

## Competitive adsorption geometries for the arsenate As(V) and phosphate P(V) oxyanions on magnetite surfaces: Experiments and theory

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### ABSTRACT

In the present study, the competitive adsorption geometries for arsenate and phosphate on magnetite surfaces over a pH range of 4–9 were investigated using in situ attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and two-dimensional correlation analysis (2D-COS). The adsorption energies and infrared vibrational frequencies of these surface complexes were also calculated by first-principles simulations. Arsenate and phosphate have different preferences for the magnetite surface in the presence of aqueous solvent at both acid and alkaline pH. For the adsorption of phosphate, mono-protonated monodentate mononuclear (MMM) complexes dominated at acid pH, while non-protonated bidentate binuclear (NBB) complexes were dominant at alkaline pH. Arsenate mainly formed bidentate binuclear (BB) complexes with some outer-sphere species, both of which were more prevalent at acid pH. The pre-absorbed inner-sphere arsenate species were scarcely affected by the introduction of phosphate. However, the pre-absorbed phosphate oxyanions, especially the MMM complexes, were significantly substituted by BB arsenate at the magnetite surfaces. The adsorption affinity of phosphate and arsenate species for magnetite surface was found to increase in the following order: MMM phosphate complex < NBB phosphate complex < BB arsenate complex, which was consistent with the calculated adsorption energies. The simulated infrared vibrational frequencies for the most favorable adsorption modes of each oxyanion display distinctive patterns, and their trends are in excellent agreement with experimental data.

The effects of pH, adsorption sequence, and mineral species on the competitive adsorption between arsenate and phosphate oxyanions are also discussed, and their different competing ability and stability on the magnetite surfaces can be ascribed to the variations in adsorption geometry and strength of binding. To the best of our knowledge, this is the first study aiming to distinguish the stability of the different phosphate and arsenate complexes on magnetite by employing a combined approach of in situ spectroscopy and DFT simulations. Our results provide molecular-level insight into the geometries and relative stabilities of the adsorption of phosphate and arsenate on magnetite surfaces, which is useful for interpretation of the mobility and bioavailability of these anions.

**Keywords:** Phosphate, arsenate, competitive adsorption, adsorption geometry, ATR-FTIR, first-principles simulations