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ADSORPTION OF SODIUM ARSENITE ON HEMATITE SURFACE (0001): A DFT STUDY

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ABSTRACT

In this work, the modeling of the adsorption of sodium arsenite over hematite was studied by using the Density Functional Theory (DFT). Since hematite is a material that presents different magnetic states, the modeling was carried out considering different magnetic configurations on the Fe-atoms in the rhombohedral unit cell of hematite. The antiferromagnetic states (AF) presented the lowest energy with respect to ferromagnetic (FM) and nonmagnetic states (NM). The adsorption of sodium arsenite was modeled over two different hematite (0001) surfaces; the first one presents a layer of superficial O-atoms, while the second one presents a layer of Fe-atoms at the surface. The adsorption energies of the sodium arsenite are favored for the model with superficial Fe-atoms. The presence of water in the system leads to the formation of $As(OH)_3$ the adsorption of which is less favorable than that of the sodium arsenite.

INTRODUCTION

The presence of arsenite in water is a problem with serious consequences for health worldwide, for this reason, the world health organization has indicated that the maximum concentration of arsenite allowed in bodies of water is 0.01 ppm. Sodium arsenite in aqueous media leads to the formation of a more stable molecule, $As(OH)_3$ [1]. Some investigations have shown that the adsorption of arsenite by iron oxides is an efficient method for the removal of this contaminant [2]. Hematite is the most stable iron oxide and an important characteristic of this material is that it can present different magnetic moments that directly influence its stability.

The objective of this work was to evaluate the energetic and electronic influence of the magnetic states on the surface (0001) of hematite in the adsorption process of sodium arsenite using DFT.

METHODOLOGY

Using the VASP program (Vienna Ab initio Simulation Package), the Perdew-Burke-Ernsernhof (PBE) interchange and correlation functional, the structures of the $NaAsO_2$ and $As(OH)_3$ molecules were energetically and structurally characterized. In the same way, the rhombohedral structure of the hematite was characterized considering the non-magnetic state (NM), ferromagnetic (FM) and the antiferromagnetic state (AF-++-). For the last model it was build a 2x2x1 hexagonal super cell with fifteen and sixteen layers and 15 Å of vacuum.
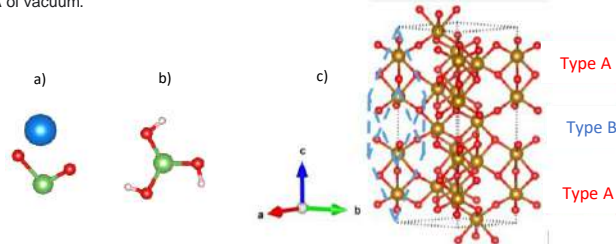

Figure 1.- *Structures of a) $NaAsO_2$, b) $As(OH)_3$ and c) hexagonal cell of hematite.*
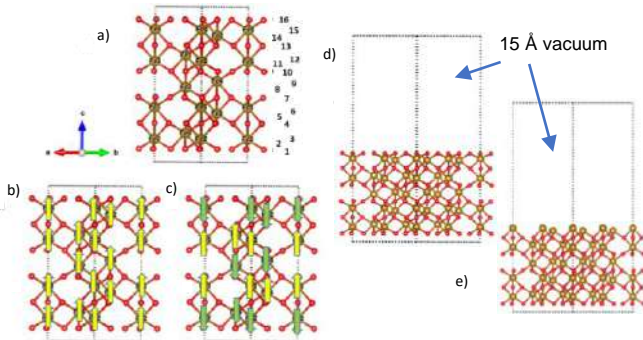

Figure 2.- *Hematite hexagonal cell a) NM, b) FM, c) AF-++-. Hematite super cells 2x2x1 d) sixteen layers and e) fifteen layers.*

Two adsorption sites were determined on the surface, in the first one there are no Fe atoms in the top layer (Type 1) and, in the second one, there is presence of Fe atoms in the top layer (Type 2). In such sites the adsorption process of $NaAsO_2$ and $As(OH)_3$ molecules were modeled for fifteen and sixteen layers.
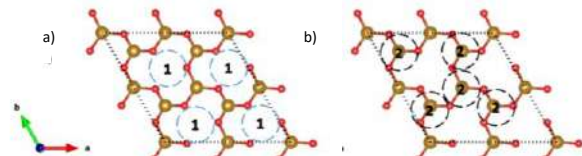

Figure 3.- *View of the upper layers of hematite super cells 2x2x1 a) sites Type 1, b) sites Type 2.*

RESULTS

Table 1.- *Energy for the magnetic states of the rhombohedral cell of hematite.*

Magnetic states	[eV/atom]
NM	-7.39
FM	-7.44
AF-++-	-7.58

Table 2.- *Energy/atom [eV/atom] obtained for supercells 2x2x1 for each magnetic state.*

Magnetic states	[eV/atom] 16 layers	[eV/atom] 15 layers
NM	-7.11	-7.10
FM	-7.22	-7.19
AF-++-	-7.26	-7.24

The adsorption modeling for the two molecules was performed in such a way that the arsenic atom interact directly with the two different sites on the surface.

Table 3.- *Adsorption energies [eV] for $NaAsO_2$ molecule.*

	16	layers			15	layers	
Sites	NM	FM	AF-++-	Sites	NM	FM	AF-++-
Type 1	1.95	6.86	8.45	Type 1	-2.49	-1.52	-0.87
Type 2	2.56	7.03	8.64	Type 2	-1.51	-1.36	-0.86

Table 4.- *Adsorption energies [eV] for $As(OH)_3$ molecule.*

	15	layers	
Sites	NM	FM	AF-++-
Type 1	0.32	0.71	1.6
Type 2	0.57	1.97	2.9

CONCLUSIONS

The AF - ++ - state turned out to be the most energetically stable, both in the rhombohedral cell and in the 2x2x1 supercell of hematite. An important aspect of this magnetic state is the formation of layers with magnetic moments in the same direction figure 2 c). The surface with sixteen layers presented a lower energy with respect to the surface with fifteen layers regardless of the magnetic state, this is attributed to the terminal oxygen layer present when sixteen layers are considered.

Considering the magnetic moments of hematite, the stability of the surface is AF - ++ -> FM> NM and, on average, the adsorption energies follow this trend regardless of the number of layers. On the other hand, the number of layers is decisive in the adsorption process. It is, since with sixteen layers a contribution of energy is necessary for the adsorption process to occur, while with fifteen layers the adsorption energies obtained were negative, which indicates that a surface with Fe atoms at the top layer favors adsorption. The adsorption energies of the $As(OH)_3$ molecule were positive, while the adsorption energies for the $NaAsO_2$ molecule were negative, therefore, the arsenic compound of the adsorbate is another important factor in the process of adsorption.

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