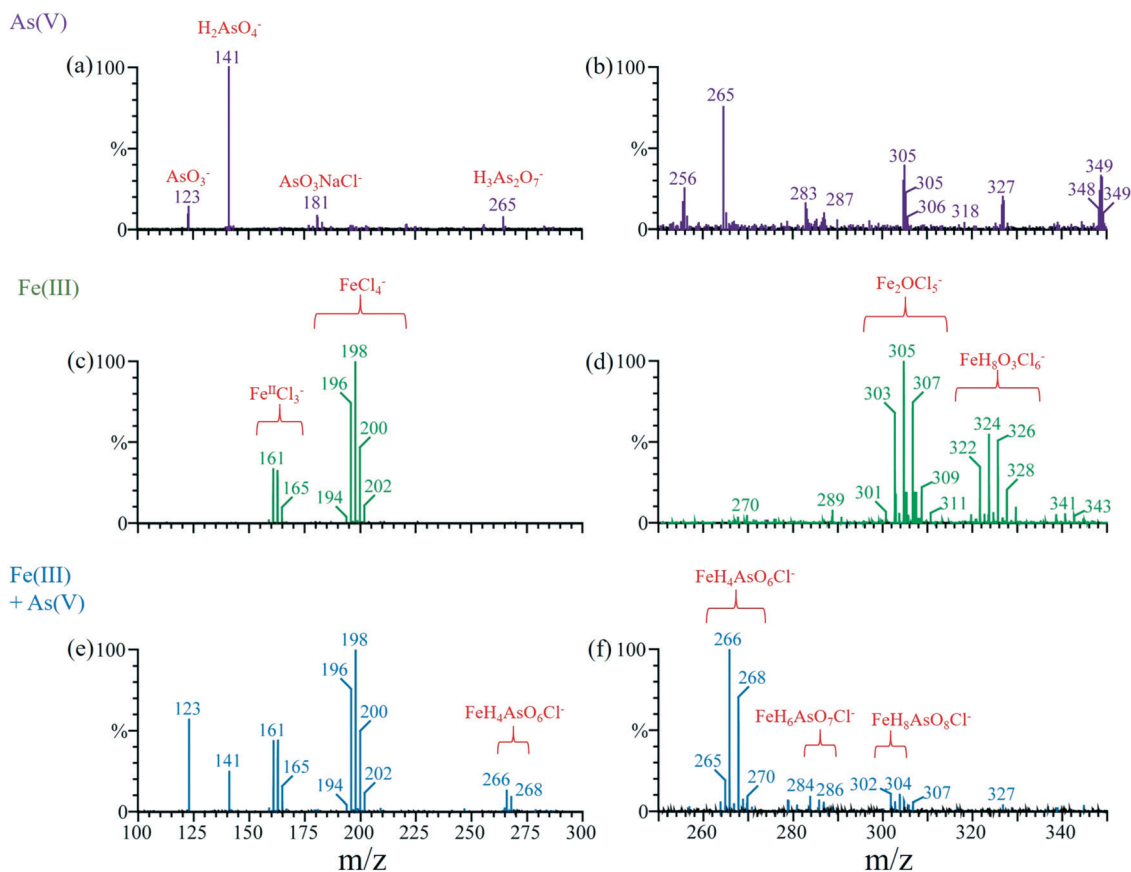


Fig. 2 Negative ESI-MS spectra in ranges of m/z 100–300 (a, c and e) and 250–350 (b, d and f) for 2 mM As(v) (a and b), Fe(III) (c and d), and As(v) + Fe(III) (e and f) solutions.

observed AsO_3^- (m/z 123), which resulted from fragmentation of H_2AsO_4^- .

The MS/MS spectra confirmed the presence of Fe–As soluble complexes with a chemical formula of $\text{FeH}_8\text{AsO}_8\text{Cl}$. Considering the solution properties might be altered during the electrospray ionization process, we further employed ATR-FTIR to characterize single and binary component solutions of FeCl_3 and As(v) mentioned above

(Fig. S6†). No significant band is observed in the IR spectrum of FeCl_3 solution. Two major bands are observed in the IR spectrum of As(v) solution, which are asymmetric vibration of As–OH at 808 cm^{-1} and symmetric vibration of As–O at 928 cm^{-1} .^{53–55} It is clear that the presence of Fe(III) in As(v) solution leads to two additional IR bands at 890 and 839 cm^{-1} , resulting from the complexation between Fe(III) and As(v).

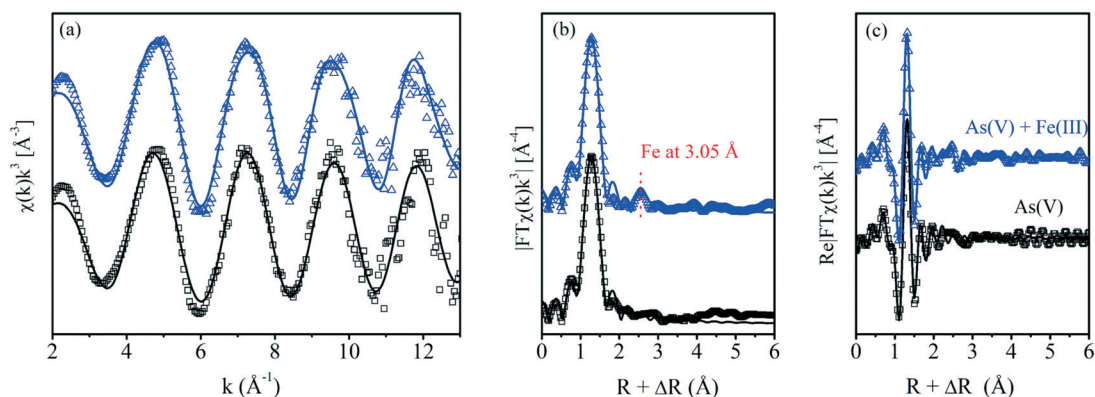


Fig. 3 Normalized k^3 -weighted experimental (symbols) and simulated (lines) As K-edge EXAFS spectra of 0.02 M As(v) solutions in the absence (black square) and presence (blue triangle) of 0.02 M Fe(III) (a) at pH 0.5 (4% HCl), the corresponding Fourier transformed magnitude (b) and real parts (c).

Because the heavy overlapped bands of the formed complexation with H_3AsO_4 , the IR bands could not be used to identify the configuration of the complex. Also, the molecular structure of soluble $\text{As(v)}\text{-Fe(III)}$ complex derived from the ESI-MS analysis cannot provide information regarding the geometric structure, *e.g.*, bond length. Therefore, EXAFS analysis was further conducted to explore the coordination shells of the Fe and As atoms in solution. Fig. 3 shows As K-edge XAS spectra for As(v) solution in the absence and presence of Fe(III) . The coordination shell of As atom in single As(v) solution show only one FT peak (Fig. 3-b), corresponding to the widely reported four O atoms surrounding As with an average bond length ($d_{\text{As-O}}$) of 1.70 Å.^{36,56} A second FT peak was observed on the FT spectrum of As(v) solution in the presence of Fe(III) . Fitting results (Table S1†) show that a Fe shell with a coordination number (CN) of 0.7 was detected with an interatomic distance ($d_{\text{As-Fe}}$) of 3.05 Å.

The EXAFS analysis of Fe K-edge for single and binary Fe(III) and As(v) solutions was also used to investigate the coordination shells surrounding the Fe atom (Fig. 4). As shown in Table S2,† two shells surrounding the Fe atom were observed for Fe(III) solution, corresponding to 5.2 ± 0.4 O and 3.8 ± 0.7 Fe atoms at 2.03 and 3.64 Å, respectively. The XAS study by Kiyotaka *et al.* reported both coordinated Cl and O surrounding the Fe atom.²⁶ Their results further indicated that $[\text{FeCl}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ dominated the species of Fe(III) in FeCl_3 solution, and the CN of Cl increased to 2 when the FeCl_3 concentration was higher than 3 M. In our study, the addition of Cl shell led to a CN of Cl with 0.3 ± 0.1 , suggesting the small fraction of Cl, and a similar phenomenon was also observed in previous XAS studies for FeCl_3 solution.^{25,57} The low fraction of coordinated Cl was mainly due to the low FeCl_3 concentration of 0.02 M in this study, suggesting that the hydration of Fe ($\text{Fe}(\text{OH})_2$) dominated the Fe(III) species under this condition. The detected second Fe shell indicated that the polymerization of Fe in FeCl_3 solution occurs even at pH <1, which agrees well with a recent study regarding the formation of Fe polymer at pH 0.15.³¹

The presence of As(v) in FeCl_3 solution led to a significant change in the coordination environment of Fe. As shown in Table S2,† a second shell was observed and fitted by 0.8 ± 0.1 As atom at 3.12 Å, within a difference of 0.1 Å compared to the value (3.05 Å) derived from As K-edge EXAFS analysis. In addition, the CN of Fe-Fe shell was reduced to 0.3, indicating the polymerization process was inhibited by the complexation of As(v) with Fe.

The additional Fe shell surrounding As and the additional As shell surrounding Fe in the binary Fe(III) and As(v) solutions imply the formation of soluble Fe(III)-As(v) complexes. The corresponded CN of Fe (0.7 ± 0.2) and As (0.8 ± 0.1) showed a ratio of 1 for Fe/As in the complex, which was consistent with our ESI-MS characterized chemical formula.

EXAFS results confirmed the complexation of As(v) and Fe(III) in aqueous solution, and provided coordination information between As(v) and Fe(III) . However, As(v) and Fe(III) may be coordinated through monodentate or bidentate by one or two bridged oxygens, respectively. To clarify this uncertainty, the possible Fe(III)-As(v) complexes with different geometric structures, which were derived from the spectroscopic measurements, were further calculated using DFT. The interatomic distance between iron and arsenic atoms ($d_{\text{Fe-As}}$) measured by EXAFS was used as a reference to justify the DFT calculated structures, as well as the DFT calculated BE calculated for the evaluation of the structures' thermodynamic stability.

3.3 Theoretical calculation of Fe(III)-As(v) complexes under acidic condition

The possible geometric structures of Fe(III)-As(v) complex were optimized by DFT calculation. The valid DFT calculated structures are consistent with the EXAFS measurements. Specifically, DFT calculated molecules of H_3AsO_4 and $\text{Fe}(\text{OH})_3(\text{OH})_2$ shows an average As-O and Fe-O bond lengths of 1.728 and 2.025 Å, respectively (Fig. S7†). These results agreed well with EXAFS measurements with a insignificant

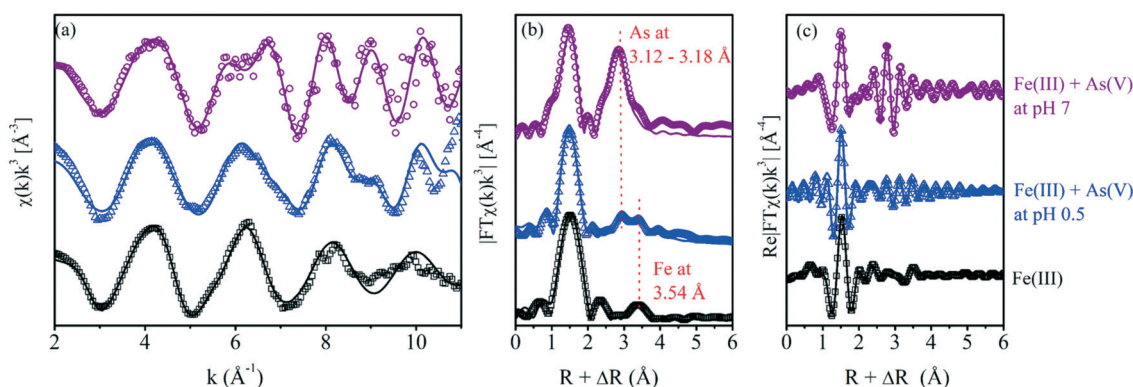


Fig. 4 Normalized k^3 -weighted experimental (symbols) and simulated (lines) Fe K-edge EXAFS spectra of 0.02 M Fe(III) solutions in the absence (black squares) and presence (blue triangles) of 0.02 M As(v) at pH 0.5 (4% HCl), and the filtered (by 0.02 μm syringe filter, purple circles) solution at pH 7 (a), the corresponding Fourier transformed magnitude (b) and real parts (c).

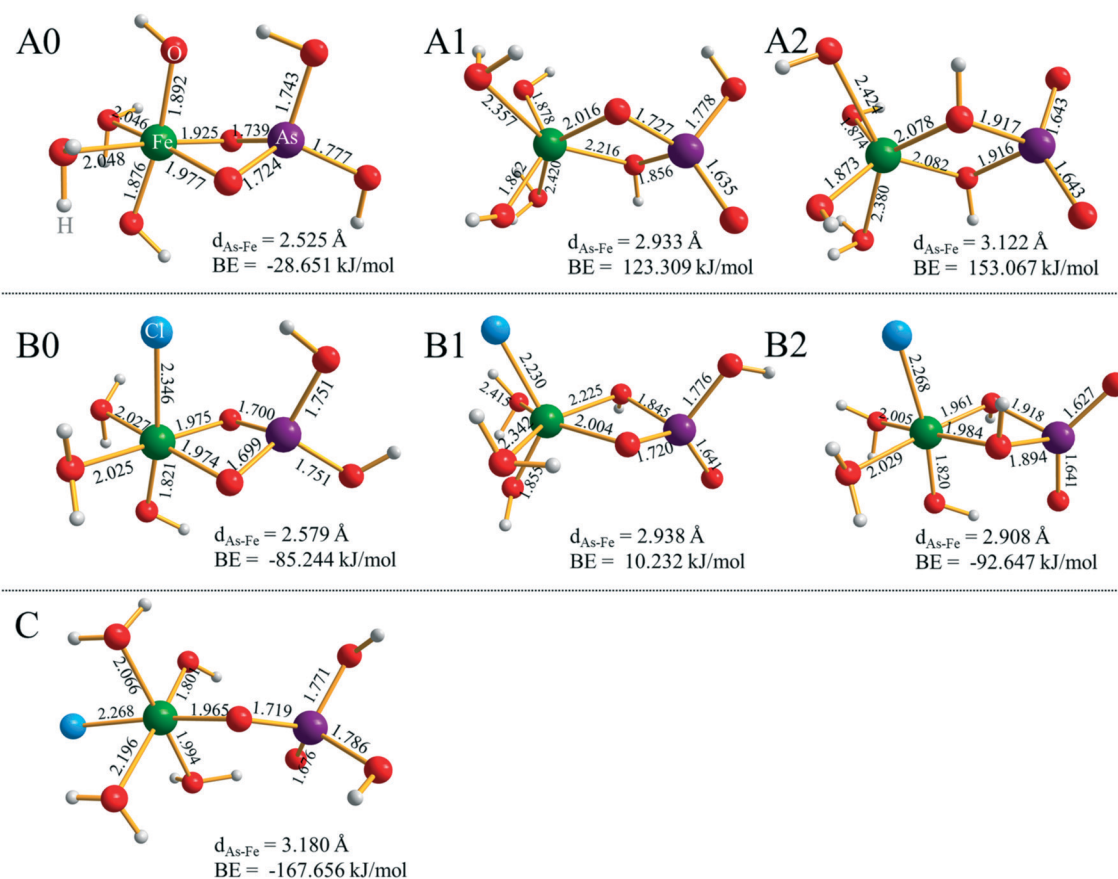


Fig. 5 DFT optimized Fe(III)-As(V) complexes in bidentate configurations without (A) and with (B) coordinated Cl, as well as monodentate configuration (C). The bidentate configurations include un- (A0 and B0), singly (A1 and B1), and doubly (A2 and B2) protonated oxygen bridged complexes. The calculated Fe-O and As-O bond lengths ($\text{\AA}$), the As-Fe interatomic distances ($d_{\text{As-Fe}}$), and binding energies (BE) are labeled, and details regarding BE calculation are listed in Tables S3 and S4.[†]

difference of less than $0.02 \text{ \AA}$ ($1.69\text{--}1.71 \text{ \AA}$ for As-O and $2.02\text{--}2.04 \text{ \AA}$ for Fe-O bond lengths, Tables S1 and S2[†]).

We firstly calculated the bidentate Fe(III)-As(V) complex without coordinated Cl atom $((\text{OH}_2)_2(\text{OH})_2\text{FeO}_2\text{As}(\text{OH})_2)$, Fig. 5-A0). The calculated interatomic distance between As and Fe ($d_{\text{As-Fe}}$, $2.525 \text{ \AA}$) is much lower than the EXAFS measured values ($3.05\text{--}3.12 \text{ \AA}$). In a previous DFT calculation of the uranyl-arsenate (U-As(V)) complex by Gezahegne *et al.*,²⁹ the protonation of the bridged oxygen atom increased the interatomic distance between U and As atoms. Hence, the Fe(III)-As(V) complexes with singly and doubly protonated bridged oxygen atoms were also calculated by DFT $((\text{OH}_2)_2(\text{OH})_2\text{FeO}(\text{OH})\text{AsO}(\text{OH}))$ shown in Fig. 5-A1 and $(\text{OH}_2)_2(\text{OH})_2\text{Fe}(\text{OH})_2\text{AsO}_2$ shown in Fig. 5-A2). The singly and doubly protonating of the bridged oxygen atoms increased the $d_{\text{As-Fe}}$ to 2.933 and $3.122 \text{ \AA}$, respectively. The accuracy of DFT calculated interatomic distance is generally considered within $\pm 0.1 \text{ \AA}$.^{47,58} Therefore, the bidentate Fe(III)-As(V) complex bridged with two protonated oxygen well matched the EXAFS measurements. However, the calculated BE ($153.067 \text{ kJ mol}^{-1}$) indicates that this structure is thermodynamically unfavorable.

The Cl coordinated Fe(III)-As(V) (Cl-Fe(III)-As(V)) complexes were also calculated by DFT. The possible existence of Cl-Fe(III)-As(V) with un-, singly-, and doubly- protonated bridged oxygen (Fig. 5-B0-B2) were all excluded, because the calculated $d_{\text{Fe-As}}$ ($2.579\text{--}2.938 \text{ \AA}$) was much smaller than EXAFS measurements ($3.05\text{--}3.12 \text{ \AA}$). It needs to be noted that the coordination with chloride significantly improved the thermodynamic stability of the Fe(III)-As(V) complex, evidenced by the decreased BE (*i.e.*, from $-28.651\text{--}153.067 \text{ kJ mol}^{-1}$ to $-92.647\text{--}10.232 \text{ kJ mol}^{-1}$, Fig. 5).

On the other hand, the optimized Cl-Fe(III)-As(V) complex in monodentate configuration shows a $d_{\text{Fe-As}}$ of $3.180 \text{ \AA}$, which is less than $0.1 \text{ \AA}$ difference from the EXAFS measurements. Meanwhile, this configuration also has a lowest BE of $-167.656 \text{ kJ mol}^{-1}$, suggesting a more stable structure than other possible configurations.

Overall, by using the EXAFS measured $d_{\text{Fe-As}}$ value as a reference, and with the consideration of the BE at the same time, the DFT calculation implies that Fe(III)-As(V) complex is in monodentate configuration with one coordinated Cl. The interesting finding from DFT is that coordination with Cl increased the thermodynamic stability of the Fe(III)-As(V) complex.

3.4 Characterization of Fe(III)–As(v) complex at neutral pH

The possible formation of Fe(III)–As(v) complexes in solution with neutral pH was also characterized by ESI-MS. However, the MS peaks at m/z 266 and 268, as well as other additional peaks observed at acidic condition, were not observed (data not shown). This might be caused by a low fraction (less than 1%) of Fe(III)–As(v) complexes (0.6 mg L^{-1} when initial As is 150 mg L^{-1} , Fig. 1) out of total soluble As concentration, so that the possible MS signal of Fe(III)–As(v) complex was covered by the high As(v) signal. Similarly, As K-edge analysis cannot provide useful information, because most As(v) molecules were not bonded to Fe(III). However, Fe K-edge EXAFS analysis can be used to acquire the coordination environment of Fe, because most soluble Fe(III) atom are from Fe(III)–As(v) complex.

The EXAFS characterization shows that the first FT peak (Fig. 3-b) is similar to the Fe solution at the acidic condition. Fitting results showed that the first FT leak was composed of 5.1 O and 0.4 Cl atoms at 1.98 and 2.33 Å, respectively. The second FT peak is stronger than that at the acidic condition, which was fitted by 2.3 As atoms at 3.18 Å. The increased CN of As surrounding Fe suggests that the Fe(III)–As(v) complex formed at neutral pH is different from that formed at acidic condition, in which the Fe:As ratio changed to 1:2.

3.5 Theoretical calculation of Fe(III)–As(v) complex at neutral pH

The possible structures of soluble Fe(III)–As(v) complexes at neutral pH, *i.e.* Fe(III) with two surrounding As(v) (As(v)–Fe(III)–As(v)), were also calculated by DFT for the structural clarification (Fig. 6). Both bidentate and monodentate configurations without and with the coordination of Cl were considered in the DFT calculation.

The difference between the DFT calculated $d_{\text{As-Fe}}$ values (2.892–2.922 Å, Fig. 6-A) and the EXAFS measurements (3.12–3.18 Å, Fig. 4) for bidentate As(v)–Fe(III)–As(v) is higher than 0.1 Å. On the other hand, although the calculated $d_{\text{As-Fe}}$ in As(v)–Fe(III)–As(v) with coordinated Cl (3.036–3.059 Å, Fig. 6-C) matches the experimental results, the calculated BE is higher than zero ($6.510 \text{ kJ mol}^{-1}$), indicating that the formation of this structure is energetically unfavorable. Therefore, both bidentate configurations with or without the coordination of Cl were excluded.

On the other hand, the calculated As(v)–Fe(III)–As(v) complex in monodentate configuration, with or without coordinated Cl, shows $d_{\text{As-Fe}}$ values of 3.036–3.142 Å, which agrees well with the EXAFS measurements. These two structures are also energetically favorable (BE: -150.931 and $-218.721 \text{ kJ mol}^{-1}$), indicating the simultaneous formation of them in the solution. It is worthy to mention that the

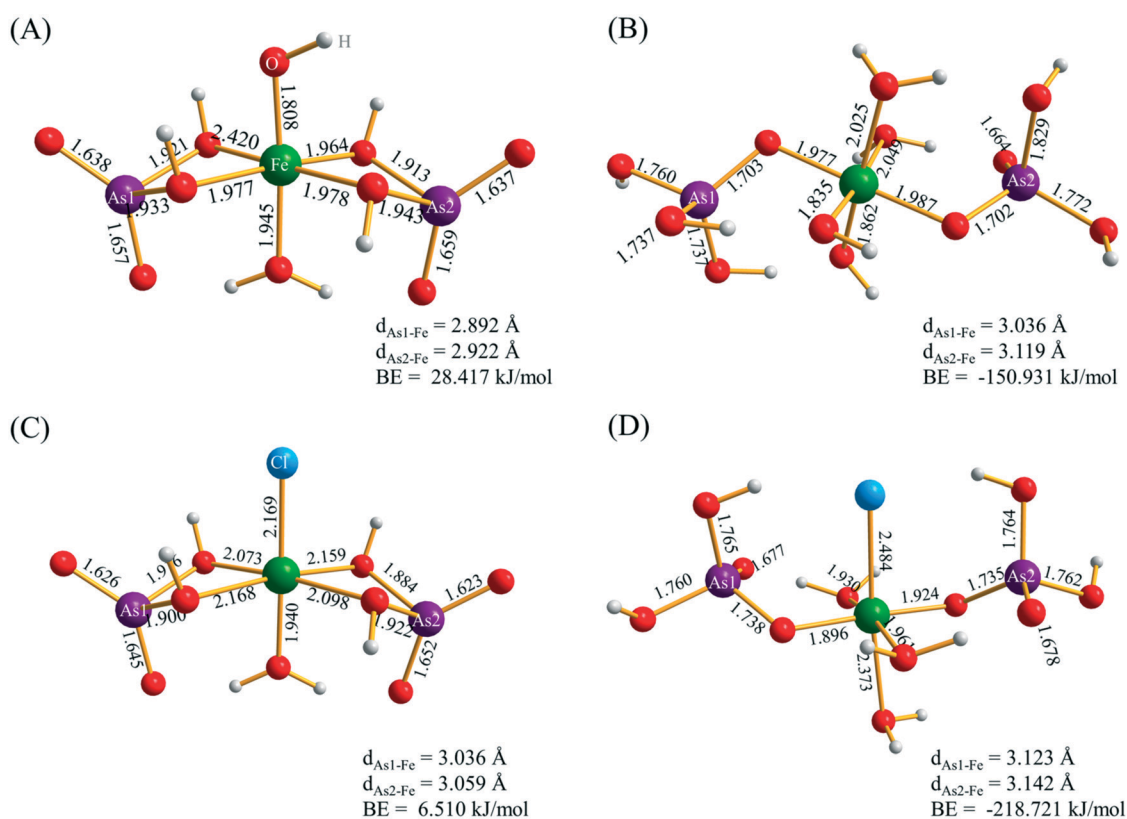


Fig. 6 DFT optimized Fe(III)–As(v) complexes with a Fe:As ratio of 1:2, including bidentate (A and C) and monodentate (B and D) configurations without (A and B) and with (C and D) coordinated Cl. The calculated Fe–O and As–O bond lengths (Å), the As–Fe interatomic distances ($d_{\text{As-Fe}}$), and binding energies (BE) are labeled, and details regarding BE calculation are listed in the Tables S3 and S4.†

calculated As(v)–Fe(III)–As(v) complex is in a size of approximate 1 nm (*i.e.*, 9.69–9.98 Å), in agreement with the measured particle size of the filtered Fe(III) and As(v) solution at pH 7 (Fig. S1†).

Overall, the DFT calculation confirmed the existence of As(v)–Fe(III)–As(v) complex at neutral pH. Compared to the Fe(III)–As(v) complex formed at acidic pH, an additional As(v) molecule was involved at neutral pH. This difference might result from the higher As/Fe ratio, because most of the ferric ions are precipitated at neutral pH. Similar to the As(v)–Fe(III) complex at the acidic condition, coordination with Cl also improved the thermodynamic stability of As(v)–Fe(III)–As(v) complex. The involvement of Cl in the soluble Fe(III)–As(v) complex also explains why the increased Cl[−] concentration promoted the solubility of FeAsO₄ precipitate in a previous study.⁵⁹

3.6 Estimation of equilibrium constant for Fe(III)–As(v) complex at neutral pH

The equilibrium constant of Fe(III)–As(v) complex at neutral pH was estimated based on the ratio of 1Fe:2As:1Cl by eqn (S1) (page S14 in ESI†). The Fe(III) in the solution without the presence of As(v) is lower than 17 µg L^{−1} (Fig. 1-a), suggesting that the mononuclear Fe(III) (*i.e.*, un-complexed with As(v)) accounting for less than 5% of the total soluble Fe (570 µg L^{−1}). Therefore, most (>95%) of the soluble Fe exists as As(v)–Fe(III)–As(v) complex at neutral pH. Hence, the concentration of As(v)–Fe(III)–As(v) complex was considered as same as the soluble Fe concentration (Fig. 1-b). The estimated equilibrium constants of Fe(III)–As(v) (log *K* in Table S5†) ranged from 1.86 to 6.45, which increased with the decreasing initial Fe and As, suggesting that the formation of Fe(III)–As(v) complex is not stable, which might be due to the interference from precipitation of FeAsO₄ and ferric oxides.

The increased equilibrium constants with decreased initial Fe and As concentrations are important to the natural systems. In the contaminated ground water, Fe and As concentrations usually range from 0–1000 µg L^{−1}.^{60,61} Based on our previous study,⁴² the presence of 50 µg L^{−1} As(v) significantly improved the soluble Fe concentration from 1.9 µg L^{−1} to 7.3 µg L^{−1}, while the presence of 500 µg L^{−1} As(v) resulted in a soluble Fe concentration of 87 µg L^{−1}. Considering that the World Health Organization (WHO) guideline value for As in drinking water is as low as 10 µg L^{−1},⁶² the existence of Fe(III)–As(v) complex is significant to the mobility of both As(v) and Fe(III) in natural systems.

4. Conclusions

The discovery of the existence of Fe(III)–As(v) complex is important to understand the fate and transport of the Fe(III) and As(v) in natural water systems. In addition, since Fe(III) based technologies (*i.e.*, nano- to mill-meter scale iron oxides adsorbents) are extensively used in treating As(v) contaminated water, the findings in this study is important to understand the role of As(v) on the dissolution of ferric

oxides and the possible leaching of As(v) from sludge. This study evidenced the formation of Fe(III)–As(v) complex at neutral pH with a size of 1 nm, providing new insights into the existence of nano-sized iron oxides particles, which could be considered as the soluble complex. The existence of such a complex has a significant effect on the fate of nano- to micro-scale iron oxides particles, *i.e.*, rethinking their solubility constants in the presence of As(v). The existence of Fe(III)–As(v) complex should be considered in fate and transport modeling studies regarding the iron oxides particles in natural systems, particularly when As(v) is present. Moreover, because the As(v)–Fe(III)–As(v) complex is soluble at neutral pH, it should be considered in the design of arsenate containing water treatment processes by the Fe(III) based nanotechnologies, as well as the disposal of treatment sludges.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory (APS) under Contract No. DE-AC02-06CH11357. The XAS spectrum for Fe at pH 7 was collected at 6 BM beamline of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated by Brookhaven National Laboratory under Contract No. DE-SC0012704. Authors thank Dr. Bruce Ravel at 6 BM beamline for his kind help on XAS spectra collection. The Extreme Science and Engineering Discovery Environment (XSEDE) supplied computational time for this study through the allocation TG-BCS180005.

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