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Microscopic insight into precipitation and adsorption of As(V) species by Fe-based materials in aqueous phase

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HIGHLIGHTS

- Outer-spheres structure of $[FeH_2AsO_4]^{2+}{}_{aq}$ species may be dominant in acidic solution.
- Low hydrophily of Fe(III) colloid is a key factor for As(V) removal efficiency.
- Charge on Fe(III) in colloid is not responsible for As(V) removal efficiency.
- Charge transfer and bidentate association are not key factors for As(V) removal.

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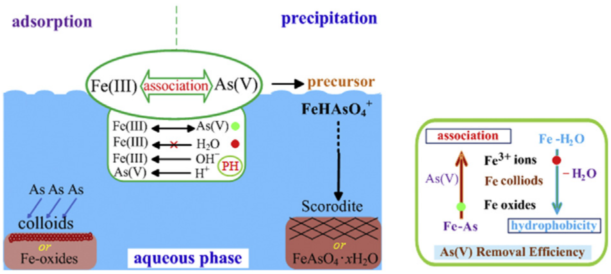
GRAPHICAL ABSTRACT



ABSTRACT

The mechanism of As(V) removal from the drinking water and industrial effluents by iron materials remains unclear at the molecular level. In this work, the association of Fe-based materials with As(V) species was explored using density functional theory and *ab initio* calculations. Solvent separated ion pair structures of $[FeH_2AsO_4]^{2+}{}_{aq}$ species may be dominant in an acidic solution of Fe–As complex. The association trend of $H_2AsO_4^-$ species by $Fe^{3+}{}_{aq}$ is found to be quite weak in the aqueous solution, which may be attributed to the strong hydration of $Fe^{3+}{}_{aq}$ and $[FeH_2AsO_4]^{2+}$ species. However, the association of $H_2AsO_4^-$ species by colloidal clusters is quite strong, due to the weakened hydration of Fe(III) in colloidal structures. The hydrophobicity of Fe-based materials may be one of the key factors for their As(V) removal efficiency in an aqueous phase. When the number of OH^- coordinated with Fe(III) increases, the association trend of As(V) by colloidal ferric hydroxides weakens accordingly. This study provides insights into understanding the coprecipitation and adsorption mechanisms of arsenate removal and revealing the high efficiency of arsenate removal by colloidal ferric hydroxides or iron salts under moderate pH conditions.

1. Introduction

Arsenic contamination of ground waters and mine wastes leads to significant environmental hazards and human diseases (Ayotte et al., 2016; Durkee et al., 2017; Olszewska et al., 2016; Rajpert

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et al., 2016). Consequently, the treatment technologies for As-containing drinking water and industrial wastewater are of great urgency and high priority in many countries (Durkee et al., 2017; Fawcett et al., 2015). One of the most commonly applied methods for removing arsenate from water is coagulation by iron salts (Qiao et al., 2012; Wang et al., 2014), which has been identified as the most effective and most economical treatment technology in mine waste treatment (Michael, 2013). Published studies on the As(V) adsorption have been conducted using Fe-based materials (Ma et al., 2015; Yu et al., 2016), such as magnetite (Chandra et al., 2010; Kango and Kumar, 2016; Luo et al., 2016; Sun et al., 2016), hematite (Kilianova et al., 2013; Zhang et al., 2017), goethite (Du et al., 2014; Watts et al., 2014), and ferrihydrite (Jiang et al., 2015; Lee et al., 2014; Mandaliev et al., 2014). The As(V) removal by Fe-based materials involves co-precipitation and adsorption (Wang et al., 2014; Zhang et al., 2016), whereas the interaction mechanisms of the Fe-based materials with As(V) are not well described at the microscopic level. Meanwhile, the efficiency of As(V) removal is highly correlated to the solution pH (Chandra et al., 2010; Ma et al., 2015; Zhang et al., 2016), which can govern the distribution of the As(V) species and affect the affinity of As(V) on the iron (oxyhydr)oxides surface. Therefore, a systematic comparative study on the mechanisms of As(V) species with Fe-based materials is of considerable significance.

Complexation of arsenate with ferric ion was proposed to exit as $FeH_2AsO_4^{2+}$, $FeHAsO_4^{+}$, and $FeAsO_4$ (Chai et al., 2017; Zhang et al., 2016). However, Wei et al. (2016) reported that $H_2AsO_4^{-}$ would occur under acidic pH conditions, $HAsO_4^{2-}$ would occur under neutral and weak basic pH conditions, and AsO_4^{3-} would only occur under high pH conditions. The work of Bhattacharjee et al. (2010a) also showed that the hydrolysis process of arsenate, results in the species $HAsO_4^{2-}$ which has been experimentally determined as the main species of As(V) in water at a neutral pH condition. Recently, the work of Chai et al. (2017) indicated that the two complexes $FeH_2AsO_4^{2+}$ and $FeHAsO_4^{+}$ are identified in acidic solutions by Ultraviolet–Visible (UV–Vis) spectra and time-dependent density functional theory (TDDFT) calculations. And Zhang et al. (2016) reported the specific adsorption and association with iron precipitate by spectroscopy, and indicated that forming inner-sphere complexes are the main mechanisms of As(V) removal, which is consistent with the result of the other spectroscopic experiments (Du et al., 2014; Zhao and Guo, 2014). However, the comparison between the ferric arsenate contact ion pair (CIP) and solvent-shared ion pair (SSIP) isomers has not been effectively discussed, which can counter-reflect the mobility of As(V) in precipitates and improve the techniques of As(V) removal. Thus, it is desirable to gain insight into characteristics of the specific arsenate complexes with Fe-based materials existed in an aqueous solution at the molecule level.

Solution pH affects the structures of iron oxide complexes (Kong et al., 2017; Sun et al., 2016; Wang et al., 2017), and iron colloids were generated during the treatment of As(V) by iron oxide materials in some studies, which is indispensable in explanation of As(V) removal (Koilraj et al., 2016; Ma et al., 2016). Kango and Kumar (2016) demonstrated that the adsorption mechanism of magnetite is OH^- on the surface exchanged with arsenate species. Nonetheless, the influence of the coordination of OH^- with Fe(III) on the adsorption and precipitation of As(V) species has not been sufficiently described at the microscopic level. The hydration behaviors of As(V) species (Bhattacharjee et al., 2010a,b) and ferric ion (Bogatko et al., 2013; Miliordos and Xantheas, 2015) have been reported previously. However, the effect of hydration on the arsenic removal by Fe-based materials, which is an important factor for ionic association in an aqueous solution (Li et al., 2015, 2017; Wang et al., 2016; Kemp et al., 2013), has not been systematically investigated. Thus, the characteristics of ferric arsenate complexes have to be evaluated to understand their roles in the transport of arsenate in an aqueous environment and its adsorption behavior on Fe-based materials.

To obtain a comprehensive understanding of the ferric arsenate structures in aqueous solutions, particularly the specific iron forms with different OH^- and various arsenate species on the As(V) removal efficiency, a systematic investigation using quantum chemistry methods was conducted in this study. The association of arsenate species with Fe-based materials, such as $Fe^{3+}{}_{aq}$, Fe-oxides and the colloidal ferric hydroxides, was investigated at the molecular level. Furthermore, the hydration characteristics of Fe(III) in Fe-based materials and charge transfer (CT) in the association of Fe(III) with As(V) were also discussed.

2. Methods

Density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) method has been successfully used to study arsenite, phosphate or sulfate adsorption on Fe-(hydr)oxide surfaces (Acelas et al., 2013; Watts et al., 2014; Zhang et al., 2005). Hence, the DFT method with Becke's three-parameter exchange potential and Lee-Yang-Parr correlation functional (B3LYP) (Becke, 1988; Miehlich et al., 1989), was applied to find the local minimum energy conformations of $[FeH_mAsO_4(H_2O)_n]^{m+}$ (m = 0–2; n = 6–8, 10, 12, 14, 30) clusters with the spin multiplicity 2, 4, and 6, in combination with 6-311G** basis sets, for As, O, H. And the Stuttgart relativistic effective core potentials and basis set used for Fe (Dolg et al., 1987). Similar calculations for Fe-oxides and the colloidal complexes with As(V) species were also considered in the study. Meanwhile, charge population analyses were performed using the natural bond orbital (Foster and Weinhold, 1980; Reed et al., 1985) (NBO) method. Goddard et al. (Bryantsev et al., 2008) and Clark et al. (Wander and Clark, 2008) employed mixed cluster/continuum models to investigate the ion hydration, and their calculated results all agreed well with the experimental observations. Recently, mixed cluster/continuum models have also been used to investigate the hydration of Fe(III) (hydr)oxides in the study by Zhu et al. (2013) and Acelas et al. (2013). Thus the mixed cluster/continuum model was employed to investigate the solvation of $[FeH_mAsO_4(H_2O)_n]^{m+}$ and the other Fe-based complexes with As(V) species in this work. The long-range electrostatic effect of the polarized continuum is considered by reaction field calculations using the integral-equation-formalism protocol (Cancès et al., 1997) (IEF–PCM). These polarized continuum model (PCM) calculations with radii and non-electrostatic terms from the SMD solvation model by Cramer et al. (Marenich et al., 2009) were done. Møller-Plesset second order perturbation theory (Head-Gordon et al., 1988) (MP2) was also employed to evaluate the adsorption energy of As(V) species by Fe-based materials with in an aqueous solution, at the B3LYP/6-311G** level. Time-dependent density functional theory (Petersilka et al., 1996) with CAM-B3LYP functional (Yanai et al., 2004) was used to study electronic spectrums of $[FeH_mAsO_4(H_2O)_n]^{m+}$ (m = 1–2; n = 12, 14, 30) clusters. All DFT and MP2 calculations were performed with the Gaussian 09 suite of programs (Frisch et al., 2009).

The association trend of Fe^{3+} with As(V) species in an aqueous phase can be evaluated by the association energies ΔE_{as}

$$\Delta E_{as} = E_{[FeH_mAsO_4]^{m+},aq} - E_{Fe^{3+},aq} - E_{H_mAsO_4{}^{3-m},aq} \tag{1}$$

which correspond the processes