



## Investigation of phosphate adsorption onto ferrihydrite by X-ray Photoelectron Spectroscopy

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### ABSTRACT

The objective of this study was to characterize phosphate adsorption onto synthetic 2-lines ferrihydrite using surface analysis by X-ray Photoelectron Spectroscopy and batch experiments. Surface analysis of ferrihydrite samples before phosphate sorption gives very reproducible Fe:O surface ratios of  $(1.3 \pm 0.1)$ . Phosphate sorption onto ferrihydrite was investigated by means of pH, initial phosphate concentration, and ionic strength effects. Additionally, potential background electrolyte influence on phosphate adsorption was also determined. Phosphate uptake by ferrihydrite significantly increases with decreasing pH, with a maximum uptake of  $104.8 \text{ mg PO}_4 \text{ g}^{-1}$  obtained at  $\text{pH} = 4$ . Phosphate removal increases with the enhancement of ionic strength in agreement with the formation of inner-sphere complexes. The presence of chloride, nitrate, and sulfate showed no competing effect on phosphate removal efficiency. Sorption kinetics follow a pseudo-second order model ( $R^2 > 0.99$ ) and the Freundlich isotherm model adequately describes sorption ( $R^2 = 0.995$ ). The careful examination of high resolution Fe 2p, O 1s, and P 2p spectra before and after phosphate sorption allows the characterization of the modifications occurring onto the ferrihydrite surface. The binding energy of the P 2p peak agrees well with that observed in Fe-PO<sub>4</sub> compounds. Additionally, binding energy shifts in the Fe 2p spectra combined to variations in the relative intensity of the components in the high resolution O 1s spectra illustrate well the formation of chemical bonding between iron and phosphate anions at the ferrihydrite surface.

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### 1. Introduction

Phosphorus is well known to be an essential nutrient for the growth of microorganisms in aquatic environments. However, excessive supply of orthophosphate (denoted phosphate in the present study) to all water bodies through agricultural, industrial, and household activities has been identified to be at the origin of alteration of nutrient ratios and thus eutrophication of lakes, rivers, and sea [1]. For example, dramatic proliferation of blue-green algae in coastal waters is one of the typical manifestations of eutrophication caused by excessive phosphorus concentration [1].

In a general way, the mobility of contaminants in groundwater systems is well known to be strongly dependent on the interaction developed with iron and aluminum based materials which are commonly encountered in soils and waterways. In particular, iron oxides display strong affinity for the sequestration of transition metals [2,3] and anions such as arsenate ( $\text{AsO}_4^{2-}$ ) [4,5], chromate ( $\text{CrO}_4^{2-}$ ) [4,6], and phosphate ( $\text{PO}_4^{3-}$ ) [7–9]. The environmental abundance of iron oxides combined to their low cost, their easy availability, and the lack of human toxicity make them excellent

candidates in contaminant removal strategies. Many studies are focused on the goethite mineral ( $\alpha\text{-FeOOH}$ ), the most common and most stable iron oxyhydroxide in natural environments. The main reason is that synthesis of goethite is now perfectly controlled in terms of size particles and geometry which makes this mineral a reference compound for numerous studies. Conversely, ferrihydrite is a poorly ordered iron oxide also commonly encountered in geochemical processes [10,11]. Ferrihydrite is a precursor to other iron minerals such as goethite and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and is thought to play a significant role in geochemical processes [12] in view of its high surface area [10,13]. However, ferrihydrite identification and characterization are difficult in view of its low crystallinity and small particles size [11]. In addition, at the laboratory scale, slightly different products may be obtained depending on the synthesis conditions which may affect the mineral reactivity and make the comparison of the literature data challenging [14].

In any way, the experimental approaches used in the previous studies relative to phosphate sorption by iron oxides involved thermodynamic modeling of sorption data and potentiometric titrations [13], Infrared IR spectroscopic investigations [5,15,16], and X-ray Absorption Near Edge Structure (XANES) investigations [9,17–19]. X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive method that has been widely used to investigate both the electronic structure and the bonding of molecules in a wide range

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of iron oxides [20,21]. However, there is only few studies that report the use of XPS to characterize phosphate sorption and bonding onto the surface of iron oxides [22,23].

The aim of the present study is thus to characterize phosphate sorption at the ferrihydrite surface using bulk solution data combined with XPS information. To the best of the authors' knowledge, such a careful XPS examination of physicochemical modification occurring at the ferrihydrite surface has never been reported in the literature before.

## 2. Materials and methods

### 2.1. Ferrihydrite synthesis

Two-line ferrihydrite (Fh) samples were synthesized using a slightly modified procedure from that reported by Cornell and Schwertmann [10]. Chloride ( $\text{FeCl}_3 \cdot 8\text{H}_2\text{O}$ , Sigma–Aldrich, 98%) was used as the source of ferric salt. Briefly, the ferric solution was prepared by dissolving ferric chloride in demineralized water to obtain a 0.8 M initial concentration. The pH of the solution was raised to  $\sim 7.5$  using 3 M NaOH and maintained to this pH value for  $\sim 3$  h under vigorous stirring. The ferrihydrite precipitates were then centrifuge-washed until the surface chloride atomic concentrations determined by XPS were reduced below 3 at.%. The pastes were then dried at room temperature and crushed in a porcelain mortar to get pulverulent compounds. XRD pattern (not shown) revealed two broad peaks with interplanar spacings of about 0.26 and 0.15 nm which unambiguously confirmed the presence of two-line ferrihydrite particles [10]. The specific surface area of synthetic ferrihydrite determined by single point BET method was  $309 \text{ m}^2 \text{ g}^{-1}$  in agreement with commonly reported values in the literature for the BET method [10].

### 2.2. Phosphate adsorption experiments

All glassware and plastic bottles used in the experiments were first cleaned in concentrated HCl and washed with demineralized water and ethanol to avoid any trace analysis. The pH of the suspensions was maintained at a fixed value by the addition of a minimum volume of 0.1–2 M NaOH or HCl at constant time intervals. A 0.1 M NaCl supporting electrolyte was used unless otherwise stated. Samples were stirred on an orbital shaker at room temperature during a 24 h reaction period determined from preliminary experiments and in agreement with literature data [9,13,15]. Experiments were carried out at pH = 7 unless otherwise specified, in agreement with municipal wastewater pH that typically ranges from 6.5 to 7.3. Samples were at different reaction times (0, 10, 20, 35, 50, 70, 105, 135, 180, 240, 360, 500, and 1400 min for kinetics experiments; 0 and 1440 min for isotherms and pH effect experiments), withdrawn from the reaction vessels and filtered through  $0.22 \mu\text{m}$  polypropylene syringe filters before phosphate determination. All experiments were carried out in duplicate, and the mean values are reported.

Phosphate adsorption was investigated at different ionic strengths (70, 200, 3000  $\text{mg L}^{-1}$  NaCl), using a  $1 \text{ g L}^{-1}$  ferrihydrite concentration and a  $70 \text{ mg L}^{-1}$  phosphate concentration ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  Aldrich, 99%). The effect of pH was examined using a  $200 \text{ mg L}^{-1}$  phosphate concentration and a  $2 \text{ g L}^{-1}$  ferrihydrite concentration while maintaining pH at different values ranging from  $4.0 \pm 0.1$  to  $9.0 \pm 0.1$ . The studies of the influence of initial phosphate concentration and the sorption kinetics were carried out at a  $1 \text{ g L}^{-1}$  ferrihydrite concentration and phosphate concentrations in the range [53–215]  $\text{mg L}^{-1}$ . Phosphate adsorption isotherm experiments were determined at a ferrihydrite concentration of  $2 \text{ g L}^{-1}$  and initial phosphate concentrations in the range

50–500  $\text{mg L}^{-1}$ . Finally, the potential competitive effect of background electrolyte anions ( $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and NaCl solutions) on phosphate adsorption onto ferrihydrite was examined by using initial phosphate, nitrate, and sulfate anions concentrations of  $70 \text{ mg L}^{-1}$  and chloride anions concentrations in the range of 0–3000  $\text{mg L}^{-1}$  at a ferrihydrite concentration of  $1 \text{ g L}^{-1}$ .

### 2.3. Ion chromatography

The concentrations of phosphate in solution were determined by ion chromatography (IC). A Metrosep A Supp 5-250 column packed with polyvinyl alcohol particles functionalized with quaternary ammonium group ( $5 \mu\text{m}$  particles diameter) was used for the separation. The mobile phase consisted of a mixture of 3.2 mM  $\text{Na}_2\text{CO}_3$  (Sigma–Aldrich, 99.5+%) and 1 mM  $\text{NaHCO}_3$  (Sigma–Aldrich, 99.7+%) in ultrapure water ( $18.2 \text{ m}\Omega \text{ cm}$  at 293 K). The flow rate was  $0.7 \text{ mL min}^{-1}$  and the sample loop volume was  $20 \mu\text{L}$ . The duplicate experiments demonstrated the high repeatability of the IC method and the experimental error could be controlled within 1–3%.

The removal efficiency [ $\text{PO}_{4\text{ads}}$ ] (%) was determined by the following equation:

$$[\text{PO}_{4\text{ads}}] (\%) = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_t$  are the initial and at time  $t$  phosphate concentrations ( $\text{mg L}^{-1}$ ), respectively.

Additionally, phosphate uptake ( $q_e$ ,  $\text{mg g}^{-1}$ ) by ferrihydrite at near equilibrium conditions was determined as follows:

$$q_e = \frac{(C_i - C_e) \times V}{m} \quad (2)$$

where  $C_e$  is the equilibrium phosphate concentration ( $\text{mg L}^{-1}$ ),  $V$  is the solution volume (L), and  $m$  is the dried weight (g) of ferrihydrite used.

### 2.4. X-ray Photoelectron Spectroscopy (XPS)

The surface physicochemical properties of ferrihydrite samples were examined by XPS. Spectra were obtained with a KRATOS Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromated Al  $K\alpha$  X-ray ( $h\nu = 1486.6 \text{ eV}$ ) operated at 150 W. The samples were pressed onto a Cu tape fixed on a holder and introduced into the spectrometer. The base pressure in the analytical chamber was about  $10^{-9}$  mbar. Spectra were collected at normal take-off angle ( $90^\circ$ ), and the analysis area was  $700 \times 300 \mu\text{m}^2$ . Wide scans were recorded using an analyzer pass energy of 160 eV and narrow scans using a pass energy of 20 eV. Ag  $3d_{5/2}$  full width at half maximum (FWHM) was determined to be 0.75 eV under these recording conditions. Charge correction was carried out using the C 1s core line, setting adventitious carbon signal (H/C signal) to 284.6 eV. Spectra of iron, oxygen, and phosphorus were fitted using a Shirley background and a Gaussian/Lorentzian (70/30) peak model. The core levels are reported from the peak maxima and have an experimental error of  $\pm 0.05 \text{ eV}$ .

## 3. Results and discussion

### 3.1. Removal of phosphate in batch experiments

#### 3.1.1. Ionic strength effect on phosphate adsorption

The phosphate adsorption increases with ionic strength under the conditions of the experiments (Fig. 1). The effect of ionic strength is usually correlated with the type of surface complexes that are involved [13,15]. In fact, ions that form outer-sphere com-

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