

## Desorption mechanisms of phosphate from iron oxide nanoparticles

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Numerous studies have been devoted to phosphate adsorption and desorption on minerals surfaces, in particular those of Al and Fe oxides. A general observation from these studies is the biphasic adsorption/desorption kinetics consisting of an initial rapid reaction followed by a sluggish one. This has been explained in terms of weak and strong surfaces sites and/or slow diffusion of phosphates into the structures and pores of the minerals (e.g. [1] [2]).

The aim of this study was to address the molecular basis of the phosphate desorption behavior using in-situ IR spectroscopy. We investigated the net forward desorption rate of phosphates from ferrihydrite and goethite surfaces in absence of competing anions over a wide pH range and over time periods of 0-24 h. Phosphate was adsorbed and pre-equilibrated with the iron oxides for ca. 20 h. The spectroscopic data sets were analyzed by multivariate curve resolution alternating least squares (MCR-ALS), thus resolving kinetic profiles and the component spectrum of the surface species.

Our collective results showed that a structural model, consisting of a series monodentate surface complexes in different protonation states, in conjunction with a model that accounts for the electrostatic effects on desorption kinetics, explained both the spectroscopic and kinetic features. The biphasic desorption behavior followed directly from electrostatic considerations. It was displayed by a single structural phosphate surface species, characterized by a unique IR spectrum, as a result of decreasing surface coverage as well as lateral repulsive interactions between adsorbed phosphate ions. Thus, biphasic desorption kinetics do not have to imply several different structural species associated either with weak and strong sites or exterior and interior surfaces.

[1] Barrow et al. *J. Soil Sci.* **1983**, 733-750 [2] Wang et al. *Soil. Sci.* **2013**, 178, 1-11