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# Density functional theory characterization of phosphate and sulfate adsorption on Fe-(hydr)oxide: Reactivity, pH effect, estimation of Gibbs free energies, and topological analysis of hydrogen bonds

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ABSTRACT

Understanding adsorption of phosphate and sulfate on Fe-(hydr)oxide surfaces is important to predict the fate of these anions in wastewater and in the design of systems to remove and recover phosphates. Quantum chemical calculations were used to estimate relative Gibbs free energies of phosphate and sulfate adsorption like inner-sphere and outer-sphere complexes using three different simulated pH conditions (acid, intermediate, and basic). Bidentate binuclear surface complexes presented the most thermodynamically favorable mode of adsorption for both phosphate and sulfate with −94.4 kJ/mol and −62.3 kJ/mol, respectively, at acid pH condition. Topological analysis was done to understand how the Fe-(hydr)oxide surfaces are affected for the different types of adsorption of phosphate and sulfate. A classification of the O—H···O hydrogen bonds (HBs) formed in all structures discriminating among the surface functional groups, solvation water molecules, and adsorbed molecules was done by the topological analysis of the electron density. HBs nature is mostly electrostatic which agrees with positive values of the Laplacian. This result indicates the existence of positive cooperative effects among these interactions which confers additional stabilization to the systems.

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## 1. Introduction

Phosphorus is a non-renewable and essential element for all living organisms. It is part of a large number of biological systems and is the main constituent of fertilizers used in agriculture [1]. A high discharge of phosphate originating in effluents from waste water treatment plants is one of the key pollutants responsible for eutrophication of receiving waterways [2]. Therefore, phosphate removal from water containing nutrients at high concentrations is important for the conservation of the natural aquatic environment. The USEPA (United States Environmental Protection Agency) has recommended a level of phosphorus in water less than 50 μg/L, while the Florida Everglades Forever Act recommends less than10 μg/L (USEPA, 1986; Florida Everglades Forever Act, 1994) for prevention water eutrophication [3,4].

Nowadays there are various techniques proposed for phosphorus removal. These are classified as either chemical precipitation by using ferric or aluminum salts or biological removal. Chemical precipitation and biological processes still have a technical difficulty to enhance phosphate removal to meet increasingly stringent regulations for phosphate discharge [5].

Adsorption using selective adsorbents is an attractive method for removal and recovery of phosphate due to its simplicity and low operational cost. For this purpose, hard Lewis metal ions like Fe(III), Zr(IV), Al(III), Mo(VI), etc., have been immobilized on different anion exchange systems. These adsorbents show a preference for phosphate in the presence of competing anions such as chloride, sulfate, and bicarbonate, with an excellent kinetic performance [6–10]. An interesting characteristic is that the oxides of polyvalent metals exhibit favorable ligand sorption properties through formation of inner sphere complexes [5,6].

The hydrated Fe(III) oxide (HFO) is an inexpensive, readily available, and chemically stable system over a wide pH range. The phosphate adsorption on such hydrated metal oxide is significantly affected by pH, hydration, and surface charge [11]. Among these parameters, pH is one of the most important to regulate the adsorption–desorption process between the hydrated metal oxide surface and the aqueous solution.

Concerning the adsorption of phosphate on iron oxides, the formation of inner-sphere complexes is suggested as the mechanism which takes place through Lewis acid–base interactions [6,12,13]. Metal oxides behave like Lewis acids which are electron pair acceptors and are capable of selectively binding to Lewis bases. Lewis bases, such as the phosphate anion, donate electron pair(s) to form

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inner sphere complexes by binding to the central metal atom of the oxide, such as the iron. This adsorption process has been also proposed for adsorption of other anions, such as, arsenate. However, there is still some discussion about the exact structure of the surface complex. For example, it is not clear if the complexes are monodentate or bidentate in nature. Other kinds of complexes that have been proposed to this adsorption process are the outer sphere complexes. The main drawback of this assumption is that it is not possible to determine these structures through experimental methods. For this reason computational methods have become a useful tool to study these kinds of complexes [12,14].

Electronic structure methods have been used to calculate the energetic data and adsorption structures of ions on mineral surfaces [11,15–17]. In a related study, He et al. [18] examined the influence of pH on the formation of inner and outer-sphere complexes during the arsenate adsorption process on titanium oxide surfaces. They predicted a process thermodynamically favored at low pH values (acid conditions). In a complementary study, He et al. [19] using Density Functional Theory (DFT) calculations found that the monodentate mononuclear (MM) and bidentate binuclear (BB) adsorption state coexisted. Their results indicated that the BB structure evolved from a MM state. Concerning the sulfate adsorption on hydrated iron and aluminum oxide surfaces a DFT study showed a thermodynamic favorability for surface complexation directly related to the pH conditions on the surfaces of these oxides [11].

Knowledge of the sulfate, phosphate, and Fe-(hydr)oxide reactivity helps to understand their reaction pathways. The Fukui function takes into account the reactivity of the frontier molecular orbital: highest occupied molecular orbital HOMO, and lowest unoccupied molecular orbital LUMO, which participate in the chemical bonds formation. The condensed Fukui function allows assigning a numerical value of a space region of an atom or molecule fragment. This numerical value gives an idea of the reactivity sites in each structure [20].

On the other hand, due to the chemical nature of the studied system and the presence of donor and acceptor hydrogen groups, there is formation of hydrogen bonds. The topological analysis using the QCT method (Quantum Chemical Topology) [21] becomes an important tool to classify and characterize hydrogen bonds (HBs). Through this analysis, it is possible to evaluate if the cooperative effect among HBs [22] plays an important role in the stabilization of the formed complexes.

To the knowledge of the authors, there have been no published studies using topological analysis of the electron density to characterize phosphate and sulfate adsorptions on Fe-(hydr)oxide which allow a better understanding of these involved interactions.

In this study, we investigated the thermodynamic favorability of the formation of different phosphate and sulfate surface complexes on hydrated iron oxides. It was considered inner as well as outer sphere complexes under different pH conditions. The condensed Fukui function was calculated to evaluate the chemical reactivity of these systems. A topological analysis of the electron density was focused on HBs.

## 2. Computational details and models

Ferric hydroxide was simulated using a cluster consisting of two iron atoms in octahedral coordination with 10 oxygen atoms. This cluster model has been used by different authors [11,15,23] for simulations of oxyanions bonded to an Fe-(hydr)oxide surface. It is worth mentioning that in a related study [18] where the size effect of $TiO_2$ clusters was investigated it was concluded that the used smallest cluster model is reliable for studying the adsorption process of arsenate ions. To eliminate boundary effects and to reduce the charge of the clusters, the dangling bonds of O atoms were saturated with H atoms. Selected stoichiometrically balanced equations were modeled to estimate relative Gibbs free energies of phosphate and sulfate adsorption on variable charge Fe-(hydr)oxide clusters. Charges on each Fe-(hydr)oxide were varied by adjusting the radio of $OH^-/H_2O$ functional groups ranging from +2 to 0 (i.e., changing the number of $H^+$ in the model). The phosphate and sulfate adsorption was modeled for reaction occurring on surfaces at or below their $pH_{pzc}$ (i.e., $pH \leqslant pH_{pzc}$), where $pH_{pzc}$ is defined as the pH at which the net surface charge density equals zero [24]. Relative Gibbs free energies of phosphate and sulfate adsorption were estimated for inner-sphere monodentate and bidentate bridging geometries and outer-sphere H-bonded geometry. The Gibbs free energies were corrected with the thermal correction factor, which includes effects of molecular translation, rotation, and vibrational at 298.15 K and 1.0 atm, as well as at zero-point vibrational energy [11].

Full optimization of every cluster and complex under different pH conditions for phosphate and sulfate was carried out at the DFT level of theory using the B3LYP hybrid functional and the 6-31 + g(d,p) basis set on O, H, P, and S atoms. The LANL2DZ relativistic effect core potential (RECP) basis set was used for Fe. Harmonic vibrational frequencies of these structures were calculated at the same level of theory to verify that they corresponded to stable structures (i.e., no imaginary frequencies). Frequencies were scaled by a factor of 0.9614 [25] to correct systematic errors, such as neglect of anharmonicity and approximating electron correlation. To improve the estimation of adsorption reaction energies, single point energy calculations were done for each optimized gas-phase geometry using the 6-31 + g(d,p) basis set for O, H, P, and S atoms and LANL2DZ basis set for Fe, in combination with the integral equation formalism polarized continuum model (IEFPCM). IEFPCM calculation has been applied to simulate the effect of water molecules on the outer coordination sphere (i.e., long-range solvent effect) and to estimate the total free energy in solution (including non-electrostatic terms) for each geometry optimized model species. The dielectric constant of bulk water ($\varepsilon = 78.4$) was used. Short-range explicit hydration, including the effect of six water molecules (gas-phase calculation) and long-range implicit hydration (IEFPCM calculation) were considered to take into account solvation effects. All calculations were carried out with the Gaussian 09 program [26].

In order to analyze the chemical reactivity of the systems investigated here, we made use of the natural bond orbital analysis (NBO) and of the condensed Fukui function ($f_{Ff}^{\pm}$) as described by Fuentealba et al. [20,27]. In this formulation, the Fukui function initially defined by Parr and Yang [28] is integrated in well defined regions of space. The ($f_{Ff}^{\pm}$) condensed Fukui function was evaluated using DGrid 4.4 set of programs [29].

Regarding the topological analysis, it is worth noting that the basic idea of Bader [21] of using a gradient vector field of the electron density to partition a system into subspaces is taken by the Quantum Chemical Topology (QCT) method [30]. We made use of this method as implemented in an extended local version of the MORPHY98 program [31]. Wave functions (as the only input information required for the topological analysis) were calculated with the same approach used for the optimization and frequency calculations. The topological properties evaluated were the electron density: $\rho(r)$ and its Laplacian: $\nabla^2\rho(r)$ at the bond critical points (BCPs) of the bond paths which represent the formation of HBs. See more information in the Supplementary material regarding kind of analysis.

## 3. Results and discussion

### 3.1. Reactivity of phosphate and sulfate species

The $H_2PO_4^-$ is one of the most important species of the $H_nPO_4^{3-n}$ type which is predominant under weak acid conditions

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