



Phosphate adsorption on goethite and Al-rich goethite



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ABSTRACT

The adsorption of phosphate complexes on pure and Al-rich goethite surfaces was studied by using density functional theory (DFT) and a periodic slab model. Several phosphate complexes are evaluated on these surfaces, which were not studied in other earlier theoretical works. The following complexes have been considered: bidentate binuclear (BB), bidentate mononuclear (BM), monodentate mononuclear (MM) and monodentate binuclear (MB), with their respective mono-protonated and non-protonated species. Our calculations indicate that the formation of all these species is possible on both goethite surfaces. Particularly, the direct correlation between calculated vibrational frequencies of phosphate complexes on pure goethite and experimental results indicates that some specific species are formed at certain pH values. For these cases we are able to provide an alternative interpretation to the experimental bands. On the other hand, the obtained vibrational frequencies of phosphate adsorbed on Al-goethite can be useful for the forthcoming experimental results. We noticed that the band shifts are extremely dependent on the kind of pretreated samples; for this reason the surface model used in calculations establishes restrictions on the IR experimental results to be compared.

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1. Introduction

Phosphate is one of the main nutrients for plants and, therefore, constitutes a fundamental component of fertilizers used with agricultural purpose in crop and fields. The indiscriminate use of these agrochemicals is object of special preoccupation in environmental chemistry, since phosphate is largely responsible for the eutrophication arising in nearby water bodies [1,2].

However, the transport and bio-compatibility of these nutrients can be controlled by the retaining ability of certain mineral surfaces. The most studied systems are iron (Fe) oxides and oxo-hydroxides found in soils and sediments. The presence of phosphate complexes in these minerals was evidenced using different experimental techniques, such as potentiometry [3,4] and X-ray absorption [5]. Goethite is the Fe oxo-hydroxide most studied, due to its crystallinity and stability in natural ambient. The phosphate adsorption on goethite is so strong that it can be produced even though the solid surface is negatively charged [6,7]. Phosphates are known by their capacity to form strongly bonded complexes with the goethite surface in a wide pH range [8–12].

The FTIR spectra of phosphate adsorbed on goethite was studied only by a limited number of authors [9–11]. As the bands originated from the O–H stretch vibrations of hydrated goethite surface are broad and overlap with the O–H stretch modes of protonated phosphate complexes, the frequencies commonly analyzed in

experiments are in the interval 1200–850 cm^{-1} . Other structural goethite bands appear also below 950 cm^{-1} .

Tejedor-Tejedor and Anderson [9] deduced, based on experimental vibrational frequencies, that the spectra are modified when increasing pH values are applied and when the phosphate surface coverage changes, indicative that different coordination of phosphate with the goethite surface ions are present. The phosphate complexes formed on goethite at different coverages are non-protonated monodentate and bidentate for a wide pH range of 3–8 [9]. At pH = 6 these species can co-exist, where the predominant surface species would be the non-protonated bidentate binuclear. Analogous species were supposed to be present on TiO_2 [13].

On the other hand, the assigned bands previously mentioned were questioned by other authors [10,14]. Persson et al. [10] reported that the IR spectra for phosphate adsorbed on goethite changes according to the pH; at lower pH values the bands are located at 1178 and 1001 cm^{-1} , while as the pH is raised, other two bands appear at 1122 and 1049 cm^{-1} . At the highest pH value studied, the spectrum showed only two new bands at 1057 and 966 cm^{-1} . In order to explain the changes of band positions as a function of pH, these authors considered the molecular symmetry of implied phosphate complexes. During the period of pH increasing, the C_{3v} , C_{2v} and C_{3v} symmetries were assigned to the same mono-coordinated phosphate with different protonation degree: di-, mono-, and non-protonated complexes. However, these authors performed IR spectra on dried goethite samples and significant shifts in bands positions could be generated by different water contents.

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Arai and Sparks [14] performed ATR-FTIR spectroscopic investigations for the phosphate adsorption on ferrihydrite surface. The results were interpreted as an evidence for the formation of non-protonated bidentate binuclear phosphate complexes at $\text{pH} \geq 7.5$, in co-existing with other surface species as monodentate mononuclear. These authors showed that when the phosphates establish hydrogen bonding with hydroxyl groups, the different surface complexes exhibit low symmetries. Moreover they reported that at $\text{pH} < 7.5$, the protonated monodentate mononuclear and/or protonated bidentate binuclear complexes could not be elucidated.

In order to solve the controversy about the phosphate frequency assignment on goethite, Kwon and Kubicki [15] studied theoretically different adsorption modes with a cluster model. The latter consists of two edge-sharing iron octahedral clusters and does not represent any specific goethite plane. Their calculated frequencies were contrasted with the experimental values extracted from Persson studies on dried goethite [10]. They proposed the presence of di-protonated bidentate complex ($\equiv\text{Fe}_2\text{O}_2\text{P}(\text{OH})_2$) at low pH, and the formation of mono-protonated monodentate ($\equiv\text{FeOPO}_2(\text{OH})$) or non-protonated bidentate complex ($\equiv\text{Fe}_2\text{O}_2\text{PO}_2$) at neutral pH.

On the other hand, Rahnemaie et al. [16] evaluated the PO_4^{3-} adsorption on goethite surface using an interfacial charge distribution (CD) approach based on ion adsorption and interfacial water ordering. The charge distribution values showed the relevance presence of a non-protonated bidentate surface complex at high pH values and the presence of a mono-protonated monodentate complex at low pH.

In a recent work, the characterization of phosphate and sulfate adsorptions on Fe-(hydr)oxide surface was carried out. The reactivity, pH effect, free energies and hydrogen bonds were evaluated through the topological analysis of the electron density (Laplacian) [17]. They indicated the existence of positive cooperative effects that bring additional stabilization to the studied systems.

In this work, the phosphate adsorption on the (110) goethite surface and on Al-goethite, substituted by 12.5%/mol of Al is evaluated theoretically. The Al content was considered taking into account the highest amount of Al substitution found in synthetic goethites. All the calculations were performed using a periodic method. It is important to emphasize this point because scarce works related to this issue were found in the open literature [18].

2. Surface models and computational details

The calculation corresponding to phosphate adsorption on goethite and Al-goethite surfaces were performed in the framework of spin-polarized DFT, using the *Vienna Ab-Initio Simulation Package* (VASP) [19–21]. In this package the interaction between core states and valence electrons is described by the projector-augmented wave method (PAW) [22,23].

In a previous work, two different approximations were considered to treat exchange and correlation: (1) the LDA+U and (2) GGA+U, following the approach of Dudarev for different values of U [24]. The results indicated that best structural and energetic description of both goethite and Al-goethite were obtained using GGA+U with $U = 6$ eV [25]. The Kohn–Sham valence states were expanded in a plane-waves basis set with a kinetic energy cutoff of 450 eV.

Both goethite and Al-goethite surfaces were represented by slab models. The (110) goethite surface is one of the its most usual crystal faces of this mineral [26]. This surface can be constructed by a stoichiometric truncation of bulk goethite, where three Fe–O and three hydrogen bonds need to be broken per unit cell. For the surface model construction the cell optimized parameters of bulk

goethite ($a = 4.601$ Å, $b = 9.994$ Å and $c = 3.035$ Å) were taken from our previous results [25]. In our slab model the bidimensional 1×2 cell has 8 (FeOOH) units, i.e. its contain 4 Fe layers. Afterwards, this surface was fully hydroxylated in such a way that all Fe ions preserve their octahedral coordination to cancel any spurious charge. Hence, the corresponding unit cell is formed by 8 (Fe–OH) units plus $2\text{H}_2\text{O}$ molecules (Fig. 1a). Earlier calculations showed that due to the small relaxations with respect to the bulk (lower than 1%), it is possible to use this relatively thin slab [27]. A vacuum gap of approximately 14 Å was used in normal direction to avoid the interaction between slabs. The optimized slab geometry was obtained relaxing all the superficial OH groups and the Fe atoms. The reciprocal space was described with a Monkhorst–Pack mesh of $2 \times 4 \times 1$ k -points for both goethite and Al-goethite surfaces. All the geometries were optimized until the calculated forces on the atoms are lower than 0.01 eV/Å.

Based on our previous work and taking into account the most stable magnetic arrangement in the bulk, the initial magnetic configuration for the goethite slab was considered anti-ferromagnetic (AFM) [25]. This magnetic phase presents the AFM + - - sequence, which corresponds to alternated magnetic moments of Fe atoms along the b -vector axis. These results are compatible with experiments [28] and previous calculations reported using the PBE (Perdew–Burke–Erzerhof) functional [27].

In case of the (110) Al-goethite surface, a 1×2 cell was constructed where one of the Fe atoms was isomorphously replaced by one Al atom, giving an Al-substitution of 12.5 mol%. The bulk optimized parameters with $U_{\text{eff}} = 6$ eV are $a = 4.572$ Å $b = 9.919$ Å and $c = 6.045$ Å. The Al-goethite surface was also fully hydroxylated (Fig. 1b). The magnetic configuration of Fe atoms was liberated, considering for the initial configuration the same as that in bulk Al-goethite with Al-substitution of 25 mol% [25]. In this case, the position of up and down iron spin projections is alternated, as it was observed for pure goethite. Hence, the most stable magnetic arrangement has the same spin projection for the two Fe atoms surrounding the Al atom.

The reaction energy of these systems was obtained taking into account the phosphate adsorbed on the goethite surface, as the

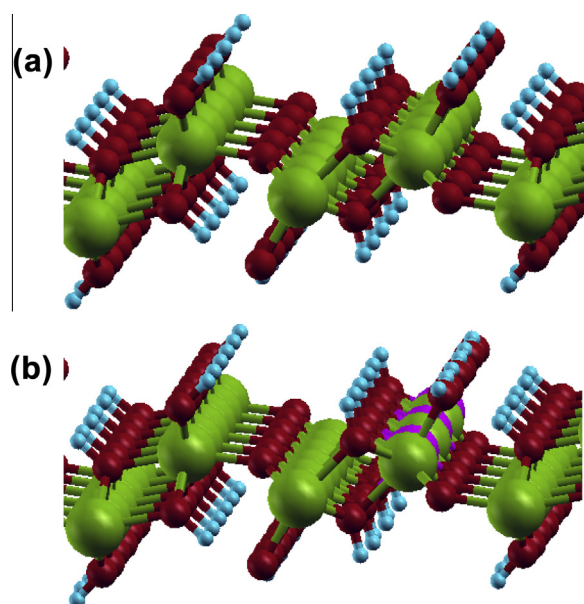


Fig. 1. (a) Hydroxylated (110) surface of goethite and (b) hydroxylated (110) surface of Al-goethite. Green, red, purple and cyan are the corresponding colors of Fe, O, Al and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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