



Desorption mechanisms of phosphate from ferrihydrite and goethite surfaces



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ABSTRACT

The fate of phosphate in the environment is governed by reactions at particle surfaces. These adsorption and desorption reactions display biphasic kinetics involving an initial rapid reaction followed by a substantially slower one extending over long time periods. In this study we have investigated the molecular mechanisms of desorption kinetics of phosphate from ferrihydrite and goethite nanoparticles in the absence of competing ligands. Desorption was studied by means of in-situ infrared (IR) spectroscopy over a wide pH range and a time period of 24 h. The spectroscopic data sets were subjected to multivariate curve resolution alternating least squares (MCR-ALS), which enabled the resolution of surface species characterized by unique IR spectra together with their corresponding kinetic profiles. The desorption results showed the typical biphasic behavior and that increasing positive surface charge of ferrihydrite and goethite slowed down desorption of the negatively charged phosphate ions. Moreover, diprotonated phosphate desorbed faster than monoprotonated phosphate at a given pH. At circumneutral pH values desorption from ferrihydrite was substantially faster as compared to goethite, and this could be ascribed to electrostatic effects and differences in charging between ferrihydrite and goethite. The collective desorption results were explained by a model, consisting of a series monodentate phosphate surface complexes in different protonation states, in conjunction with a description that accounts for the electrostatic effects on desorption kinetics at charged mineral-water interfaces. The fast and slow desorption followed directly from this model and indicated that biphasic kinetics can be caused by a single phosphate surface complex as a result of decreasing surface coverage along with the lateral repulsive interactions between adsorbed phosphate groups. Hence, in contrast to previous models our study has shown that biphasic desorption kinetics do not have to involve several different structural complexes related to either weak and strong sites or a distribution of phosphate between external surfaces and mineral pores.

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1. Introduction

Phosphorus is one of the essential elements needed to sustain life and thus a key to understanding the function of many ecosystems. It occurs in nature mainly as phosphates, either inorganic or as organic esters of phosphoric acids, and a unique property of those inorganic phosphates and the organic monoesters are their large tendency to react with environmental particles (Tiessen, 1995). This reactivity is due to the high stability of phosphate surface complexes and the propensity to form insoluble compounds with common metal ions. As a result phosphates often are hard to acquire for microbes and plants, and despite sufficiently high total concentrations phosphate fertilizers need to be applied to agricultural soils in order to sustain crop production. This, however, may also cause well-known adverse effects such as

eutrophication as excess phosphate fertilizers may be transported downstream into lacustrine environments.

In light of the central role of phosphorus in the environment, it is no surprise that phosphate reactions in soils have been thoroughly studied (Barrow, 1983; Torrent et al., 1992; Hinsinger, 2001; Arai and Sparks, 2007). One focus area has been the extent and rate of adsorption on and desorption from soil mineral particles, and it has been established that both reactions commonly display a biphasic behavior with one rapid and one slow reaction phase (Willett et al., 1988; Torrent et al., 1992; Colombo et al., 1993; Freese et al., 1995; Strauss et al., 1997; Luengo et al., 2006; Puccia et al., 2009; Bhadha et al., 2012; Wang et al., 2013a; Neupane et al., 2014). Barrow has formulated a general model for phosphate adsorption and desorption onto soil that captured these characteristics (Barrow, 1983). The foundation of the model rests on three basic concepts: 1. A description of the surface charge-dependent adsorption; 2. A normal distribution of parameters needed to model the adsorption such as surface potentials and binding constants; 3. The formation of a diffusion gradient from adsorbed species

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to species incorporated in the solids, resulting in a slow diffusion into the solids. The first two concepts are invoked to model the extent of phosphate adsorption whereas the assumption of adsorbed and absorbed fractions, displaying different kinetics, explains the biphasic phosphate adsorption/desorption kinetics.

Numerous studies on phosphate adsorption and desorption, covering time regimes from minutes to several months, have used Barrow's model to explain the kinetic behavior (Freese et al., 1995; Strauss et al., 1997; Bhadha et al., 2012). Thus, biphasic kinetics have been ascribed to solid-state diffusion, but this interpretation has been complemented or even replaced by the idea that adsorption and desorption occur from both strong and weak surface sites (Barrow, 1983; Willett et al., 1988; Colombo et al., 1993; Puccia et al., 2009; Wang et al., 2013a; Neupane et al., 2014). Recently, the possible effects of surface charge on phosphate adsorption kinetics onto ferrihydrite were also qualitatively discussed (Wang et al., 2013b). Although the presented explanations are all plausible, the definitive molecular-scale evidences are largely missing. For instance, there is little evidence that solid-state diffusion into pure minerals such as goethite actually occurs (Staunton et al., 2015), and so far the existence of phosphate adsorbed to strong and weak surface sites, which should be spectroscopically different, has not been clearly established.

Another area of intense debate has been the structure and composition of phosphate surface complexes formed primarily on the iron oxides, which are thought to be among the most reactive surfaces towards phosphate ions in the environment. Much of this discussion has concerned whether predominantly bridging bidentate structures where each phosphate ion coordinates two iron atoms (Tejedor-Tejedor and Anderson, 1990; Arai and Sparks, 2001; Antelo et al., 2010; Kim et al., 2011; Wang et al., 2013a), or monodentate species where only one phosphate oxygen interacts with one surface iron are formed (Tejedor-Tejedor and Anderson, 1990; Persson et al., 1996; Olsson et al., 2010). The protonation state of the adsorbed phosphate ions has also been a matter of concern (Tejedor-Tejedor and Anderson, 1990; Hiemstra and Van Riemsdijk, 1996; Persson et al., 1996; Luengo et al., 2006; Zhong et al., 2007). A recent study of phosphate surface complexes on iron oxides suggested that adsorption occurs via a range of different mechanisms that depend on the crystal faces present in the micro- or nano-particulate mineral powders (Kubicki et al., 2012). Thus, the structure of the phosphate surface complexes is then not only controlled by the type of mineral but also by the particular properties of the mineral powder. If this is the case, the various complexes formed on the different crystal faces may also be expected to display different adsorption and desorption kinetics.

Partly missing in this area of phosphate research is a connection between the detailed studies of structural characteristics of phosphate surfaces complexes and the overall adsorption and desorption kinetics. One reason has been the lack of appropriate in-situ techniques to monitor spectroscopic properties in real-time during the adsorption and desorption reactions. Recently, the potential of in-situ IR spectroscopy to study these reactions was demonstrated (Luengo et al., 2006; Puccia et al., 2009; Carabante et al., 2010; Olsson et al., 2010; Tofan-Lazar and Al-Abadleh, 2012). In the present work we have further developed this approach in order to study the spectroscopic changes during the net forward desorption of phosphate in absence of competing ligands. We have used this technique to study desorption of phosphate from ferrihydrite and goethite nanoparticles over a wide pH range and at a time resolution of minutes for 24 h. Moreover, the spectroscopic data sets were de-convoluted by means of multivariate curve resolution alternating least squares (MCR-ALS), hence the kinetic profile for each phosphate surface complex with a unique IR spectrum was resolved. With this analytic approach we have been able to test previous hypotheses concerning the biphasic desorption kinetics, and we have also put our results in the context of an electrostatic kinetic model for processes at charged water-solid interfaces (Koopal and Avena, 2001).

2. Materials and methods

2.1. Synthesis and characterization of the iron oxides

The 6-line ferrihydrite was synthesized according to the method of Schwertmann and Cornell (2000). Briefly, 20 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 2 L preheated distilled water during rapid stirring. The solution was kept at 75 °C for 10–12 min and thereafter rapidly cooled to room temperature. The obtained suspension was transferred to a dialysis bag and dialyzed for three to four days, changing the water several times daily. The solid concentration of ferrihydrite in the final suspension was 1.4 g L⁻¹ and the pH of the suspension was between 5 and 6. The suspension was thoroughly purged with nitrogen gas to remove carbonate species in solution or at the ferrihydrite surface. This nitrogen purge was repeated before each experiment.

One part of the suspension was transferred into a polyethylene bottle and was stored in the fridge at 4 °C, while the other part was freeze dried and kept in the desiccator prior to sample characterization. The ferrihydrite powder was characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and IR spectroscopy (Figs. S1 and S2, Supplementary Material (SM)). XRD was collected with a Bruker AXS d8 using Cu K α radiation. A small amount of grease was applied to secure the sample on the holder. The diffractogram displayed 6 peaks at 1.46, 1.51, 1.70, 1.97, 2.23, and 2.48 Å characteristic of 6-line ferrihydrite (Schwertmann and Cornell, 2000). The ferrihydrite particle morphology and size were analyzed by a TEM JEM1230 Jeol limited (Japan). The TEM images displayed roughly spherical particles, and from these images the average particle size was estimated to be 4–5 nm, which is in agreement with previous results (Schwertmann and Cornell, 2000). The surface area was estimated to 380 m² g⁻¹, based on an average particle size of 4.2 nm, spherical morphology and a density of 3.8 g cm⁻³. IR spectra of wet ferrihydrite pastes were recorded in attenuated total reflectance (ATR) mode using the experimental setup described below in 2.2. Characteristic bands of goethite and lepidocrocite were absent in these IR spectra (Fig. S2, SM).

Goethite was prepared as described by Hiemstra and van Riemsdijk (1996). A solution of 2.5 M NaOH (EKA Chemicals) was slowly pumped into a solution of 0.5 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) under stirring and bubbling with N₂ (g) until the pH reached approximately 12. The product was aged at 60 °C for one week prior to ca. two months dialyzing in Millipore 12–14,000 D tubes and then it was stored in polyethylene bottles. The precipitate was identified as goethite by X-ray diffraction and IR spectroscopy, and the needle-like particle morphology (width ca. 10 nm and length ca. 60 nm) was confirmed by TEM (Figs. S1 and S2, SM). The surface area was determined to be 90.1 m² g⁻¹ by the BET N₂ (g) single point method using a Micrometrics Flowsorb II 2300. A suspension of 9.8 g L⁻¹ was acidified to pH 4.2 and thoroughly purged with nitrogen gas to remove carbonate species in solution or at the goethite surface.

2.2. IR spectroscopic desorption experiments

Desorption experiments are an adaptation of an existing method for simultaneous infrared and potentiometric titration (SIPT) experiments, as described previously by Loring et al. (2009). The ferrihydrite and goethite experiments were carried out with two slightly different versions of this setup schematically described in the Supplementary Material (Fig. S3, SM). The ferrihydrite experiments were carried out at pH 4, 5, 6, 7, 8, and 9 while goethite data were collected at pH 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12. All experiments were done in 0.1 M NaCl medium and pH was adjusted with 40 mM HCl and NaOH solutions in 0.1 M NaCl.

A goethite suspension was pumped peristaltically in a closed loop through fluoroelastomer (Chemsure Gore Industries) and PTFE tubing from a thermostated (25 ± 0.05 °C) titration vessel to a flow-through attenuated total reflectance (ATR) cell. The flowthrough attachment was custom built of inert materials (e.g. Pyrex glass, PEEK, PTFE) and

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