Adsorption of As(III) and As(V) compounds on $\text{Fe}_3\text{O}_4(001)$ surfaces: A first principle study

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Keywords: Arsenic, Iron oxides, Adsorption, Density functional theory

ABSTRACT.

The adsorption of arsenic species on magnetite has been studied by first principles calculations. From the considered anionic species, a higher adsorption energy was found for the complexation of $\text{Fe}_3\text{O}_4(001)$ with As(III) being 1.3 eV higher than the adsorption energy for As(V). In the case of As(III), a large partial band charge density was found, which was associated to the O-Fe bond formation, while more delocalized electron density was found in the adsorption of As(V) subspecies, with the formation of two Fe-O bonds. A comparison with sorption of neutral arsenic

atoms and O₂ molecule was also considered. As(V) is mainly adsorbed on the surface with a double O-Fe bond formation, similar to the case of O₂ in the most stable configuration.

1. Introduction

In the last few years, the presence of metalloids and heavy metals in aqueous sources has been a major concern and it is going to be even more important as the water consumption increases. In this context, several pollutants found via natural processes such methylated arsenicals, or heavy metals (Pb, Cd, Cr, etc.) from several anthropogenic activities have been investigated [1-4]. Arsenic is a metalloid which can be found in contaminated water in two different oxidation states: arsenite As(III) and arsenate As(V) and with different protonated subspecies going from AsO(OH)₃ to AsO₄³⁻ and As(OH)₃ to AsO₃³⁻. These subspecies are controlled by the acidic conditions present in water from which can be related to the pH and pK values. These arsenic species are considered as carcinogen agents by the World Health Organization and their ingestion are considered treats to the human health [5], as for example, in the disruption of the production of adenosine triphosphate, which is the responsible of energy transportation in cells [6]. The high toxicity of the pollutants has demanded new alternatives to purify water resources. In particular, a great attention has been put into the application of iron nanoparticles to capture these arsenic compounds [7,8]. The atomic nanoparticle surface reconstruction, obtained from its natural oxidation process, is observed at different pH conditions. These conditions promote the nucleation of iron oxides polycrystals on the surface of the nanoparticles, which happen to be related to their sorption capabilities [9]. This surface reconstruction has been experimentally characterized by considering several external conditions [10]. The obtained results show the

presence of magnetite, hematite, lepidocrocite and other iron oxyhydroxide structures at the nanoparticle surface. In the case of magnetite, it was demonstrated that this compound grows on the nanoparticle with a (001) orientation which is the dominant orientation, even though, in small rate, it is possible to find the (111) and (110) orientations [11-13].

The presence of different Fe oxidation states has been directly related to the sorption capacity of the nanoparticles [1,7,9,14,15] as it interacts with different metallic atoms (Cr, Cu, Pb, etc.) or metalloids such as Arsenic molecular species. The interaction between arsenic molecules with iron oxides and oxy(hydr)oxides surfaces leads to the formation of inner-sphere complexes during the adsorption process and eventually the formation of covalent bonds between the adsorbed species and the surface atoms.

In this work, we study the interaction of arsenic complexes in contact with iron oxide surfaces at the atomic scale. Even though the hydrated iron oxide surface is a more realistic condition in the sorption process, an ideal surface can be suitable to study specific interactions between arsenic species and the magnetite.

Our results clarify how the different associated oxidation states of the adsorbed molecules are chemisorbed by iron nanoparticles, which is a relevant process for the pollutant problem as previously discussed. A detailed analysis of the structural changes due to the interaction between arsenic compounds and the Fe_3O_4 surface is presented. Electronic and magnetic properties such as charge density and magnetic moments are reported as a function of different arsenic complexes. We have selected only two different As complexes with two different oxidation states as they are the most common when As is present as water pollutant, as it has been concluded in experimental measurements [16-18].

2. Methodology

2.1. Computational Methods

In order to calculate the total energy and simulate the structural optimization of pristine magnetite and the adsorption of different molecules we have performed first principle calculations based on the density functional theory (DFT)[19] within the generalized gradient approximation (GGA) and with the exchange-correlation functional proposed by Perdew et al. and also known as PBE [20]. DFT has been extensively used to study iron oxides crystals and surfaces [13,21] as well as molecular adsorption. In general, good agreement with experimental results have been reported [22,23]. The numerical simulations as well as the electronic description are obtained by using an expansion of the Kohn-Sham orbitals with the augmented wave based method (PAW) as implemented in the VASP package [24].

Although spin-polarized system has been considered in our calculations, spin-orbit coupling contribution was neglected, mainly because it is expected that changes in the electronic properties are small with respect to it. In this context, initial magnetic moments were defined following the ferrimagnetic configuration associated to magnetite, which means that Fe atoms occupy octahedral and tetrahedral sites with opposite magnetic moments, as it has been recognized by interpreting the experimental results for bulk magnetite [25-27]. Due to the strong correlation present in the localized d-states of Fe, standard LDA and GGA functionals are unable to describe correctly the electronic configuration of these systems. Therefore, we have considered the DFT+U method to correct the lack of strong correlation in these functionals by following the approach given by Dudarev et al. [28]. This method introduces a correction to the used functional by adding a term obtained from the Hubbard Hamiltonian, where the on-site Coulomb repulsion, U , was set 4.5 eV and the exchange parameter, J , was set to 0.89 eV. Both parameters have been already used in the literature with good agreement in structural and

electronic properties of iron oxides between theoretical predictions and experiments [22, 29]. In order to consider possible effects of van der Waals corrections in the sorption study, due to fluctuations in charge density of the surface, we have added the correction optPBE-vdW of a non-local correlation functional proposed by Klimes et al. [30]. The energy cutoff for the plane wave expansion part of the PAW functions was set to 400 eV, where well converged results were obtained (0.01 meV per unit cell for the energy and 0.001 eV/Angs for interatomic forces). The forces and stresses were minimized by following the conjugated gradient algorithm. In order to have a good representation of the Kohn-Sham orbitals in the reciprocal space, our simulations considered a Monkhorst-Pack grid with a grid of 8x8x1 for all surface calculations. A empty space of 14 Angs was considered to avoid periodic interactions of the considered slab geometry.

3. Results

3.1 Fe_3O_4 bulk structure

In order to validate the parameters considered in our study, we started our work with the bulk structure of Fe_3O_4 . The ground state of this material corresponds to an inverse spinel structure with space group $Fd3m$, where the 32 oxygen anions crystallize in a close-packed fcc lattice and the Fe atoms are located at the interstitial sites grouped in 8 Fe^{3+} (tetrahedral sites) and 16 Fe^{2+} (octahedral sites) ions. The obtained interatomic distances were $d(O-Fe^{tet})=2.056$ Angs. and $d(O-Fe^{oct})=1.892$ Angs., while the octahedral planes are separated by 2.09 Angs. and the optimized lattice parameter was $a= 8.934$ Angs, which are consistent with the experimental results [31]. The magnetic moments associated to tetrahedral and octahedral sites are -4.02 and 3.92 respectively and are depicted as blue arrows in Fig. 1A, which result on slightly higher values than experimental results [32]. The calculated density of states (DOS) (see Fig. 1B) shows a half-metallic behavior due to the insulating behavior of the majority spin band (black line) and the

metallic behavior due to the presence of the minority spin band (red line) around the Fermi level E_F , which is in agreement to the results previously reported by Arras *et al.* [33].

Figure 1. Fe_3O_4 Magnetite crystal structure and total electronic DOS. Figure A shows the optimized atomic structure with the atomic magnetic moments (represented by blue arrows). Golden and red atoms correspond to Fe and O atoms respectively. Right hand side (B) shows the electronic density of states, where the spin majority is plotted in black, while the spin minority in red and with a negative sign for the total DOS.

3.2. $\text{Fe}_3\text{O}_4(001)$ surface

The Fe_3O_4 structure mainly grows, at natural conditions, along the (111) and (001) directions, being (110) a less common orientation of the structure [11]. Theoretical studies have suggested that $\text{Fe}_3\text{O}_4(001)$ (see Fig. 2) is thermodynamically more favorable than other orientations [12,13]. This orientation can be identified as a stacking sequence of alternating layers of octahedral (odd L in Fig. 2 a) and tetrahedral (even L in Fig. 2 a) coordination sites. From the (001) orientation, the octahedral Fe termination is energetically more favorable than the tetrahedrally coordinated Fe [12, 34]. In our work we have considered a system in a simulation unit with lateral dimension of 8.39 x 8.39 Angs, while the perpendicular axis was set up to 22.39 Angs, given an actual slab dimension of 8.5 Angs and a periodic image distance of 14 Angs

vacuum, to avoid spurious slab interactions. Eight layers were considered to build the simulated slab as depicted in Fig. 2a, where the first 4 layers were allowed to fully geometrically relax and the last 4 were kept fixed during the geometry optimization process to simulate the bulk behavior. Therefore, we are assuming that the surface relaxation occurs within the first top layers, a fair assumption which has proven to be quite accurate in similar systems [13, 35]. In this context, a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction of $\text{Fe}_3\text{O}_4(001)$ has been obtained after the surface relaxation (see Fig. 2b and 2c), in agreement to experimental results [36]. This has been attributed to a Jahn-Teller distortion effect from the different d -orbital occupation [12]. On the top layer there is a Fe atom with two O atoms bonds at 1.99 Angs and two O atoms at 2.01 Angs, which shows a nonequivalent distortion with respect to the 2.06 Angs obtained in the bulk structure. Fig. 2d shows the projected DOS of the relaxed surface, depicting only the contributions of the relaxed layers, where majority states near the Fermi level were associated to the unrelaxed and fixed atoms of the last layers (L7 and L8) and identified as orange lines in the bandstructure (see Fig.2e), therefore their contribution can be separated of the sorption analysis. These results are in agreement with the study of stability and electronic structure reported by Fonin *et al.* [36].

Figure 2. Top left side (a) shows a lateral view of a relaxed $\text{Fe}_3\text{O}_4(001)$ surface indicating the considered slab of eight layers, (b) top center depicts the surface reconstruction after the relaxation and (c) top right side shows the (001) orientation. Red balls denote oxygen atoms while orange and grey balls are octahedral and tetrahedral Fe atoms respectively. Bottom left (d) shows the resolved projected DOS per atom and orbital. Bottom right side (e) shows the electron band structure along the most important symmetry points and orange lines are associated to the non-relaxed and fixed atoms of the bottom layers.

3.3 O_2 molecule on $\text{Fe}_3\text{O}_4(001)$ surface

The adsorption of O_2 molecules on $\text{Fe}_3\text{O}_4(001)$ surface under vacuum conditions was considered. Two different initial configurations were taken into account: (i) Oxygen atom on top of the surface Fe atom and in the other O between of two Fe atoms, and (ii) An oxygen dimer sits between two Fe atoms. The most energetically favorable configuration was obtained when the

two O atoms were bounded to the octahedral Fe atoms at a distance $d(\text{Fe-O})=1.983$ Angs (see Fig 3c), while the O-O inter molecular distance was 1.414 Angs, a bit longer than the isolated equilibrium O-O distance (1.246 Angs). The atomic projected DOS obtained in this case shows two specific peaks associated to the O molecule and located around the Fermi level and 0.3 eV below the Fermi level respectively (depicted as blue lines in the projected DOS Fig. 3A). To identify the bond formation between the O_2 molecule and the surface, the partial charge density was calculated within -0.4 to -0.2 eV energy range, this analysis allowed us to associate the peak at 0.36 eV below Fermi level to adsorbed oxygen, which is consistent with the depicted blue lines of the bandstructure (Fig. 3b). The partial band charge density isosurface is evaluated around the first molecular peak (at 0.2 eV below Fermi level), showing the partial electronic density localized between the molecular Oxygen atoms and the Fe atoms from the surface. The adsorption energy is evaluated in order to estimate the strength of the interaction between the surface and O_2 molecule and obtained from

$$E_{ads} = E_{Surf} + E_{Mol} - E_{Total},$$

where the E_{Surf} and E_{Mol} are the energies of the surface and the molecule respectively and calculated with the same cell, k points and energy cutoff as in the joined system. Therefore, a positive value is associated to a stable adsorption. In our case the adsorption energy for O_2 was 1.116 eV (25.736 kJ/mol). In the case of the magnetic moments, there is no significant change after the adsorption of O_2 , being the largest variation produced at the octahedral Fe ($4.122 \mu_B$) of the third layer with an increase of 4% respect to the reconstructed surface ($3.958 \mu_B$).

Figure 3. Top left figures shows the projected DOS of $\text{Fe}_3\text{O}_4(001) + \text{O}_2$ system per species. Bottom left side shows the corresponding band structure while the bottom right side depicts the optimized atomic structure and the partial band charge density associated to the bond between O_2 and the surface. Golden and red atoms correspond to Fe and O atoms respectively. The isosurface value of the partial charge density is $0.0005 \text{ e}/\text{\AA}^3$.

3.4 As(III) and As(V) species

We have considered two species of Arsenic typically studied in polluted water: Arsenate and Arsenite. These species are capable to form inner-sphere complexes on the surface of iron oxides [37,38]. Under normal and moderated acidic conditions, Arsenate ($\text{AsO}_2(\text{OH})_2^-$ and $\text{AsO}_3(\text{OH})^{2-}$) and Arsenite ($\text{AsO}(\text{OH})_2^-$ and $\text{As}(\text{OH})_3$) are some of the dominant subspecies found in contaminated water [39]. In order to compare the adsorption energies of the anionic species, we

have included the study of two neutral cases ($\text{AsO}_2(\text{OH})_2$ and $\text{AsO}(\text{OH})_2$). Before adsorption, the isolated molecules are geometrically optimized under the same conditions of the simulated slab. The As-O bonds obtained for $\text{AsO}(\text{OH})_2^-$ were one short bond at 1.71 Angs (unprotonated O atom) and two larger bonds (protonated O atoms) at 1.92 Angs, compared to the experimental average As-O bond 1.77 Angs obtained with EXAFS spectra analysis of As(III) by Ramirez-Solis and coworkers [40]. These interatomic distance values agree with other DFT calculations performed for $\text{AsO}(\text{OH})_2^-$ by Wei *et al.* [41]. If we consider the neutral $\text{As}(\text{OH})_3$ molecule, the As-O distance is almost the same and averaged to 1.84 Angs. Similarly, in the case of $\text{AsO}_2(\text{OH})_2^-$, the As-O distance shows a substantial difference between the OH group (1.87 Angs) and unprotonated O atoms (1.68 Angs). Finally, the $\text{AsO}_3(\text{OH})^{2-}$ has a As-O distance of 1.89 Angs for OH group and a shorter As-O distance (1.72 Angs) for unprotonated O atoms. From these results we have obtained optimized isolated molecules where the energy difference between HOMO and LUMO levels was 0.78 eV for $\text{AsO}(\text{OH})_2^-$, 5.35 eV for $\text{As}(\text{OH})_3$, 1.39 eV for $\text{AsO}_2(\text{OH})_2^-$ and finally 0.01 eV for $\text{AsO}_3(\text{OH})^{2-}$ respectively for each anionic case, and being therefore $\text{As}(\text{OH})_3$ the most stable molecule subspecies under vacuum conditions. The obtained partial charge density revealed a LUMO contribution mainly localized around the O atoms with no H bonds, and therefore associated with the more reactive sites of the molecule.

Figure 4. Side and top views of the possible configurations considered for arsenic molecules on $\text{Fe}_3\text{O}_4(001)$ surface. The possible adsorption cases (a), (b), (c), (d), (e) and (f) are referred to As(III) subspecies while (g), (h), (i), (j) and (k) are the configurations for As(V) subspecies. Golden, red, yellow and light-blue balls correspond to Fe, O, As and H atoms respectively.

3.5 $\text{AsO}(\text{OH})_2$ on $\text{Fe}_3\text{O}_4(001)$ surface

The adsorption of arsenite species on $\text{Fe}_3\text{O}_4(001)$ surface was considered with two subspecies: $\text{AsO}(\text{OH})_2^-$ and $\text{As}(\text{OH})_3$. Six different configurations of these molecules on the surface were considered (see Fig. 4): (a) oxygen atom on top of surface Fe atom, (b) Arsenic atom on top of surface Fe atom, (c) O atom on top of surface Fe atom with a different molecular orientation than

(a), (d) O atom between two surface Fe atoms, (e) As atom on top of O atom, and finally (f) H atom on top of O atom. The lowest energy of $\text{AsO}(\text{OH})_2^- + \text{Fe}_3\text{O}_4(001)$ system was obtained with the oxygen atom bounded to the octahedral Fe atom (c case in Fig. 4) and $d(\text{Fe-O})=1.907$ Angs. as shown in Fig. 5c. The associated adsorption energy of $\text{AsO}(\text{OH})_2^-$ was 2.067 eV, which is smaller than the adsorption of neutral $\text{AsO}(\text{OH})_2$ (2.907 eV). Interatomic and interlayer distances for the selected configurations are summarized in Table 1 and 2. The surface structural rearrangement, after the $\text{AsO}(\text{OH})_2^-$ adsorption, has the major impact on the first surface layer (L1) generating a separation of 1.005 Angs., which represents a 16% expansion with respect to the pristine surface while the rest of the interlayer distances are changed by less than 6% (Table 1). Projected DOS of the surface after complexation, as depicted in Fig.5a, shows some peaks around 1.4 eV below the Fermi level which are associated to the oxygen atoms from the arsenic molecule. In particular, we have obtained a partial band charge density around -1.7 eV associated to minority states (blue line in band structure Fig. 5B) with an important concentration located around the oxygen atom of Arsenic molecule that is connected to the Fe surface atom (see Fig. 5C). The obtained isosurface is mainly associated to a high density of states of p minority states. The magnetic moment of the surface Fe atoms has no major difference after the arsenic sorption being the variation much less than 2% for the adsorption of anionic and neutral molecules.

Table 1. Interlayer relaxations after sorption of molecules on $\text{Fe}_3\text{O}_4(001)$.

Layers	Distance (Angs.)							
	$\text{Fe}_3\text{O}_4(001)$	O_2	$\text{AsO}(\text{OH})_2^-$	$\text{AsO}(\text{OH})_2$	$\text{As}(\text{OH})_3$	$\text{AsO}_2(\text{OH})_2^-$	$\text{AsO}_2(\text{OH})_2$	$\text{AsO}_3(\text{OH})^{2-}$
L1-L2	0.863	1.138	1.005	1.037	0.884	1.037	1.078	1.105
L2-L3	1.133	1.056	1.125	1.101	1.162	1.108	1.092	1.127
L3-L4	1.217	1.276	1.241	1.242	1.218	1.222	1.227	1.258
L4-L5	1.107	1.106	1.092	1.111	1.083	1.101	1.111	1.084
L5-L6 (Bulk)	1.049	1.049	1.049	1.049	1.049	1.049	1.049	1.049

Figure 5. $\text{Fe}_3\text{O}_4 + \text{AsO}(\text{OH})_2^-$ system. Figure A shows the atomic projected density of states. Figure B corresponds to the associated band structure after adsorption, where blue line corresponds to the O (p) states of the Arsenic molecule and orange lines are associated to the Fe (d) of the bottom layers of the slab. Figure C depicts the optimized atomic structure and the electron density associated to the Fe-O bond. Golden and red balls correspond to Fe and O atoms

respectively while the molecule includes yellow and light-blue atoms associated to Arsenic and Hydrogen respectively. Isovalue for the electronic density was taken to be 0.0005 e/Ångs^3 .

Figure 6. $\text{Fe}_3\text{O}_4 + \text{AsO(OH)}_2$ system. Figure A shows the projected density of states after adsorption. Figure B corresponds to the associated band structure after adsorption, while the right side depicts the optimized atomic structure and the partial charge density associated to the bond between O and the Fe atom. Golden, red, yellow and light-blue spheres correspond to Fe, O, As and H atoms respectively.

The adsorption study of neutral AsO(OH)_2 molecule showed a lower energy than the anionic case where the stable atomic configuration corresponds to a structure similar to the one obtained for AsO(OH)_2^- (see Fig. 6C). This case shows an adsorption energy of 2.91 eV, 0.84 eV higher than the anionic case. The Fe-O distance is 1.866 Å, 2.1% closer than AsO(OH)_2^- . Fig. 6B shows the corresponding band structure and right side depicts the optimized atomic structure and

the partial band charge density associated to the bond between O and the Fe atom. The Fe atom is displaced 0.77 Angs from its equilibrium value at 2.06 Angs of layer L1 due to the Fe-O bond formation while the optimized spacing between first atomic layer (L1) and the second one (L2) is 1.037 Angs., being expanded by a 20%, respect to the isolated surface.

3.7 As(OH)₃ on Fe₃O₄(001)surface

The second As(III) subspecies considered was As(OH)₃ with two atomic configurations (Fig. 4 e and f). The lowest atomic configuration energy gives a O-Fe bond formation (Fig. 7B) with d(O-Fe)=2.21 Angs. and d(As-Fe)=3.54 Angs. which is slightly longer than the distances reported for As(OH)₃ on Pyrite [42]. The adsorption energy of As(OH)₃ shows the highest value (4.62 eV) of the studied As(III) subspecies. The relaxed surface after adsorption conveys the shortest interlayer displacement between L1, L2 and L3 as compared to the pristine surface (see Table 1), and when it is compared to the other considered molecules. In the energy range close to the Fermi level, the projected DOS of the relaxed structure (Fig. 7A) shows the contribution of the d states of Fe atoms of layers 3 and 5. In contrast, the O atoms coming from the arsenic molecule contribute with peaks at 3.6 and 4.0 and 4.7 below Fermi level (blue lines). The magnetic moment per formule after the adsorption was 4.424 μ_B , which is the lowest for all sorption cases, and where the atomic magnetic moment is 4.04 μ_B for octahedral Fe atoms and -3.998 μ_B for tetrahedral atoms, similar to the clean surface (see Table 3).

Figure 7. $\text{Fe}_3\text{O}_4 + \text{As}(\text{OH})_3$ system. Figure A shows the atomic projected DOS. Right side depicts the optimized atomic structure. Golden, red, yellow and light-blue spheres correspond to Fe, O, As and H atoms respectively.

3.8 $\text{AsO}_2(\text{OH})_2$ on Fe_3O_4 surface

The sorption study of As(V) on $\text{Fe}_3\text{O}_4(001)$ was considered with five different configurations of $\text{AsO}_2(\text{OH})_2^-$ and $\text{AsO}_3(\text{OH})_2^-$ (see right side of Fig. 4): First $\text{AsO}_2(\text{OH})_2^-$ with (g) oxygen atom on top of surface Fe atom, (h) two oxygen atoms on top of Fe atoms, (i) Arsenic atom on top of surface Fe atom, and finally $\text{AsO}_3(\text{OH})_2^-$ with (h) one O atom on top of Fe atom and (k) two oxygen atoms on top of Fe atoms. The most energetically stable configuration of $\text{AsO}_2(\text{OH})_2^-$ corresponds to the adsorption mediated by two pairs of O-Fe bonds (h case in Fig. 4). The interatomic distance of O-Fe bond was 2.09 Å as depicted in Fig 8B, while the Fe-As distance was 3.199 Å. The associated adsorption energy of $\text{AsO}_2(\text{OH})_2^-$ was 2.404 eV, which is lower than the adsorption of neutral $\text{AsO}_2(\text{OH})_2$ (3.333 eV). In the case of the atomic magnetic moment values, the percentage variation with respect to the pristine surface values is less than 3% (see Table 3), which is the highest difference with respect to all adsorption cases. Therefore, the molecular adsorption has no significant contribution to the ferrimagnetic behavior of the $\text{Fe}_3\text{O}_4(001)$. The adsorption of $\text{AsO}_2(\text{OH})_2^-$ promotes a rearrangement of the surface, where the interlayer distance L1-L2 is increased a bit more than 20% with respect to the cleaned surface conditions. The displacements of the next layers L2, L3, and L4 show variations smaller than 3% (see Table 1). The analysis of partial band charge density after the adsorption of As(V) shows a delocalization of the electrons, in contrast to the highly localized density of states associated to

the As(III)-surface bond. This could be caused by the double bond of the sorption and the number of electrons involved in the sorption process.

Table 2. Intraparticle distance after O₂ and arsenic adsorption on Fe₃O₄(001) surface.

Atoms	Atomic Distances (Angs.)							
	Fe ₃ O ₄ (001)	O ₂	AsO(OH) ₂ ⁻	AsO(OH) ₂	As(OH) ₃	AsO ₂ (OH) ₂ ⁻	AsO ₂ (OH) ₂	AsO ₃ (OH) ²⁻
Fe ₁ -O ₁	2.006	2.052	2.064	2.070	2.018	2.034	2.024	2.044
Fe ₁ '-Fe ₁ '	2.934	2.880	2.995	2.995	2.969	2.989	2.998	2.964
Fe ₁ -O ₃	2.062	2.698	2.777	2.836	2.264	2.410	2.512	2.700
Fe ₂ -O ₁	1.897	1.871	1.898	1.889	1.912	1.893	1.885	1.872
Fe ₁ -O ₁ ^m	---	1.983	1.907	1.866	2.214	2.087	2.031	1.961
Fe ₁ '-O ₂ ^m	---	1.983	---	---	---	2.097	2.034	1.961
As-O ₁ ^m	---	---	1.785	1.810	1.902	1.706	1.712	1.755
As-O ₂ ^m	---	---	1.841	1.838	1.837	1.699	1.707	1.755
As-O ₃ ^m	---	---	1.850	1.841	1.813	1.791	1.782	1.838
As-O ₄ ^m	---	---	---	---	---	1.808	1.784	1.666
Fe ₁ -As	---	---	3.405	3.414	3.537	3.199	3.191	3.331
Fe ₁ '-As	---	---	---	---	---	3.212	3.204	3.329
O ₁ ^m -O ₂ ^m	---	1.414	---	---	---	2.906	2.882	2.841

Figure 8. Figure A shows the projected DOS of Fe₃O₄ + AsO₂(OH)₂⁻ system. Figure B depicts the optimized atomic structure and the interatomic distances associated to the bond between O

and the Fe atoms. Golden, red, yellow and light-blue balls correspond to Fe, O, As and H atoms respectively.

Table 3. Atomic Magnetic moments for each layer of $\text{Fe}_3\text{O}_4(001)$ before and after the adsorption of different O_2 and Arsenic species.

Layer	Magnetic Moment per atom (μ_B)							
	$\text{Fe}_3\text{O}_4(001)$	O_2	$\text{AsO}(\text{OH})_2^-$	$\text{AsO}(\text{OH})_2$	$\text{As}(\text{OH})_3$	$\text{AsO}_2(\text{OH})_2^-$	$\text{AsO}_2(\text{OH})_2$	$\text{AsO}_3(\text{OH})^{2-}$
$\text{L}_1(\text{Fe}^{\text{oct}})$	4.103	4.088	4.058	4.115	4.117	4.076	4.079	4.117
$\text{L}_2(\text{Fe}^{\text{tet}})$	-4.019	-3.996	-3.962	-4.017	-4.021	-3.961	-3.963	-4.010
$\text{L}_3(\text{Fe}^{\text{oct}})$	3.958	4.122	3.971	4.017	4.015	3.975	4.005	4.098
$\text{L}_4(\text{Fe}^{\text{tet}})$	-3.994	-3.992	-3.930	-3.988	-3.993	-3.932	-3.934	-3.984
$\text{L}_5(\text{Fe}^{\text{oct}})$	4.09	4.094	4.022	4.093	3.987	4.025	4.066	4.001
$\text{L}_6(\text{Fe}^{\text{tet}})$	-3.977	-3.977	-3.912	-3.980	-3.98	-3.911	-3.914	-3.973
$\mu/\text{formule}$	4.442	4.611	4.472	4.527	4.424	4.551	4.483	4.533

The adsorption study of the neutral $\text{AsO}_2(\text{OH})_2^-$ has shown that the most stable configuration was found to be the h case as in Fig. 4, where the pair of Fe-O bonds have a distance of 2.03 Angs. (Fig. 9B). The optimized interlayer spacing between first atomic layer and the second one (L1-L2 in Table 1) is 1.078 Angs, being expanded by a 25% with respect to the isolated surface, while the next interlayer distances are modified by less than 4%. The projected density of states shows that the main contributions are coming from the d states of Fe at L1 and L3 layers. In particular, for the Fe atoms at L3, most of their contributions are manifested just below the Fermi level energy (Fig. 9A). The molecular p states of oxygen atoms were blue shifted 0.5 eV, compared to the anionic case (see Fig. 8A).

Figure 9. Figure A shows the projected DOS of the $\text{Fe}_3\text{O}_4 + \text{AsO}_2(\text{OH})_2$ system. Figure B depicts the optimized atomic structure after the molecular adsorption and the interatomic distances associated to the bond between O and the Fe atoms. Golden, red, yellow and light-blue spheres correspond to Fe, O, As and H atoms respectively.

3.8 $\text{AsO}_3(\text{OH})^{2-}$ on Fe_3O_4 surface

The second As(V) subspecies considered was $\text{AsO}_3(\text{OH})^{2-}$ with two atomic configurations (Fig. 4 j and k). The obtained lowest atomic configuration energy corresponds to the system with two O-Fe bonds (Fig. 10b), with $d(\text{O-Fe})=1.96$ Angs and $d(\text{As-Fe})=3.33$ Angs. The adsorption energy of $\text{AsO}_3(\text{OH})^{2-}$ was 3.046 eV, being higher than the anionic $\text{AsO}_2(\text{OH})_2^-$ but lower than the neutral $\text{AsO}_2(\text{OH})_2$. The relaxed surface after adsorption shows the largest interlayer displacement of the first layer L1 (see Table 1) with a L1-L2 distance of 1.105 Angs, compared to the sorption of other molecules, and 28% larger than clean surface conditions. The projected DOS of the relaxed atomic structure (Fig. 10A) shows the contribution of the d states of Fe atoms of layers 1 and 3 around the Fermi level. In contrast, the O atoms coming from the arsenic molecule contribute mainly with peaks at 1.6 and 1.8 and 2.6 below Fermi level (blue lines). The average magnetic moment per formula after the adsorption was $4.533 \mu_B$, where the atomic

magnetic moment is $4.07 \mu_B$ for octahedral Fe atoms and $-3.99 \mu_B$ for tetrahedral Fe atoms, being slightly smaller than the anionic $\text{AsO}_2(\text{OH})_2^-$ (Table 3) and higher than clean $\text{Fe}_3\text{O}_4(001)$ surface.

Figure 10. $\text{Fe}_3\text{O}_4 + \text{AsO}_3(\text{OH})_2^-$ system. Figure A shows the projected DOS. Figure B depicts the optimized atomic structure and the interatomic distances associated to the bond between O and the Fe atoms. Golden, red, yellow and light-blue spheres correspond to Fe, O, As and H atoms respectively.

Table 4. Adsorption energies obtained after adsorption of O_2 and Arsenic species.

Energy	Adsorption energies						
	O_2	As(III)			As(V)		
		$\text{AsO}(\text{OH})_2^-$	$\text{AsO}(\text{OH})_2$	$\text{As}(\text{OH})_3$	$\text{AsO}_2(\text{OH})_2^-$	$\text{AsO}_2(\text{OH})_2$	$\text{AsO}_3(\text{OH})_2^{2-}$
$\Delta E(\text{eV})$	1.116	2.067	2.907	4.620	2.404	3.333	3.046
$\Delta E(\text{kJ/mol})$	107.679	199.438	280.442	445.769	231.955	321.619	293.899

4.1 Discussion

Figure 11. Total DOS of Fe_3O_4 + Arsenic species. Electronic configuration of the complexation with As(III) (A, B and C) and As(V) (D, E and F) species with anionic and neutral cases. Red and blue lines correspond to minority and majority spin states respectively, and zero energy is adjusted to the Fermi level.

The adsorption of As(III) and As(V) obtained after the relaxation process revealed the formation of O-Fe bonds in each case. The projected DOS of $\text{AsO}(\text{OH})_2^-$ adsorbed on magnetite surface features the presence of specific peaks at 1.8 eV below the Fermi level (see Fig. 5A) and associated to the p states of oxygen atom bound to the surface Fe atom. These states are identified in the band-structure and the partial band charge density showing a localized distribution of electrons around the O-Fe bond. A similar partial charge density was calculated with the neutral As(III), where projected states around 0.7 eV are associated to the bond. Figure

6A shows that the projected density of states of $\text{AsO}(\text{OH})_2 + \text{Fe}_3\text{O}_4(001)$ system is related to the O(p) states and were found at 0.7 and 1.0 eV below Fermi level. The highest adsorption energy was obtained for $\text{As}(\text{OH})_3$ (4.62 eV) with a Fe-O bond of 2.21 Å. In the case of As(V), the adsorption occurs with a double Fe-O bond formation, in agreement with experimental results [43]. Also a more spread DOS is obtained and therefore it is more complicated to identify the states associated to the bond formation. The magnetic response of tetrahedral and octahedral Fe sites obtained after the adsorption process has small variations with respect to the clean surface (see Table 3), being the larger variation produced after $\text{AsO}_2(\text{OH})_2^-$ adsorption with an average magnetic moment of 4.025 μ_B for octahedral and -3.93 μ_B for tetrahedral sites, compared to the clean surface (4.05 μ_B and -4.0 μ_B respectively). In contrast, the interlayer distances (see Table 2) have shown an important variation after all different molecular adsorption, mainly at the first layer, with an increased L1-L2 distance going from 16 to 25 % with respect to the original separation. If we consider an interlayer displacement between a fixed layer L5 and the L1, the distance is expanded from 2% to 4% respect to the clean surface. The adsorption of $\text{AsO}_3(\text{OH})_2^{2-}$ has the L1-L2 distance of 1.105 Å, being the greatest for our studied arsenic molecules. The changes in the total density of states of $\text{Fe}_3\text{O}_4(001)$ after the arsenic sorption are summarized in Fig. 11. The adsorption of anionic species of As(III) and As(V) has promoted the appearance of electronic states around the Fermi level, compared to the small contribution from the neutral species. The addition of molecular states is also distributed in a different way in each case, where $\text{AsO}(\text{OH})_2^-$ adsorption shows the p states of oxygen mainly localized between 1.5 and 3.0 eV below Fermi level, $\text{As}(\text{OH})_3$ has p states very far from the Fermi level (below -3.7 eV). In the case of $\text{AsO}_2(\text{OH})_2^-$ adsorption, p states of oxygen atoms are distributed between 2.5 and 4.5 eV below Fermi level. The adsorption of $\text{AsO}_3(\text{OH})_2^{2-}$ on magnetite surface shows a projected DOS

with p states of O atoms mainly located from -1.7 eV up to -5 eV (blue lines in Fig. 10A). The O(p) states, of Arsenic molecules, are energetically blue shifted at the adsorption of neutral As(III) and As(V) molecules, compared to the anionic cases, nevertheless they are still energetically below the Fermi level.

Summary and conclusions

Density functional theory calculations were performed on (001) surface of Fe_3O_4 in order to identify the adsorption details of molecular species of As(III) and As(V). Adsorption of O_2 molecule and Arsenic species (Arsenate and Arsenite) were obtained after a surface complexation of the magnetite surface (001). In particular, the highest adsorption energy was found for $\text{As}(\text{OH})_3$ as compared with other considered species. In this configuration, a more localized electronic density was found for As(III) and associated to the formation of one O-Fe bond. In the case of the O_2 molecule, O-Fe bonds are responsible of the adsorption energy of 1.106 eV found in this case, which is smaller than in the case of the arsenic species. For As(V), the highest adsorption energy for the considered anionic molecules (stable under normal pH conditions) was obtained for $\text{AsO}_3(\text{OH})^{2-}$ with a double O-Fe bond. The atomic magnetic moments show no significant difference after the complexation of the magnetite surface at each case. This is an important observation given the fact that it is possible to consider possible magnetic processes to remove the iron oxide particles from water. These results suggest a highly stable process of Arsenic adsorption at normal pH conditions of these anionic arsenic species, a result that is in agreement with the experimental results of arsenic sorption on iron oxide surfaces [7-9,17]. The consequences of these results are important in order to determine the optimal adsorption process conditions of arsenic species in contact with iron oxide nanoparticles and to predict the dominant adsorption mechanism.

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ACKNOWLEDGMENT

The authors thank the support of FONDECYT under grants 11100439, Proyecto DICYT, Código 041631BR, Vicerrectoría de Investigación, Desarrollo e Innovación. Also S. B. R. would like to thank to the Basal Funding for Scientific and Technological Centers under project FB0807 and NSF with project 1434897 and Donors of the American Chemical Society Petroleum Research Fund under contract 54075-ND10. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575.

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As(V)

As(III)

$\text{Fe}_3\text{O}_4(001)$