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Proton interaction in phosphate adsorption onto goethite

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Abstract

The adsorption of phosphate on goethite is generally modeled by assuming a simple ligand exchange reaction with surface hydroxyl groups. This study investigates the binding forms of phosphate on goethite by evaluating the proton interaction and surface charge change during phosphate adsorption. It is found that OH^- release stoichiometry increases with phosphate coverage, which suggests that different mechanisms predominate at different phosphate loadings. It demonstrates that surface binding changes from monodentate complexation to bidentate complexation with increasing surface phosphate coverage. The net OH^- release accompanying this transformation is best interpreted with a $2pK_a$ multisite model.

Keywords: Phosphate; Goethite; Adsorption; OH^- release stoichiometry; Monodentate complex; Bidentate complex

1. Introduction

Phosphate adsorption on natural adsorbents is of particular importance in regulating the transport, mobility and bioavailability of phosphates in environmental systems [1]. Therefore, phosphate adsorption on naturally existing adsorbents, such as iron oxides and aluminum oxides, is widely investigated to evaluate their performance in controlling phosphate concentration in aqueous solutions and to elucidate the adsorption mechanisms using various macroscopic and spectroscopic techniques [2–11]. Goethite, one of the most common forms of iron oxides in nature, is found to exhibit a strong affinity to phosphate. Its strong affinity to phosphate is allegedly attributed to ligand exchange reaction on the adsorbent surface, in which phosphate ions consistently exchange with surface structural hydroxyl groups [2].

However, there are controversies over phosphate speciation on surface in terms of its complexation forms with surface hydroxyl groups at different experimental factors (e.g., pH, ionic strength, and surface coverage). Spectroscopic methods have been employed to qualitatively study the inner-sphere phosphate species adsorbed on goethite surface [3–12]. Tejedor-Tejedor and Anderson [9] observed dominated protonated and unprotonated bidentate on goethite surface with an in situ cylindrical internal reflection Fourier transform infrared (FTIR) spectroscopy. Conversely, Persson et al. [11] identified inner-sphere monodentate as the dominant phosphate species by employing a diffuse reflectance FTIR technique. The ambiguous phosphate species will bring about plausible explanation of the phosphate adsorption mechanisms on goethite.

Anion adsorption on goethite surfaces is known to be accompanied by proton adsorption. Therefore, the H^+/OH^- release stoichiometry can be used to quantitatively deduce the surface species and the surface complexation during anion adsorption onto goethite. Rietra et al. [13] observed that the proton consumption was less than stoichiometric and nonlinearly related to adsorbed oxyanion amount while the anion coverage ranged from 0 to 0.7 $\mu mol/m^2$. Jain et al. [14] claimed that varied reaction mechanisms predominated at different oxyanion loadings since the ratio of released OH^-/H^+ to adsorbed oxyanion changed with the surface oxyanion loadings ranging from 0 to 6 $\mu mol/g$ ferrihydrite. However, the macroscopic H^+/OH^- release stoichiometry was investigated at a relatively low surface phosphate coverage. A further study of the H^+/OH^- release stoichiometry at a high surface phosphate coverage on goethite becomes important to the better understanding of the phosphate

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adsorption mechanisms. The experimental data can provide information for modeling and simulation of phosphate adsorption.

This study aimed to unveil the proton interaction in phosphate adsorption onto goethite. The macroscopic H^+/OH^- release stoichiometry and surface charge change at both low and high surface phosphate coverages were determined. The stoichiometry was evaluated at four pH values and varying phosphate surface loadings in the absence of atmospheric CO_2. The results were then employed to evaluate the consistency of a surface complexation model (SCM).

2. Materials and methods

All the chemicals used were from the Merck unless specified otherwise. In order to eliminate the influence of dissolved carbonates on phosphate adsorption, all experiments were carried out in a closed nitrogen glove box in the absence of atmospheric CO_2. All prepared goethite suspensions and phosphate solutions were purged with nitrogen gas at approximately pH 3.0 for at least 24 h. The nitrogen gas was initially passed through distilled deionized water to avoid loss of water in the purged solution for humidifying the dry gas [12].

2.1. Preparation of goethite

Goethite used in this study was synthesized using the method described by Atkinson et al. [15]. $Fe(NO_3)_3$ solution was rapidly neutralized by adding to NaOH solution to form iron hydroxide at pH of around 12. The resultant suspension was then aged at 60 °C for 72 h followed by continuing washing [16]. The goethite stock solution was diluted with a deionized water to desired solid concentrations and stored in plastic bottles for further use. Contact with glassware was avoided as much as possible to prevent silicate contamination to goethite.

The specific surface area of the solid was investigated by using physical adsorption of nitrogen on an automatic volumetric sorption analyzer (Quantachrome, NOVA1200). Prior to measurements, the sample was degassed at 200 °C for 5 h in vacuum. The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) method. The X-ray diffraction (XRD) (XRD-6000, Shimadzu, Japan) and transmission electron microscope (TEM) (JEOL JEM-2010F) techniques were used to study the structure of the prepared solid.

2.2. Potentiometric titration

A potentiometric titration of 10.0 g/L goethite suspension was performed by an auto-titrator (Metrohm 718 STAT Titrino). The goethite solution of 100 mL was adjusted to ionic strength of 0.001, 0.01 and 0.1 M with $NaNO_3$, respectively. The solution was then placed in a shaker for 24 h. The titrants were 0.1 N NaOH and 0.1 N HNO_3.

2.3. Phosphate adsorption and OH^-/H^+ release stoichiometry

Phosphate adsorption experiments were conducted with the automatic titrator in pH-STAT mode at four pH values of 3.5, 4.7, 6.8, and 8.0. This commonly studied pH range covers the dominant species distribution of three surface oxygen groups of goethite [14]. Phosphate solutions with initial concentrations ranging from 10 to 400 μmol/L were prepared using reagent-grade $Na_2HPO_4 \cdot 2H_2O$, which would result in both low and high phosphate loadings from 3.5 to 86.5 μmol per gram goethite after the adsorption. Goethite suspension of 2.0 g/L was ultrasonicated (NEY ULTRAsonik 57 X) for at least 2 h before the adsorption. Goethite suspension and phosphate solution of different initial concentrations were adjusted to ionic strength of 0.01 M by adding $NaNO_3$ and to desired pH value by adding HNO_3/NaOH solution. A 50 mL phosphate solution was then mixed with a goethite suspension of 50 mL for the adsorption. Blanks with same initial phosphate concentration and ionic strength were also prepared at various pH values without mixing with goethite suspension to compensate possible phosphate loss via adsorption onto the plastic bottles. The pH of the phosphated goethite suspension was automatically titrated back to its original pH by adding HNO_3/NaOH solution during adsorption reaction. The OH^-/H^+ release stoichiometry was the ratio of total amount of consumed NaOH/HNO_3 to the determined phosphate surface coverage on goethite.

The phosphate surface coverage was determined by calculating the difference between the initial phosphate concentration and the final phosphate concentration in the mixture suspension. The goethite suspension was filtered through a 0.45 μm Whatman® autovial filter after 72 h adsorption. The filtrate was then acidified and analyzed for the final phosphate concentration with an Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 3000 DV).

2.4. Zeta potential measurement

Zeta potential of phosphated goethite suspensions obtained in the above phosphate adsorption experiments were analyzed using a ZetaPlus analyzer (Brookhaven Instruments Corporation). The instrument was calibrated with the zeta potential reference material BI-ZR1 before the measurements. At least eight runs were conducted for each sample and the averaged values were used in this study.

3. Results and discussion

3.1. Basic physical properties

The specific surface area by the BET measurement is 36.4 m^2/g. The XRD analysis confirms that the prepared solid is goethite. The TEM results given in Fig. 1 show long, acicular (needle-like) goethite crystals with multidomain structure along their needle axis.