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## Adsorption of arsenate on Fe-(hydr)oxide

N Y Acelas<sup>1</sup> and E Flórez<sup>1</sup>

<sup>1</sup> Universidad de Medellín, Medellín, Colombia

E-mail: nyacelas@udem.edu.co

**Abstract.** Adsorption using metal oxide 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. The high number of oxyanions in aquatic ecosystems causes serious pollution problems. Removal of arsenate ( $\text{H}_2\text{AsO}_4^-$ ), is one of the major concerns, since it is a highly toxic anion for life. Within the metal oxides, the iron oxide is considered as a suitable material for the elimination of oxyanions. The adsorption of  $\text{H}_2\text{AsO}_4^-$  on Fe-(hydr)oxide is through the formation of inner or outer sphere complexes. In this work, through computational methods, a complete characterization of the adsorbed surface complexes was performed. Three different pH conditions were simulated (acidic, intermediate and basic), and it was found that, the thermodynamic favourability of the different adsorbed complexes was directly related to the pH. Monodentate complex ( $\text{MM}_1$ ) was the most thermodynamically favourable complex with an adsorption energy of  $-96.0\text{kJ/mol}$  under intermediate pH conditions.

### 1. Introduction

Arsenic (As) is mobilized to the environment through natural processes (weathering, biological activities, volcanic emissions), and anthropogenic (mining, fossil fuels, pesticides, etc.) and, even at low concentrations is toxic to humans [1]. The presence of arsenic in surface (rivers, lakes, reservoirs) and underground waters (aquifers) constitutes a major threat to health. Therefore, the World Health Organization (WHO), the European Union (Directive 98/83) and the US Environmental Protection Agency (USEPA) have established a reduction of the permitted limit of arsenic in drinking water from  $50$  a  $10\mu\text{g/l}$  [2].

Arsenic is mainly found as the oxyanion,  $\text{H}_2\text{AsO}_4^-$ , when the pH value in water is  $<6.9$ . An efficient method to control the contamination of aquatic ecosystem caused by arsenate is to binding it at water/mineral interfaces. Infrared (IR) spectra is particular useful to explore protonation and adsorption mechanism at solid/liquid interfaces [3]. Previous studies have indicated that the IR vibrational spectra of arsenate on several minerals (such as goethite, ferrihydrite and anatase) contain abundant coordination information [4,5]. It has been reported that the predominate adsorption species when arsenate interacts with hydrated iron oxides are inner sphere complexes [6,7]. However, the exact geometry of the surface complex (monodentate or bidentate) is unknown.

There is still some discussion on this topic and the effect of factors such as, pH and thermodynamic favourability of each surface complex is not clear. Therefore, computational methods are an alternative to study adsorption problems [8-10]. The goals of this work are: (i) to help in the understanding of the factors driving thermodynamic preferences for the adsorption of arsenate over Fe-(hydr)oxide and (ii) to understand the modes of adsorption in inner and outer sphere complexes as a function of pH.



## 2. Computational details and models

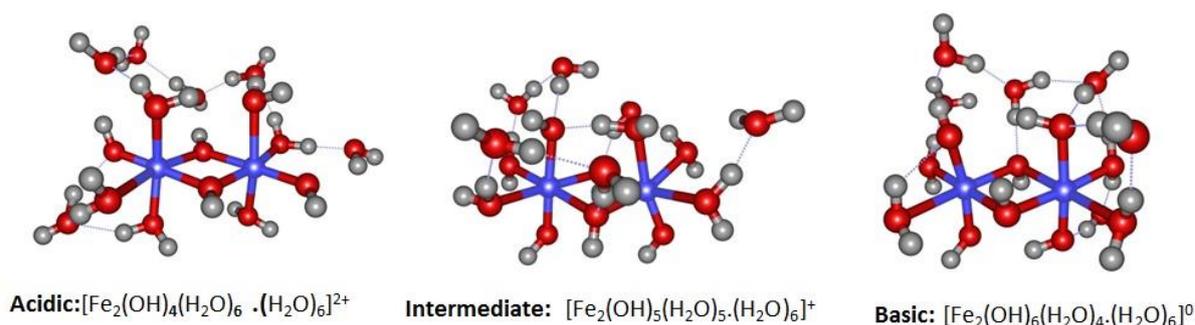
Following models previously worked by some authors [8,9] the iron oxide was simulated using two iron atoms in octahedral coordination with 10 atoms of oxygen. In order to simulate various pH conditions, the  $\text{-OH}^-/\text{-H}_2\text{O}$  ratios was adjusted in the initial clusters as follows: cluster with 4/6  $\text{OH}^-$  to  $\text{H}_2\text{O}$  with net charge of +2 correspond to acidic pH; 1/1 ratio have net +1 charges corresponding to intermediate pH conditions, and basic conditions correspond to those with the 6/4 ratio and a net charge of 0. The Gibbs free energies of adsorption (equation 1) for the different surface complexes under the three simulated pH conditions were estimated using a series of stoichiometric ratios.

$$\Delta G_{\text{ads}} = G_{\text{complex}} - [G_{\text{H}_2\text{AsO}_4^-} + G_{\text{cluster}}] \quad (1)$$

The specie of Arsenate used for the adsorption process was the oxyanion,  $\text{H}_2\text{AsO}_4^-$ . To simulate its molecular properties in aqueous phase it was microsolvated with six water molecules. The other species involved in the adsorption processes such as:  $[\text{OH}(\text{H}_2\text{O})_7]^-$ ,  $[(\text{OH})_2(\text{H}_2\text{O})_6]^{2-}$ ,  $[\text{OH}(\text{H}_2\text{O})_6]^-$ ,  $(\text{H}_2\text{O})_8$ ,  $(\text{H}_2\text{O})_7$ , and  $(\text{H}_2\text{O})_6$  were obtained by the use of the ASCEC algorithm, a stochastic-like search strategy [11]. The optimization of each complex under different pH conditions was carried out using the PBE0 functional and the DEF2TZVP basis set on O, H, and as atoms. The LANL2DZ relativistic electron core potential (RECP) was used for Fe. To verify that the optimized structures were minimal in the potential energy surface harmonic vibrational frequencies were calculated (i.e., no imaginary frequencies). Taking into account that the adsorption process occurs in aqueous medium, the short-range solvent effect was simulated by the inclusion of six molecules of water during the optimization process of each specie. We have shown before [8] that long-range solvent effects heavily influence adsorption free energies. To account long-range solvent effect polarized continuum model (IEFPCM) was used. All calculations were performed with the Gaussian 09 program [12]. In our previous work [9] it was shown that for clusters containing  $\text{Fe}^{3+}$  atoms, their stability is favoured in high spin states and therefore, all the calculations carried out here were made in the cluster of iron in multiplicity of 11.

## 3. Results and discussion

Figure 1 shows the clusters used to simulate the different adsorption processes of arsenate anion under the three simulated pH conditions. All the geometric parameters in our calculations for the Fe-(hydr) oxide clusters are in very good agreement with the experimental geometric parameters reported for goethite [13]. It indicates that this is a suitable model to do the simulations.



**Figure 1.** DFT-calculated clusters of Fe-(hydr) oxide under acidic (charge+2), intermediate (charge +1), and basic (charge 0) pH conditions. Red, blue, and grey spheres denote O, Fe, and H atoms, respectively. The total spin multiplicity of 11 was considered for all cases.

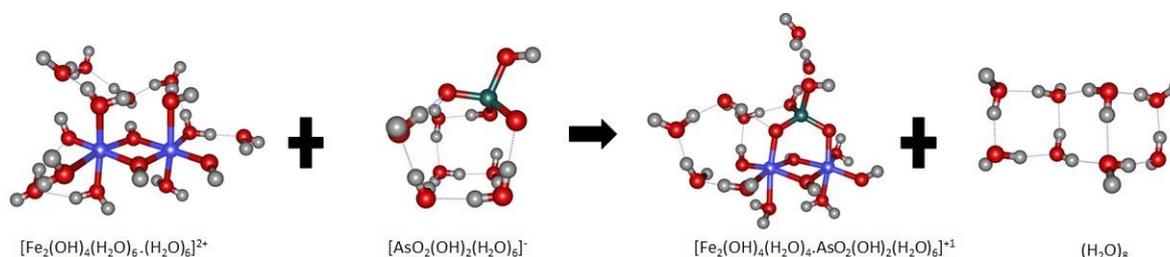
### 3.1. Formation of surface complexes

In the literature there are several reports related to the surface models for arsenate complexation on oxides [1,14]. Inner sphere complexes, Monodentate Mononuclear (MM) and Bidentate Binuclear (BB) have been reported as the most likely adsorption modes of arsenate species when they are coordinated

with metal oxides [14]. Figure 2 shows the adsorption reaction to form the inner sphere complex, BB, under acidic pH conditions.

The arsenate adsorption on Fe-(hydr)oxide as inner sphere complexes (BB or MM) can be explained as a ligand exchange process between the oxide surface functional groups and the oxygen atoms of the anion. BB complexes are formed by exchanging two functional groups present on the oxide surface while MM complexes are formed by the exchange of one functional group of the oxide surface.

The functional group present on the oxide surface depends on the pH conditions, as follows: under acidic pH conditions  $\text{-H}_2\text{O}$  functional groups will be exchanged; at basic pH conditions the exchanged will be with only  $\text{-OH}^-$  functional groups and at intermediate pH conditions, both groups  $\text{-H}_2\text{O}$  and  $\text{-OH}^-$  are exchanged, which leads to the possibility to form two types of monodentate complexes,  $\text{MM}_1$  complexes if the group  $\text{-H}_2\text{O}$  is exchanged and  $\text{MM}_2$  with the exchange of  $\text{-OH}^-$  group.



**Figure 2.** Adsorption of arsenate as bidentate complex on Fe-(hydr)oxide under acidic pH conditions. Red, blue, green, and grey denote O, Fe, As and H atoms, respectively.

The adsorption of arsenate as outer-sphere complex (H-bonded), it is suggested that occurs by intermolecular interaction (hydrogen bonds) of the reactive oxygen atoms of arsenate and the surface functional groups of the oxide, without ligand exchange. Similar pathways have been reported in the literature for the adsorption of oxoanions on metal oxides [1,8-10]. Figure 3 shows optimized structures of all inner and outer sphere complexes.

The prediction of the thermodynamic favourability of the different adsorption modes by experimental tools is difficult and through IR spectroscopy is possible to obtain a mix of all adsorption modes [15]. Therefore, these experimental models need to be complemented by computational results. Surface complexation modelling [1,8-10,14,16] has the capability to predict the behaviour and the nature of adsorbed arsenate species as a functions of environmental parameters, such as pH.

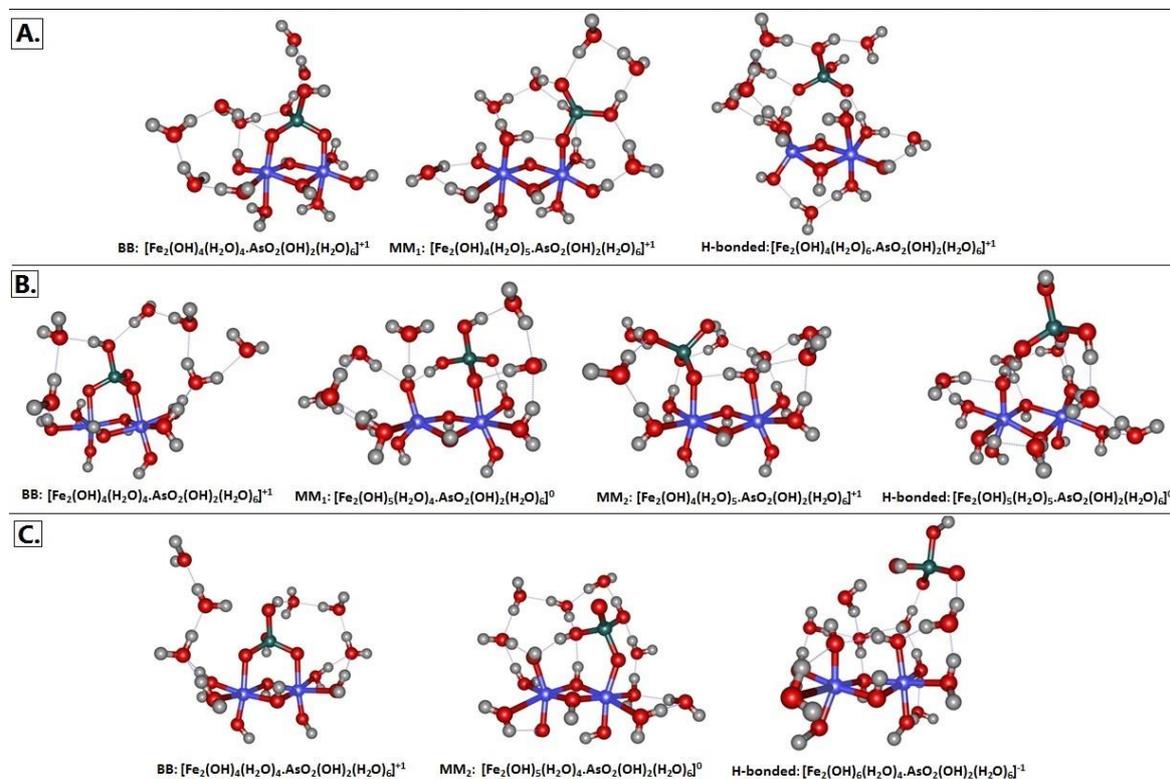
### 3.2. Gibbs free energies of adsorption

It is important to determinate the Gibbs free energy to identify the most favourable adsorption mode under certain experimental conditions. Gibbs free energy was calculated according to equation (1), by subtracting the total energy of the reactant species from the total energy of the product species in aqueous phases (Figure 3).

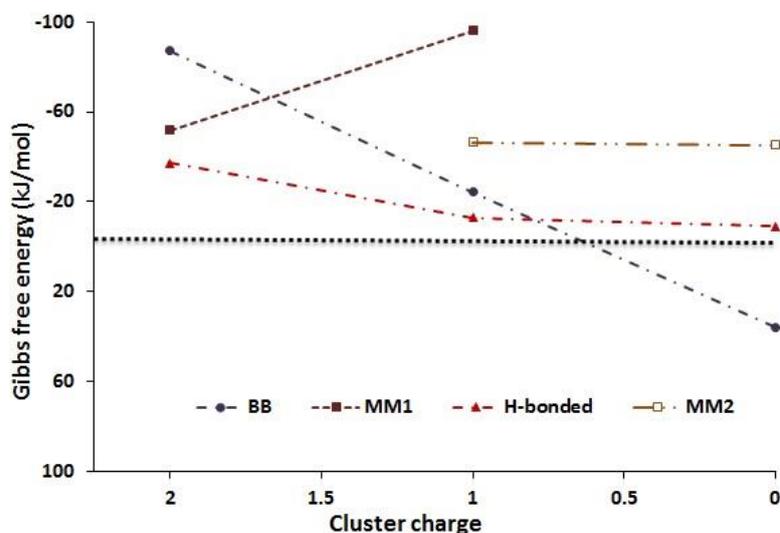
Figure 4 shows the energy curves of arsenate adsorption on Fe-(hydr)oxide. It can be seen that the thermodynamic favourability for adsorption as an inner and outer sphere complexes is directly related to pH. Under acidic pH conditions both types of adsorption are energetically favourable from  $-87.01\text{kJ/mol}$  to  $-37.03\text{kJ/mol}$ , whereas at basic pH conditions the thermodynamic favourability for the different adsorption modes decreases. For BB complex an adsorption energy of  $+36.10\text{kJ/mol}$  was found.

From Figure 4, it can be concluded that although at intermediate pH conditions the most thermodynamically favourable compound ( $\text{MM}_1 = -96.00\text{kJ/mol}$ ) is found, under acidic pH conditions there are high variety of favourable complexes. BB complex formed under acidic pH condition is only  $+9\text{kJ/mol}$  more energetic that the  $\text{MM}_1$  complex generated under intermediate pH conditions. Our results are in agreement with those reported by some authors as follows: (i) Ladeira *et. al.* 2001. [17] demonstrated that during the adsorption of arsenate on aluminium oxide clusters, the BB specie was more stable than the MM complexes. (ii) Sherman and Randall, 2003. [18] using DFT and EXAFS data,

suggested that the adsorption of arsenate on iron hydroxide clusters was as a BB complex. And, (iii) Kubicki, 2005 [19] showed by using computational methods that the formation of BB complexes during the adsorption of arsenate on iron hydroxide clusters resulted in good agreement with spectroscopic data.



**Figure 3.** DFT-calculated structures of inner and outer sphere adsorption products of arsenate on Fe-(hydr)oxide (a) acidic; (b) intermediate; and (c) basic pH conditions. Note: Red, blue, green, and grey denote O, Fe, As and H atoms, respectively. MM<sub>1</sub>: Monodentate mononuclear complex exchanged to one  $-\text{H}_2\text{O}$  surface functional group and MM<sub>2</sub>: Monodentate mononuclear complex exchanged to one  $-\text{OH}^-$  surface functional group.



**Figure 4.** Gibbs free energies of arsenate adsorption on various protonated Fe-(hydr)oxide surfaces at different pH conditions. MM<sub>1</sub>: Monodentate mononuclear complex exchanged to one  $-\text{H}_2\text{O}$  surface functional group and MM<sub>2</sub>: Monodentate mononuclear complex exchanged to one  $-\text{OH}^-$  surface functional group.

According to above, it is possible to conclude that during the adsorption process of arsenate on Fe-(hydr)oxide a mixture of thermodynamically favourable surface complexes is generated and computational tools allow to characterize them separately. BB configuration is most consistent with spectroscopic data, but Gibbs free energies of adsorption suggested that the MM<sub>1</sub> configuration is energetically more stable.

#### 4. Conclusion

In this work, a characterization of the potential energy surface for the adsorption of arsenate on Fe-(hydr)oxide surfaces under aqueous environments at three different pH conditions (acidic, intermediate and basic) was made. Our results show that monodentate (MM<sub>1</sub>) complex under intermediate pH conditions and bidentate complex (BB) under acidic pH conditions are preferred, and we support this claim by the calculated adsorption energies of -96.00kJ/mol and -87.01kJ/mol for MM<sub>1</sub> and BB, respectively.

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