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Tridentate arsenate complexation with ferric hydroxide and its effect on the kinetics of arsenate adsorption and desorption

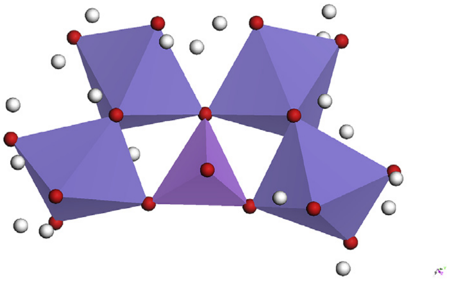
James Farrell

Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ 85721, USA

HIGHLIGHTS

- Quantum chemistry modeling indicates that arsenate may form several different tridentate complexes with ferric hydroxide.
- Tridentate complexes involve arsenate bridge formation between ferric hydroxide octahedra.
- Activation barriers for tridentate complex formation range from 13 to 51 kcal/mol.
- Breaking of tridentate complexes requires overcoming activation barriers of 18–62 kcal/mol.
- High activation barriers associated with tridentate complexation can explain previously observed slow sorption phenomena.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption reactions of arsenate with ferric hydroxide minerals and amorphous ferric hydroxide play an important role in affecting the transport and fate of arsenate in the environment. Previous studies have investigated formation of mono- and bidentate complexes between arsenate and ferric hydroxide. Based on As–Fe coordination numbers, there is spectroscopic evidence that arsenate may also form tridentate complexes with ferric hydroxide. However, the nature of these complexes and the reaction energies and activation barriers for their formation have not been investigated. This research used density functional theory (DFT) calculations to determine the structure of possible tridentate complexes and to determine reaction energies and activation barriers for forming different structures. Tridentate binding between arsenate and ferric hydroxide was found to be thermodynamically favorable for arsenate binding to two or three adjacent dioctahedral ferric hydroxide clusters. In addition, arsenate was also observed to form As–O–As bonds simultaneously to forming bidentate binuclear bonds with ferric hydroxide. The As–Fe distances in the tridentate complexes differed from those calculated for bidentate complexes by an average distance of only 0.045 Å. This suggests that spectroscopic methods (EXAFS) may not be able to distinguish bidentate from tridentate complexes based on interatomic distances. Formation of tridentate complexes required overcoming activation barriers ranging from 13 to 51 kcal/mol. Breaking of tridentate complexes had even greater activation barriers ranging from 18 to 62 kcal/mol. This suggests that tridentate complexation may contribute to previously observed extremely slow adsorption and desorption reactions of arsenate with ferric hydroxide.

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1. Introduction

Arsenate complexation reactions with iron oxide minerals and ferric hydroxide coated aquifer sediments play an important role in determining the transport and fate of arsenic in the environment. Furthermore, arsenate complexation with adsorbents containing ferric hydroxide is commonly used to remove arsenic from potable water. Thus, the types of complexation reactions of arsenate with ferric hydroxide have received considerable research attention. However, there still remain some unexplained phenomena associated with arsenate reactions with ferric hydroxide. The foremost of these are very slow adsorption kinetics for a fraction of the arsenate, and the apparent irreversible binding of some fraction of the adsorbed arsenate (O'Reilly et al., 2001; Chaudhary and Farrell, 2015).

Arsenate adsorption to ferric hydroxide occurs via several mechanisms that include both physical and chemical adsorption. X-ray absorption fine structure (EXAFS) spectroscopy along with density functional theory modeling have been used to deduce the adsorption mechanisms of arsenate on ferric hydroxide (Kubicki, 2005; Sherman and Randall, 2003). Several studies indicate that physical adsorption occurs via electrostatic interactions between the negative charges on $H_2AsO_4^{1-}/HAsO_4^{2-}$ species and areas of positive charge on ferric hydroxide (Farrell and Chaudhary, 2013). These electrostatic interactions can be enhanced by charge-assisted hydrogen bonding, in which one or more hydrogen bonds form between the O-atoms of arsenate and the H-atoms of ferric hydroxide. Chemical adsorption involves a ligand exchange between arsenate and a $-OH$ or $-OH_2$ ligand bound to the central Fe atom in a 6-coordinated octahedral structure. Chemical adsorption may involve formation of a monodentate complex in which a single Fe—O—As bond forms between iron and arsenate (Waychunas et al., 1993, 1995). These monodentate bonds are described as ^1C if the Fe—O—As bond is on a corner site (i.e., at the apex of the octahedral unit) or ^1E, if the bond is at the edge site of the octahedral unit (Sherman and Randall, 2003). Complexation may be bidentate-binuclear (^2C) where a single arsenate species forms two Fe—O—As bonds to two adjacent corner Fe atoms. Bidentate-mononuclear complexes (^2E) may also form where an arsenate species forms two Fe—O—As bonds with a single Fe atom along the edge of the octahedral unit (Fendorf et al., 1997).

Although there is no definitive evidence for tridentate arsenate complexes, based on As—Fe coordination numbers, Waychunas et al. (1993) have speculated that arsenate adsorption by ferrihydrite may involve tridentate complexes. The difficulty in identifying tridentate complexes is that they have similar As—Fe distance as bidentate complexes (Foster, 2003). In the Waychunas et al. (1993) study, the As—Fe coordination numbers on ferrihydrite averaged 3.02, suggesting that 3 of the 4 apices of the arsenate tetrahedra were attached to an Fe octahedral unit. However, these conclusions based on coordination numbers can not be considered definitive, since EXAFS spectroscopy is not very sensitive to coordination numbers (Foster, 2003).

The formation of tridentate complexes may be aided by the nanocrystalline nature of ferrihydrite. Crystallites lengths of 8–15 Å have been observed in x-ray scattering studies (Fuller et al., 1993). These crystallites aggregate and are held together by van der Waals forces, forming gelatinous flocs of 100 nm or larger in size (Bottero et al., 1991; Tchoubar et al., 1991). Some investigators have proposed that arsenate may form bridges between ferrihydrite crystallites (Fuller et al., 1993). For arsenate adsorption to ferrihydrite, observations of As—Fe coordination numbers as high as 4.25 suggest that disordered aggregates of ferric oxyhydroxyl units can form as many bonds with arsenate tetrahedra as the local geometry permits (Waychunas et al., 1993). In crystalline ferric hydroxides, such as, goethite, tridentate complexes appear to be less likely, as evidenced by lower coordination numbers than those observed for ferrihydrite (Waychunas et al., 1993).

When examined on the time scale of laboratory experiments, arsenate adsorption does not exhibit reversible equilibrium or kinetic behavior (Yean et al., 2005; Yang et al., 2012; He et al., 2011). The rate of arsenate adsorption to ferric hydroxide has been shown to display biphasic kinetics, with the majority of arsenate uptake occurring on a time scale of minutes, while the remaining uptake occurs on a time scale of weeks to months (Zhang and Stanforth, 2005; Zhang and Selim, 2005; Grossl et al., 1997; Yang et al., 2012). For example, Fuller et al. (1993) found ~75% of arsenate uptake by ferrihydrite occurred in less than 5 min, but additional adsorption continued to occur over at least 8 days. Desorption of arsenate from ferric hydroxide has also been found to display biphasic kinetics. Regeneration of a variety of ferric hydroxide adsorbents loaded with arsenate showed that 75–90% of the adsorbed arsenate was released from the adsorbents by 0.1–5 M NaOH solutions within minutes, but the remaining arsenate was released at rates that were more than two orders of magnitude slower (Chaudhary and Farrell, 2015).

Several mechanisms have been proposed to explain the biphasic kinetics for arsenate adsorption and desorption. Fast adsorption followed by a slow surface precipitation process has been proposed for explaining biphasic adsorption kinetics (Jia et al., 2006; Hongshao and Stanforth, 2001). Other investigators have proposed that slow intraparticle diffusion to and from remote adsorption sites limits rates of arsenate adsorption and desorption (Fuller et al., 1993; Raven et al., 1998 Luengo et al., 2007). Contradicting the diffusional hypothesis is the fact the rate of slow arsenate uptake has been observed to be independent of the effective particle size of the ferric hydroxide (Zhang and Stanforth, 2005). Zhang and Stanforth (2005) proposed that heterogeneity in the surface site binding energies or other surface reactions can explain the biphasic kinetics. Supporting the surface reaction hypothesis as the rate limitation for arsenate adsorption are DFT calculations of the activation barriers for different modes of arsenate adsorption (Farrell and Chaudhary, 2013). Physical adsorption promoted by electrostatic effects was found to have no activation barrier, with adsorption energies ranging from −5 to −14 kcal/mol, depending on the surface charge. Formation of monodentate complexes was found to have activation barriers ranging from 15 to 17 kcal/mol. Conversion of monodentate to bidentate complexes had even higher activation barriers ranging from 19 to 27 kcal/mol, with lower barriers at more negative surface charges.

The goal of this research was to investigate the reaction energies and activation barriers for tridentate arsenate complexes on ferric hydroxide, and to assess their effects on the kinetics of arsenate adsorption and desorption from ferric hydroxide. Towards those ends, DFT simulations were performed for a variety of possible tridentate adsorption complexes. Calculated reaction energies and activation barriers were use to assess the likelihood of different binding modes, and to asses their contributions to kinetically slow adsorption and desorption reactions. Formation of several different tridentate complexes was found to be energetically favorable, with some of the complexes having high activation barriers for both adsorption and desorption.

2. Materials and methods

DFT simulations were performed to determine the Gibbs free energy changes for complexation reactions and to determine the activation barriers for forming or breaking surface complexes. Amorphous ferric hydroxide was simulated using clusters identical to those used in several previous DFT studies of arsenate binding to