



Enhanced immobilization of phosphate by ferrihydrite during the photoreductive dissolution process

Ying Lv^{a,b,c}, Jing Liu^d, Chaorong Chen^{a,b,c}, Xiaojun Lin^{a,b,c}, Xiao Wu^{a,b,c}, Qingze Chen^{a,b,c}, Hongping He^{a,b,c}, Runliang Zhu^{a,b,c,*}

^a CAS Key Laboratory of Mineralogy and Metallogeny, Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China

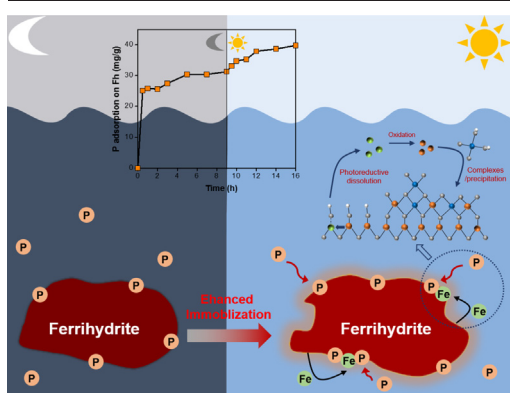
^c University of Chinese Academy of Sciences, Beijing 100049, China.

^d Macau University of Science and Technology, State Key Laboratory of Lunar and Planetary Sciences, Avenida Wai Long, Taipa, Macau, China

HIGHLIGHTS

- The immobilization of phosphate on Fh was enhanced by light irradiation.
- Photoreductive dissolution of Fh accelerated the formation of surface complexes and surface precipitation on Fh.
- Light irradiation enhanced the retention of phosphate on Fh.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Baoliang Chen

Keywords:

Photoreductive dissolution
Ferrihydrite
Phosphate immobilization
Ternary complex
Surface precipitation

ABSTRACT

The surface interactions of iron (hydr)oxides with various environmental chemicals play a vital role in controlling their environmental transport and fate. As a bioessential element, phosphorus and its biogeochemical cycling are usually controlled by its adsorption on iron (hydr)oxides. Photoreductive dissolution of iron (hydr)oxides can change their surface structure and properties, but its influence on the adsorption of phosphate remains unknown. Here, an enhanced removal of phosphate during the photoreductive dissolution of ferrihydrite (Fh) was investigated. The K_d value of phosphate adsorption on Fh under light irradiation is evidently larger than that in the dark (21 vs 13 L/g). Zeta potential determination in combination with X-ray photoelectron spectroscopy analysis suggested that the released Fe^{2+} from Fh surface during photoreductive dissolution can be oxidized to Fe^{3+} , which then co-adsorb with phosphate back to Fh surface, enhancing the immobilization of phosphate on Fh. In situ ATR-FTIR results disclosed that light irradiation could further facilitate the formation of ternary complexes and surface precipitation on Fh, even after the increment of phosphate adsorption becoming negligible in the dark, and the relative content of surface precipitation increased evidently. The desorption ratio of phosphate from the irradiated Fh sample was reduced, which should be attributed to a high content of surface precipitation that can tightly bind phosphate on Fh. The findings of this study highlight an important yet previously unappreciated pathway that light irradiation can enhance the immobilization of phosphate on iron (hydr)oxides.

* Corresponding author at: CAS Key Laboratory of Mineralogy and Metallogeny, Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.

E-mail address: zhurl@gig.ac.cn (R. Zhu).

1. Introduction

Due to their large specific surface area, high surface reactivity, ubiquity and abundance, iron (hydr)oxides are important geosorbents for environmental chemicals (e.g., nutrients, contaminants, and organic matter) (Cornell and Schwertmann, 2003; Hochella et al., 2008, 2019). The immobilization pathways of environmental ions by iron (hydr)oxides generally includes: (1) direct adsorption of ions (e.g., oxyanions, heavy metals, and organic ligands) on the surface through surface complexation and electrostatic interaction (Arai and Sparks, 2007; Barrón and Torrent, 2013; Johnston and Chrysoschoou, 2014; Liu et al., 2018; Mikutta et al., 2014; Shi et al., 2021; Wang et al., 2017). (2) Alteration of the valence of chemicals, such as Mn, Cr, through surface-catalyzed or sunlight-induced redox reactions (Junta and Hochella, 1994; Lan et al., 2017; Liu et al., 2019, 2021a). (3) Capture of target ions (e.g., Zn^{2+} , Cu^{2+} , Pb^{2+} , arsenate, and chromate) during the formation of iron (hydr)oxides by co-precipitation reactions (Lu et al., 2020; Sun et al., 2021; Yu et al., 2021; Zhu et al., 2019). These three pathways are constrained by a variety of factors, such as valence and ionic form of the chemicals, the mineral species and surface properties of iron (hydr)oxides. Besides, these pathways may also co-operate under natural environments, making the immobilization of environmental ions on iron (hydr)oxides a rather complex process (Fei et al., 2018; Yu et al., 2016; Zeng et al., 2017).

Previous studies have shown that sunlight irradiation of iron (hydr)oxides can influence the migration of environmental ions as well. Iron (hydr)oxides as semiconductors can generate photoelectrons to reduce high-valent ions, and generate holes and reactive oxygen species (ROS) to oxidize low-valent ions (Bhandari et al., 2011, 2012; Jiang et al., 2012; Liu et al., 2019; Schuttlefield et al., 2011). The change of ion valence, therefore, may affect their interactions with iron (hydr)oxides and subsequently their environmental migration as well (Bhandari et al., 2011, 2012; Liu et al., 2019). On the other hand, some iron (hydr)oxides, particularly those with low crystallinity (e.g., ferrihydrite, Schwertmannite), can also undergo photoreductive dissolution, simultaneously generating Fe^{2+} and ROS (Bhandari et al., 2011; Ren et al., 2018; Shi et al., 2021). Meanwhile, the effects of structural changes of iron (hydr)oxides, as caused by photoreductive dissolution, on the immobilization process have been overlooked. Theoretically, the photochemically generated Fe^{2+} can be easily re-oxidized to Fe^{3+} , which should affect the surface properties of iron (hydr)oxides, and subsequently the adsorption of concurrent ions. This process may be an overlooked pathway for immobilizing ions on iron (hydr)oxides, particularly for those with stable valence (e.g., phosphate).

Phosphorus as a necessary nutrient for the photosynthetic organisms and also a pollutant to cause eutrophication, its environmental transportation and fate have been widely concerned (Compton et al., 2000; Ruttenberg, 2019). The prevalent iron (hydr)oxides can well immobilize phosphorus (mainly in the form of phosphate) through both surface adsorption and co-precipitation, affecting its environmental transportation and bioavailability (Arai and Sparks, 2001; Sverjensky and Fukushima, 2006; Wang et al., 2017). The high surface area and reactivity of ferrihydrite (Fh) makes it good sorbent for immobilizing phosphate. The adsorption of phosphate by Fh can be affected by various factors, such as pH, ionic strength, and coexisting ions, which have been well studied in previous publications (Arai and Sparks, 2001; Hayes et al., 1988; Liu et al., 2016, 2018; Wang et al., 2017). Under certain environmental settings (e.g., in the riverine and atmospheric transport processes), Fh may experience long-term sunlight irradiation while interacting with phosphate. As such, clarifying the effects of sunlight irradiation on the interactions between Fh and phosphate species is of high importance to understanding the environmental transport and fate of phosphorus. On the other hand, a few earlier studies suggested that during the adsorption of phosphate on iron (hydr)oxides, Fe^{3+} might release from iron (hydr)oxides to facilitate the adsorption of phosphate by forming ternary complexes (Ler and Stanforth, 2003; Li and Stanforth, 2000). In this view, the photoreductive dissolution of Fh should be able to enhance the adsorption of phosphate.

In this work, the influence of light irradiation on the adsorption of phosphate on Fh and the underlying mechanisms were investigated. Batch adsorption experiments were first carried out to examine the immobilization efficiency in the systems with or without light irradiation. Then zeta potential and X-ray photoelectron spectroscopy were used to figure out the change of Fh structure as caused by light irradiation. To understand the adsorption mechanisms at molecular level, in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to explore the adsorption geometries of phosphate on Fh surfaces and characterize the formation of surface precipitation. Desorption of the immobilized phosphate from Fh samples collected from different reaction systems was further compared. Our results, for the first time, showed that light irradiation can enhance the adsorption of phosphate on Fh, while the desorption of adsorbed phosphate is less efficient. Overall, this work shows a widely occurring but overlooked pathway for immobilizing oxyanions on iron (hydr)oxides.

2. Methods

2.1. Reagents and materials

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaOH, KH_2PO_4 , HNO_3 (68%), 1,10-phenanthroline, $\text{CH}_3\text{COONH}_4$, CH_3COOH , and NH_4F of analytical grade (purity >99%) were purchased from Aladdin Reagents (China). All solutions used in experiments were prepared with 18.25 MΩ cm (Milli-Q Gradient, Millipore, USA) pure water.

2.2. The synthesis of Fh

Fh was synthesized by simultaneously adding 100 mL 1 M $\text{Fe}(\text{NO}_3)_3$ and 50 mL 6 M NaOH into a beaker containing 20 mL ultra-pure water with vigorous stirring, and the final pH was adjusted to 7. After aging for 24 h, the mixture was centrifuged (4000 rpm, 10 min) and washed with pure water and alcohol for 5 times. After being freeze-dried, the obtained material was ground and sieved to below 75 μm. After using a Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, German) to identify Fh, the samples were stored in the amber bottle at 4 °C.

2.3. Photochemical and adsorption experiments

Photoreductive dissolution of Fh was investigated using batch experiments in triplicates in a photoreaction instrument (BL-GHX-V, Shanghai Depai Biotech. Co. Ltd., China). A 1000 W Mercury lamp (28.5–30 mW/cm²) was used as a solar simulator, which was placed in a cylindrical Pyrex vessel surrounded by a circulating water cooling jacket, and our photochemical experiments were conducted in a room with air conditioner. No obvious temperature change was observed during the whole photoreaction process. Photoreductive dissolution experiments were carried out with suspensions of 0.2 g/L Fh, and the pH was adjusted to 3 before reaction. To disclose the effect of O_2 on the photoreductive dissolution of Fh, experiments were conducted in anaerobic environment, before and throughout which the solutions were deaerated with high purity N_2 . The experiment conducted under dark condition was used as a control. Samples were collected at 0.5, 1, 2, 3, 5, 7, 9 h intervals to analyze the concentrations of dissolved Fe^{2+} and total Fe (TFe). Fe^{2+} concentration was analyzed using 1,10-phenanthroline photometric method (Stucki, 1981), and TFe concentration was measured by transforming all Fe ions to Fe^{2+} before analysis.

To determine the influence of light irradiation on the adsorption of phosphate on Fh, 50 mL of phosphate solution with an initial concentration of 10 mg/L was added into each quartz tube. Subsequently, 0.01 g Fh was added to the solution, and the initial pH of solution was adjusted to 3.0 using dilute nitric acid (0.1 M). Then, photochemical reactions were initiated by exposing the above-prepared suspensions to a 1000 W Mercury lamp. The control experiment was conducted under dark condition. To distinguish the adsorption processes with and without light irradiation, another photochemical experiment was conducted after the adsorption of

phosphate reaching equilibrium in the dark. Specifically, the suspension was first reacted under dark condition for 9 h using the same setting, and then the system continue to expose to a 1000 W Mercury lamp for 7 h. During phosphate adsorption under different conditions, aliquots of suspension were taken out at certain time intervals and filtered for the concentration analysis of phosphate, Fe^{2+} , and TFe. The concentration of phosphate (P) was determined by a UV–Vis spectrophotometer (UV2400, Shanghai Sunny Hengping Scientific Instrument Co., Ltd., China) with the molybdenum blue method (Murphy and Riley, 1962). Adsorption coefficient ($K_d = [\text{P}]_{\text{adsorbed on Fh}} (\text{mg/g}) / [\text{P}]_{\text{dissolved in water}} (\text{mg/L})$) of phosphate in different systems was calculated.

2.4. Desorption experiments

Desorption experiments were conducted to examine the retention of phosphate on Fh surface. Two samples pre-sorbed with phosphate were prepared according to the methods of adsorption experiments in the absence or presence of light irradiation, respectively. After adsorption for 9 h, the suspension was centrifuged, and the supernatant was filtered with 0.22 μm pore-sized membrane filters for phosphate analysis. Then, the collected solid samples were washed with pure water and reserved for desorption experiments. The solid samples were resuspended in 10 mL NaCl solution (0.5 M, pH = 8), to simulate the release of phosphate in high ionic-strength water (e.g., seawater). Moreover, to simulate the process of phosphate release from Fh in anoxic environments, the collected solid samples were resuspended in 10 mL Na_2S solution (0.5 mM). Aliquots of suspension were taken out at certain time intervals and filtered for phosphate analysis.

2.5. Zeta potential measurement of Fh with or without phosphate

Zeta-potential reflects the effective net charge of particles, which depends on the properties of particles and the solution conditions (Hunter, 1981). The zeta potential of Fh in different systems (dark, light irradiation, and adsorption of phosphate) was measured by a Zetasizer Nano-ZS instrument (Malvern, UK). Specifically, 0.01 g Fh was added to the solution with or without phosphate, respectively, and the pH of the two suspension was adjusted to pH 3. After reacting for certain time intervals (0.5, 1.0, 2.0, 3.0, 5.0, 7.0, and 9.0 h), aliquots were collected from the two Fh suspensions, and immediately transferred to the sample cell for zeta potential measurements. At least three runs were conducted for each sample and the average value was recorded. After photoreductive dissolution and adsorption experiments, the pH of each suspension was also measured and found to be almost constant. Specifically, in the absence of P, the pH was 2.97 and 2.95 under dark and light condition, respectively; in the presence of P, the pH was 3.03 and 3.05 under dark and light condition, respectively.

2.6. In situ ATR-FTIR spectroscopy

ATR-FTIR experiments were conducted on a Bruker Vertex-70 FTIR spectrophotometer, equipped with a liquid N_2 -cooled MCT detector and a single-reflection ATR accessory (Quest-VU, Specac Technology). Monolithic diamond ATR crystal (with an incidence angle of 45°) was used as a sample carrier in the experiments in the absence or presence of light irradiation. Each spectrum was collected at room temperature over a range of $850\text{--}1200\text{ cm}^{-1}$ (200 scans with a resolution of 4 cm^{-1}).

The Fh film was coated on the surface of monolithic diamond ATR crystal. 4 μL of Fh suspension (2.5 g/L) was dropped on the crystal surface and dried in air for 1 h, which was followed by rinsing the film with pure water for several times to remove the loosely deposited particles. Then, the Fh film was allowed to equilibrate in the background solution (dilute nitric acid, pH 3.0) until no further change was observed in the spectrum, and the background spectrum was collected. Subsequently, the adsorption experiments were conducted by replacing background solution with 10 mg/L phosphate solution (pH 3).

After the adsorption reaching equilibrium, the system then underwent photochemical adsorption experiments. Simulated solar illumination (320–780 nm) in the photochemical experiments was performed using a 1000 W Xe lamp (PLS-SXE300, Perfectlight). The light source and flow cell were connected by an optical fiber (Perfectlight), which enables the light irradiation to pass through the transparent window and reaches the surface of monolithic diamond ATR crystal. After the transmission in optical fiber, the practical solar light intensity at the position of the sample surface was approximately 20 mW cm^{-2} , as measured with an illuminometer (PSP, Eppley Laboratory, USA). After experiments, the Fh film was checked and no obvious erosion of the film was observed. Spectra acquisition, subtraction, normalization and baseline correction were performed via Bruker OPUS software (version 6.5, Bruker, Billerica, MA, USA). Curve fitting analysis of the overlapping peaks was conducted using a Gaussian line shape.

3. Results and discussion

3.1. Increased adsorption of phosphate on Fh under light irradiation

The adsorption kinetics of phosphate on Fh were investigated in the absence or presence of light irradiation, respectively (Fig. 1a). A rapid adsorption of phosphate at the initial stage ($\leq 0.5\text{ h}$) was observed, with a phosphate removal ratio of $\sim 50\%$. In the subsequent slow phosphate removal stage, gradual enhancement of phosphate removal was observed for all systems, and those with light irradiation evidently obtained better removal efficiency. In particular, after 9 h's reaction, the removal efficiencies of phosphate reached $\sim 80\%$ and $\sim 70\%$ under light and dark conditions, respectively. Besides, the removal efficiency of P increased with the intensity of incident light (Fig. S1). The calculated K_d values in the two systems after 9 h's

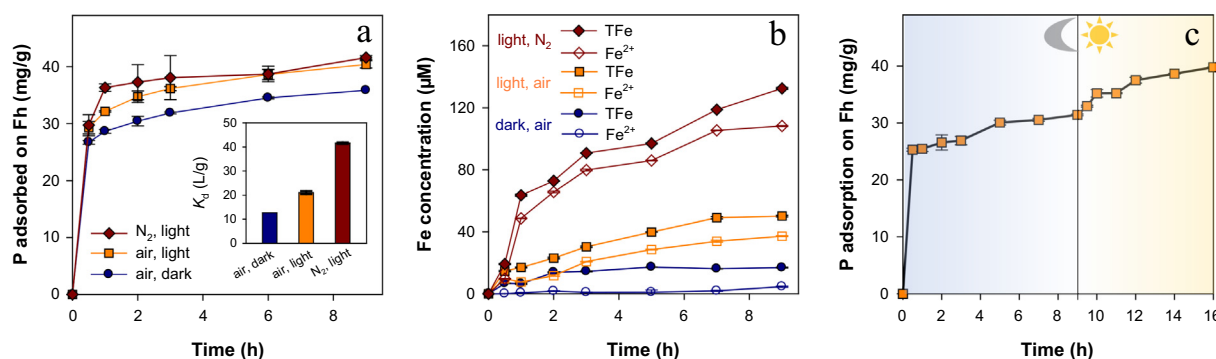


Fig. 1. (a) Phosphate (P) adsorption kinetics and adsorption coefficient K_d (inserts). The adsorption experiments were conducted under three conditions: dark and oxic condition (air, dark), irradiated and oxic condition (air, light), and irradiated and O_2 free condition (N_2 , light) (pH = 3, Fh = 0.2 g/L Fh, [P] = 10 mg/L). (b) The detected concentrations of Fe^{2+} and TFe in the three reaction systems (with 0.2 g/L Fh). (c) Change of phosphate adsorption kinetics on Fh before and after light irradiation (pH = 3, Fh = 0.2 g/L, [P] = 10 mg/L).

reaction are 13 and 21 L/g (insets in Fig. 1a), respectively. These results well showed the enhanced adsorption of phosphate on Fh as caused by light irradiation. Interestingly, the adsorption of phosphate on Fh in the presence of light irradiation under anoxic condition (i.e., purging with N_2) was further enhanced, with a K_d value of 42 L/g at the same reaction time (Fig. 1a). These results indicated that light irradiation could enhance the adsorption of phosphate, which should be related to the generated Fe ions during the photoreductive dissolution of Fh. According to previous studies on photoreductive dissolution of Fh, the typical photoreductive dissolution process include the generation of Fe^{2+} and ROS and the oxidation of Fe^{2+} to Fe^{3+} by O_2 /ROS (Borer et al., 2009; Sulzberger and Laubscher, 1995; Xing et al., 2019). Both processes may contribute to the enhanced adsorption of phosphate in this study. The aqueous Fe^{3+} can help the immobilization of phosphate on Fh through co-adsorption (Elzinga and Sparks, 2007; Liu et al., 2016, 2018). However, in the presence of oxygen, part of the generated Fe^{2+} on Fh can be directly oxidized before it is released into water (Borer et al., 2009; Sulzberger and Laubscher, 1995), which clearly is not beneficial to the adsorption of phosphate. With the purging of N_2 , more Fe^{2+} can be released to water and then be further oxidized to Fe^{3+} by ROS, and thus enhanced phosphate immobilization in the anoxic system can be obtained.

To confirm the generation of Fe ions in different systems, the aqueous concentrations of both dissolved Fe^{2+} and total Fe ($Fe^{2+} + Fe^{3+}$) were measured (Fig. 1b). For the system without light irradiation and phosphate, proton-promoted dissolution of Fh is the only pathway for generating Fe ions (i.e., Fe^{3+}), and the concentration reached a low and constant ($\sim 10 \mu M$) value within 2 h. Under light irradiation, the concentration of Fe^{2+} was significantly increased, particularly in the N_2 purging system, while that of Fe^{3+} almost remained steady for both systems. As Fe^{3+} can originate from proton-promoted dissolution of Fh and the oxidation of generated Fe^{2+} (from photoreductive dissolution) by O_2 /ROS, the low concentration of Fe^{3+} should be attributed to its low solubility, i.e., precipitation of Fe^{3+} back to the surface of Fh. The relatively low concentration of Fe^{2+} in the air system (compared with that in the anoxic system) strongly supported the oxidation of photochemically produced Fe^{2+} (by O_2). These results well correlated with the adsorption capacity of phosphate in these systems, and higher concentration of generated Fe ions would result in more phosphate adsorption. Indeed, in the presence of phosphate, the concentrations of both Fe^{2+} and Fe^{3+} decreased evidently to very low levels (Fig. S2), which could result from the co-adsorption of Fe ions and phosphate on Fh surface, and/or the inhibition of photoreductive dissolution of Fh by the adsorbed phosphate (will be further discussed below).

In another set of experiment, light irradiation was applied after the adsorption of phosphate reaching equilibrium in the dark after 9 h (Fig. 1c). After 7 h of light irradiation, the values of adsorption capacity and K_d increased from 31.4 to 39.8 mg/g, and from 8.5 to 19.5 L/g, respectively. These results further showed that light irradiation can enhance the adsorption of phosphate on Fh, even after the phosphate adsorption reached equilibrium in the dark. In other words, the photoreductive dissolution of Fh after adsorbing phosphate in the dark should still be feasible, and thus the observed low concentration of Fe ions in the system containing phosphate with light irradiation (Fig. S2) should be attributed to the co-adsorption of Fe ions and phosphate.

3.2. Light irradiation-induced change of Fh structures

During light irradiation, the crystal structure of Fh did not change evidently (Fig. S3). Because of the unfavorable adsorption of Fe(II) ion on Fh surface and the slow transformation rate of Fh at pH 3 (Appelo et al., 2002; Das et al., 2011; Yee et al., 2006), Fe(II) produced by photoreductive dissolution has negligible effect on the transformation of Fh in the limited time. Besides, the adsorption of phosphate on the surface can form Fe-phosphate complexes to stabilize Fh (Fang et al., 2021), preventing the transformation of Fh. Therefore, it is reasonable to believe the involved reactions (e.g., phosphate adsorption, photoreductive dissolution, and surface precipitation) happen on the surface of Fh. In this view, the light irradiation-induced change of surface properties, and the surface charge of Fh particles in the

systems with or without phosphate were investigated (Fig. 2). In the absence of phosphate, the zeta potential of Fh suspension in the dark was ~ 33 mV, while it gradually increased in the presence of light irradiation, reaching a constant value at ~ 38 mV after 9 h's reaction. One possible explanation for the increase of zeta potential during photoreductive dissolution of Fh is the release of Fe ions caused by photoreductive dissolution. The detachment of Fe ions ($Fe^{2+} + Fe^{3+}$) from Fh surface can expose broken Fe—O bonds (Klyukin et al., 2018; Zarzycki and Rosso, 2019), which will protonate under acidic condition, resulting in the formation of more Fe-OH on the surface and thus the increase of zeta potential. Besides, previous studies also found that photogenerated holes can oxidize surface Fe-OH to $(Fe-OH)^+$, leading to formation of net surface positive charge (Boxall et al., 1996; Zhang et al., 1993). The enhanced surface positive charge of Fh should benefit the adsorption of phosphate.

In the presence of phosphate, the rapid adsorption of phosphate on Fh (within a few minutes) neutralized part of the positive charge on the surface of Fh, leading to an immediate drop of zeta potential value (Fig. 2). After that, the zeta potential gradually increased (comparing with the first point after adding phosphate), particularly for the system with light irradiation. In specific, the zeta potential value for the samples with and without light irradiation increased from ~ 17 to ~ 29 mV and from ~ 15 to ~ 20 mV, respectively. The gradual rise of zeta potential of iron (hydr)oxides during the adsorption of phosphate was also observed in several previous studies, which was attributed to the rebinding of released Fe^{3+} back to the surface of Fh (forming a ternary complex/surface precipitation) (Ler and Stanforth, 2003; Li and Stanforth, 2000). Accordingly, the more evident rise of zeta potential in the presence of light irradiation suggests the re-binding of more Fe^{3+} with adsorbed phosphate on the surface of Fh. This is in accordance with the enhanced adsorption of phosphate as caused by light irradiation (Fig. 1a).

The chemical state of surface elements was further investigated using X-ray photoelectron spectroscopy (XPS). The Fe 2p_{3/2} spectra for the samples collected from different systems were obtained (Fig. 3). For the samples without light irradiation, Fh is only composed of Fe^{3+} (binding energy at ~ 710.5 and ~ 711.7 eV) (Fig. 3a and b) (Zhang et al., 2014; Zhu et al., 2018). After the adsorption of phosphate under light irradiation, however, the Fe 2p spectra of Fh on the surface was broadened by extending to low binding energy (Fig. 3c). This should be attributed to the generation of Fe^{2+} , which has a lower binding energy due to lower valence state than Fe^{3+} (Mills and Sullivan, 1983). The differential spectrum of Fe 2p spectra before and after the light irradiation showed a signal with the binding energy at ~ 709.5 eV (corresponding to the Fe^{2+} state), which confirmed the generation of Fe^{2+} on Fh after light irradiation (insets in Fig. 3c), and the photoreduction of Fh. The generated Fe^{2+} on Fh may release into solution (Fig. 1b) or be in situ oxidized to Fe^{3+} by O_2 /ROS (Borer et al., 2009;

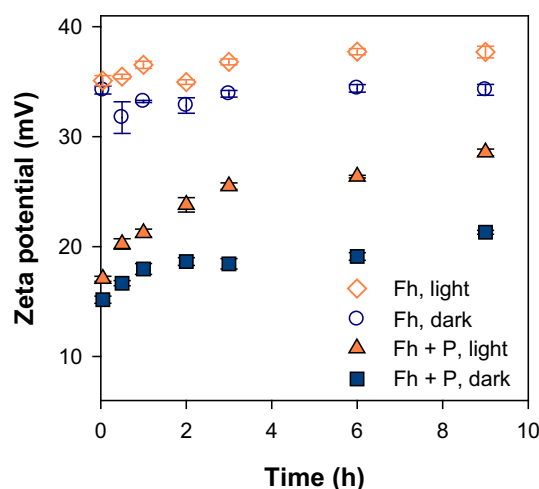


Fig. 2. Zeta potentials of Fh and Fh + P (Fh in phosphate solution) under dark and light conditions (exposed to air), as a function of reaction time.

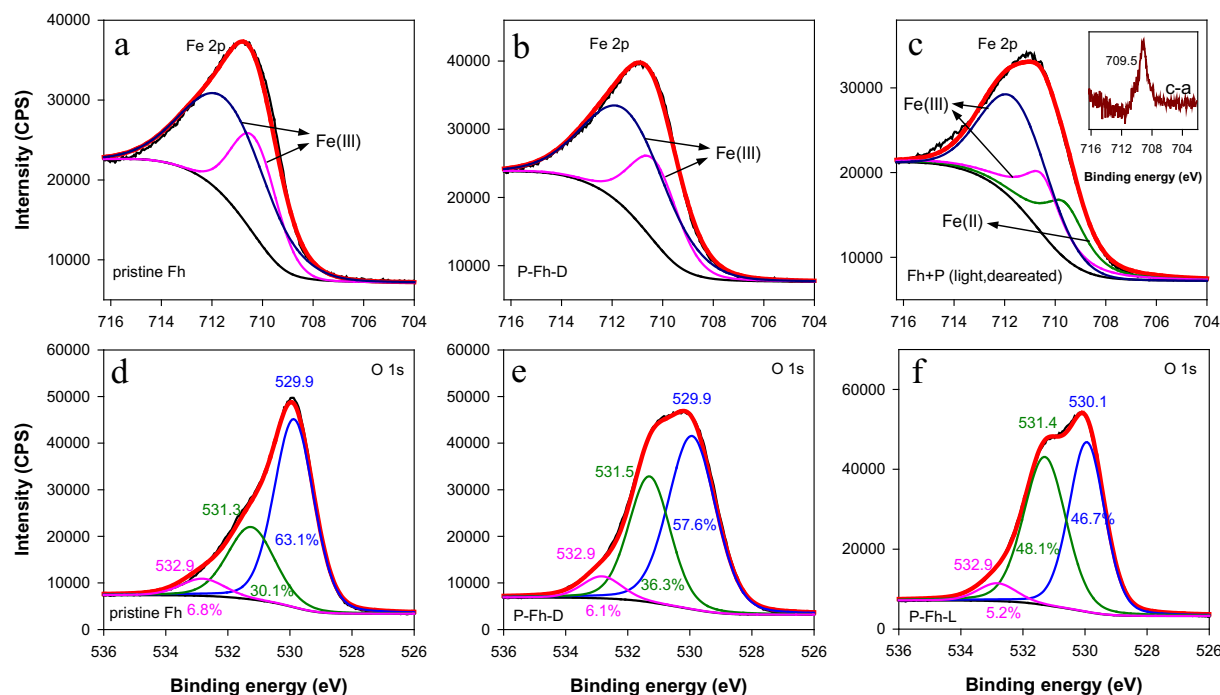


Fig. 3. XPS spectra of Fe 2p_{3/2} in the samples of (a) pristine Fh, (b) Fh after the adsorption of phosphate (P) under dark condition, (c) Fh after the adsorption of phosphate under light irradiation (N₂) and differential spectrum obtained by the subtraction of (a) from (c) (both XPS spectra were normalized before subtraction). O 1s XPS spectra of in the samples of (d) pristine Fh, (e) Fh after the adsorption of phosphate under dark condition (P-Fh-D), and (f) Fh after the adsorption of phosphate under light irradiation (P-Fh-L).

Sulzberger and Laubscher, 1995). The released Fe²⁺ will be re-oxidized and then participate in the immobilization of phosphate on Fh surface.

The binding energies of the P 2p after phosphate adsorption with and without irradiation are at ~133.7 and 133.9 eV, respectively, which are larger than that of the pure NaH₂PO₄ sample (132.2 eV) but close to that of FePO₄ (133.6 eV) (Fig. S4), confirming the formation of Fe–O–P bond on Fh. O 1s spectra of pristine Fh and collected Fh after phosphate adsorption were fitted with three peaks at ~529.9, ~531.3, and ~532.8 eV, corresponding to Fe–O in the crystal lattice, surface –OH (+ O–P) bond, and adsorbed water, respectively (Fig. 3 d–e) (Fu et al., 2018; Mallet et al., 2013). After the adsorption of phosphate, the relative content of the fitted peak at ~531.3 eV increased while that at ~529.9 eV decreased, which was attributed to the formation of Fe–O–P after phosphate binding with Fe–O. In particular, the sample collected after adsorbing phosphate on Fh under light irradiation (P-Fh-L) (Fig. 3f) has a higher component at ~531.3 eV than the sample collected after adsorbing phosphate on Fh in the dark (P-Fh-D) (Fig. 3e), reflecting the higher adsorption content of phosphate on Fh in the former system, which is consistent with the results from macroscopic adsorption experiments.

3.3. Light irradiation-induced change in phosphate species on Fh

Fig. 4a shows the time dependent evolution of phosphate adsorbed on Fh in the absence or presence of simulated solar irradiation. During the adsorption process in the dark, the spectral intensity of adsorption band increased rapidly in the first 30 min, and then increased slowly until the adsorption reaching negligible increment, the trend of which is consistent with that of macroscopic adsorption experiments. The collected spectra show a broad adsorption band between 1200 and 900 cm⁻¹, which might be attributed to the formation of phosphate complexes of low symmetry (Arai and Sparks, 2001, 2007).

According to the peak deconvolution results, nonprotonated bidentate binuclear complex (NBB) and protonated bidentate binuclear complexes (PBB) were recognized as the main phosphate complexes on Fh surface, which is consistent with previous studies (Arai and Sparks, 2001; Liu et al., 2018, 2021b). Spectra deconvolutions with Gaussian profile fitting

were performed for each collected spectrum in Fig. 4a. In Fig. 4b, the bands at 1075, 1050, and 947 cm⁻¹ are assigned to NBB, and those at 1100, 1000, and 976 cm⁻¹ are due to PBB (Abdala et al., 2015; Arai and Sparks, 2001; Zeng et al., 2008). Besides, the band at ~1030 cm⁻¹ is close to that of the spectra of amorphous ferric phosphate (AFP) in previous FTIR studies (Cai et al., 2013; Wang et al., 2017). Accordingly, the spectra fitting with different phosphate adsorption species at the reaction time of 90 min (endpoint of adsorption under dark condition), 180 min (endpoint of adsorption under light condition), and their differential spectra were obtained (Fig. 4b–d). The intensity of these bands increased evidently after light irradiation, suggesting that the content of all the phosphate species increased. Besides, the adsorption intensity of the band located at 1030 cm⁻¹ was significantly higher than those of other bands, which indicated the evident increment of AFP species after light irradiation.

The relative content of each phosphate species on Fh as a function of reaction time was further calculated in this work (Fig. 4e). Peak area was used to denote the content of the corresponding species (Jain et al., 1989; Lin et al., 1999), and accordingly the proportion of different phosphate species on Fh was calculated. Among the three adsorbed phosphate species, PBB is the dominant species, which should be attributed to the low pH in this work (~pH 3). Antelo et al. (2010) combined phosphate adsorption experiments with modeling calculations to figure out phosphate bonding configuration on Fh over a wide range of pH, and they also found protonated complex (FeO)₂(OH)PO was the major species at low pH (pH ≤ 4.5).

ATR-FTIR results also suggest that phosphate adsorption on Fh has two stages under dark condition (Fig. 4e). During the fast adsorption stage in the first 30 min, the content of three complexes increased, and the formation kinetics and content of phosphate species was in the order: PBB > NBB > AFP. The formation of both PBB and NBB on Fh surface was through a ligand exchange process, and low pH was conducive to the protonated process, leading to the faster formation of PBB than NBB. The formation of AFP needs the release of Fe³⁺ from Fh first (Luengo et al., 2006; Martin et al., 1988; Torrent et al., 1992), which then resulted in much slower formation of AFP than both PBB and NBB. After that, each phosphate species on Fh further increased slowly in the second stage (30–90 min), and the increment of AFP species was more apparent than both that

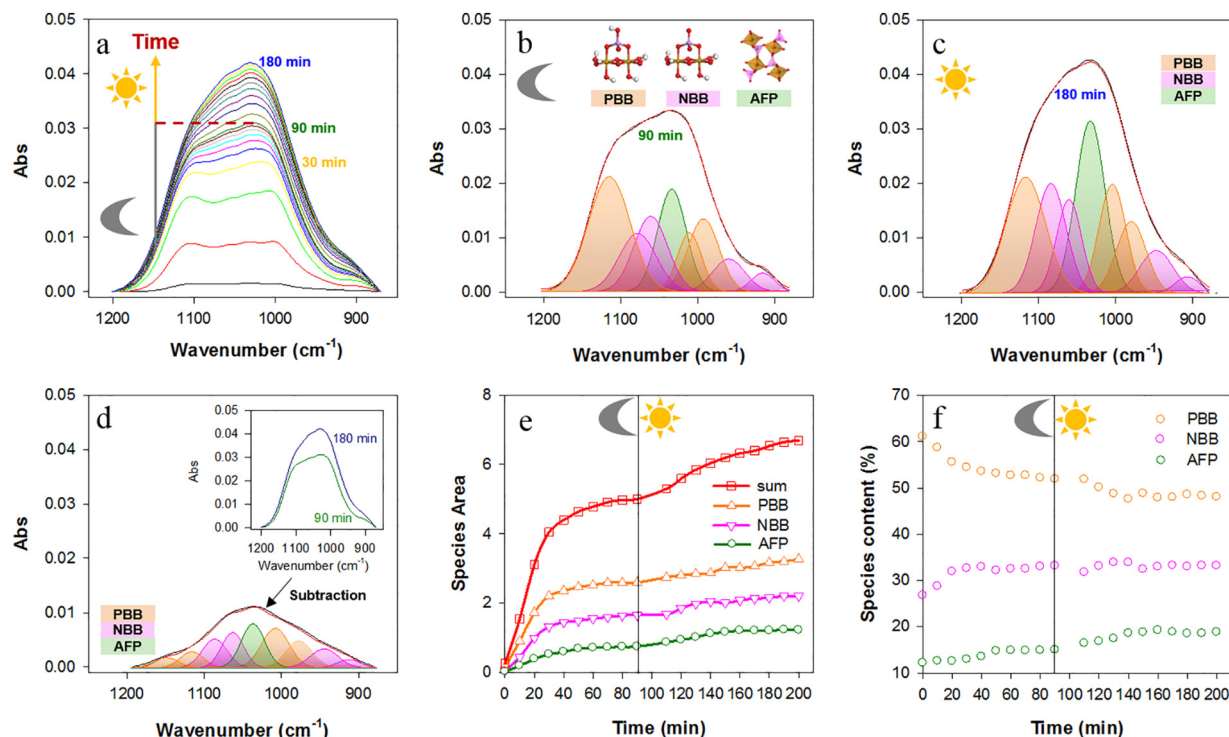


Fig. 4. (a) Infrared spectra of phosphate at the Fh-water interface as a function of time. The adsorption under dark condition is shown below the red dotted line, and photoreaction begins after the increment of phosphate adsorption becoming negligible in the dark. (b) The FTIR spectrum of the adsorbed phosphate on Fh after adsorption under dark condition ($t = 90$ min). The adsorbed phosphate species were determined according to the fitted spectra, i.e., nonprotonated bidentate binuclear complex (NBB), protonated bidentate binuclear complex (PBB), and amorphous ferric phosphate (AFP). The peaks with the same color refer to the phosphate complexes in the same molecular symmetry. (c) The FTIR spectrum of the adsorbed phosphate on Fh after adsorption under light condition ($t = 180$ min). (d) The differential spectrum of the adsorbed phosphate on Fh. The differential spectrum was obtained by subtracting the spectrum recorded at the adsorption endpoint of dark condition ($t = 90$ min) from that recorded at the adsorption endpoint of light condition ($t = 180$ min) (inserts). (e) Changes of the fitted spectrum areas relating to the NBB, PBB, AFP species and their summarized area during the adsorption of phosphate (i.e., the spectra in a). (f) The change of relative content of AFP species during phosphate adsorption on Fh before and after light irradiation.

of PBB and NBB species. Interestingly, in the whole adsorption process in the dark, the relative content of PBB species decreased while those of NBB and AFP species increased (Fig. 4f).

After the increment of phosphate adsorption becoming negligible in the dark, light irradiation was introduced into the system. In this stage, all of the three phosphate species contributed to the enhanced adsorption (Fig. 4e). Noticeably, the relative content of AFP increased (from $\sim 15\%$ to $\sim 19\%$) while that of PBB decreased (from $\sim 52\%$ to $\sim 48\%$); the relative content of NBB, however, kept constant ($\sim 33\%$) (Fig. 4f). The more evident increase of AFP species caused by light irradiation can be attributed to the photoreductive dissolution of Fh, which generates Fe^{3+} , benefiting the formation of surface precipitation with phosphate (Fang et al., 2018, 2020).

3.4. Light irradiation-improving the retention of Fh-bound phosphate

Light irradiation can improve the generation of surface precipitation/complexes of phosphate on Fh, which may affect the long-term stabilization of phosphate on Fh. The desorption experiments, therefore, were carried out to investigate the release of phosphate from Fh. The desorption of phosphate may occur while the Fh particles transport from fresh water to high ionic-strength waters and/or from oxic environment to anoxic environment (Ruttenberg, 2019). As such, NaCl and Na_2S solution were used to simulate high ionic-strength water (e.g., seawater) and anoxic environment (e.g., sediments), respectively, in which the release of phosphate from Fh was investigated (Li et al., 2016; Ruttenberg and Sulak, 2011). The desorption kinetics of phosphate from the phosphate pre-sorbed Fh in the absence or presence of light irradiation were shown in Fig. 5. All systems with the phosphate pre-sorbed Fh displayed a similar desorption trend. In specific, desorption of phosphate showed an initial rapid rate occurring within 10

min, which was followed by a slow desorption process between 10 min and 10 h. Then, the desorption of phosphate remained almost constant within 24 h. In the Na_2S desorption system, Na_2S can attack the structure of Fh by reducing structural Fe^{3+} (Li et al., 2016), and thus the generation of Fe^{2+} can be clearly detected (Fig. S5).

Noticeably, the desorption efficiency from the sample collected from the light irradiated system was less efficient than that collected from the dark system, in both NaCl and Na_2S solutions, which suggested the more effective immobilization of phosphate as caused by light irradiation. It is reasonable to believe that AFP is more stable than the surface complexes in resisting the desorption (Arai and Sparks, 2007), and the higher content of AFP on the light-irradiated Fh samples will lead to a better immobilization efficiency.

3.5. Mechanisms for the enhanced phosphate adsorption during the photoreductive dissolution of Fh

Above results showed that light irradiation, being introduced either at the beginning of the adsorption process or after the adsorption reaching equilibrium in the dark, can evidently enhance the adsorption of phosphate on Fh (Fig. 1a and c). By integrating all of the characterization results, the underlying adsorption mechanisms are proposed in Fig. 6. Under light irradiation, photoreductive dissolution of Fh occurs (Step 1 in Fig. 6) and the generated Fe^{2+} ($K_{sp} \text{Fe}(\text{OH})_2 = 4.9 \times 10^{-17}$) will release into solution due to its higher solubility than Fe^{3+} ($K_{sp} \text{Fe}(\text{OH})_3 = 2.8 \times 10^{-39}$) (Step 2 in Fig. 6). The detected Fe^{2+} on Fh by XPS (Fig. 3c) and the high concentration of Fe ions in solution (Fig. 1b) caused by light irradiation well supported the presence of these reactions. Indeed, Fh as a nanomineral with low crystallinity can easily undergo photoreductive dissolution, which

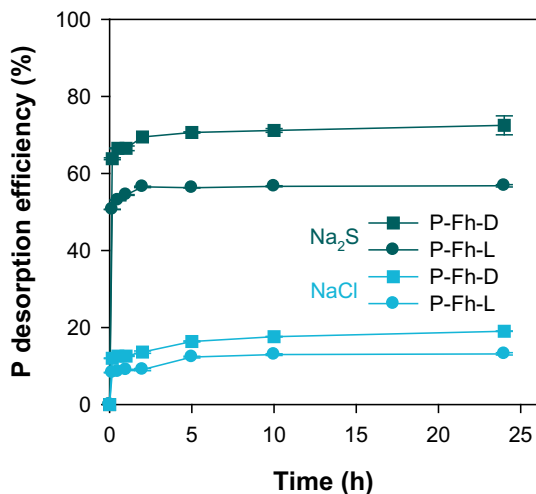
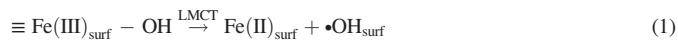


Fig. 5. The desorption kinetics of phosphate from the phosphate pre-sorbed phosphate Fh in the presence of NaCl and Na₂S. P-Fh-D: the sample collected after adsorbing phosphate on Fh in the dark; P-Fh-L: the sample collected after adsorbing phosphate on Fh with light irradiation.

has been proved by a number of previous studies (Bhandari et al., 2010; Jambor and Dutrizac, 1998; Ren et al., 2019; Xu et al., 2019).

Then, the released Fe²⁺ caused by photoreductive dissolution will be further oxidized to Fe³⁺ by O₂/ROS (Step 3 in Fig. 6), which may directly precipitate back to Fh surface with OH⁻ due to its low solubility (Step 4 in Fig. 6), or co-adsorb with phosphate to form ternary complexes/precipitation on Fh (Step 5 in Fig. 6). The low Fe³⁺ concentrations in all of the three systems with varying Fe²⁺ concentrations (Fig. 1b) suggested the precipitation back of Fe³⁺ to Fh surface (Step 4). Due to the low solubility of Fe³⁺, it can go through fast homogeneous precipitation process, i.e., Fe³⁺ precipitates with OH⁻ to form precipitation (Li et al., 2020). The extremely low concentrations for both Fe³⁺ and Fe²⁺ in the presence of phosphate (Fig. S2) indicated the co-adsorption/precipitation of Fe³⁺ with phosphate

(Step 5), which can be further supported by the increase of zeta potential of Fh during the adsorption process and the presence of AFP (as proved by XPS and FTIR results). On the other hand, the significant decrease of zeta potential of Fh after adsorbing phosphate (Fig. 2) proved the direct adsorption of phosphate on Fh surface (Step 6 in Fig. 6). The related reaction equations are as follows:



According to above proposed mechanisms, the increased content of Fe³⁺ through photoreductive dissolution process is vital to the enhanced adsorption of phosphate on Fh during light irradiation, as it can be co-adsorbed with phosphate to form surface precipitation/complexes. Although previous studies also proposed that the release of Fe³⁺ from iron (hydr)oxides under acidic condition can improve the adsorption of phosphate (Antelo et al., 2010; Arai and Sparks, 2001; Wang et al., 2017), the photoreductive dissolution process provides an additional pathway in generating available Fe³⁺. Besides, the chemical reductive dissolution of Fh (e.g., caused by Fe(II)) is common in the nature (Pedersen et al., 2005), and the re-oxidation of released Fe(II) to Fe(III) theoretically may help the immobilization of P on Fh as well. Further studies are needed to verify this deduction.

The influence of photoreductive dissolution on the immobilization of redox sensitive ions (e.g., As(III), Sb(III)) during the photoreductive dissolution of Fh has been investigated in previous studies (Bhandari et al., 2011; Kong et al., 2016). Light irradiation can excite electron transfer from the sorbed As(III)/Sb(III) to Fe(III), leading to the photoreductive dissolution of Fh, the oxidation of As(III)/Sb(III), and subsequently the enhanced adsorption on Fh (Bhandari et al., 2011; Kong et al., 2016). Compared with the

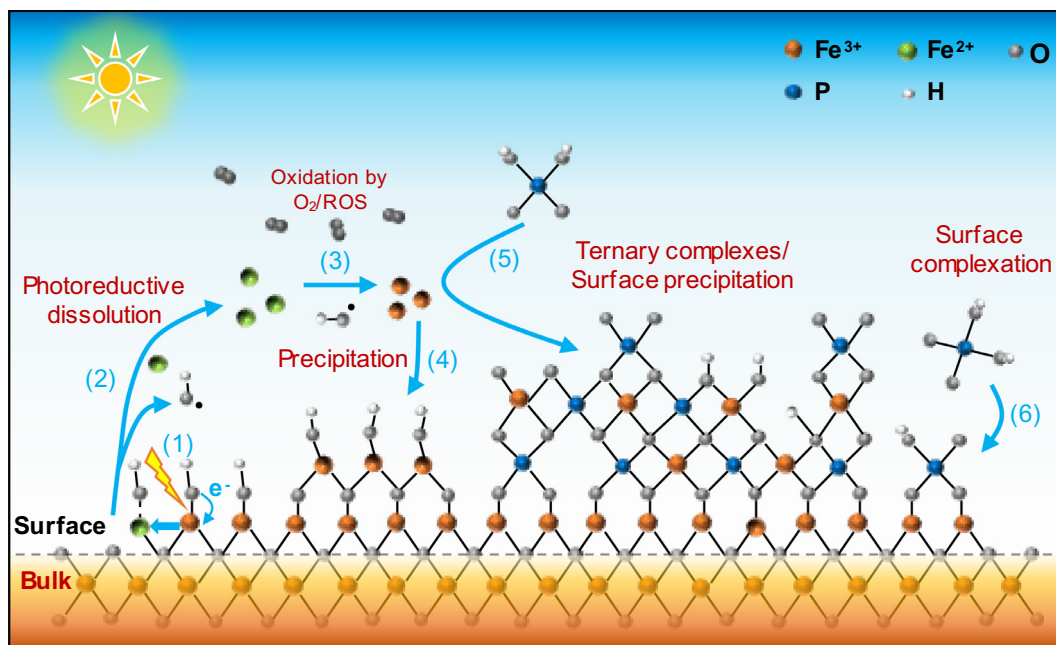


Fig. 6. The schematic of the mechanism of phosphate adsorption on ferrihydrite under light irradiation. Photoreductive dissolution of Fh includes surface Fe³⁺ reduction by ligand to metal charge transfer (1), the subsequent surface Fe²⁺ is released into solution (2), and further oxidized to Fe³⁺ (3). The dissolved Fe³⁺ may precipitate back to Fh surface (4) or re-adsorb with phosphate back to Fh surface as ternary complexes/surface precipitation (5). Phosphate can also directly adsorb on Fh surface as surface complexes (6).

immobilization of As(III) and Sb(III) through oxidation, the immobilization of phosphate in this study was achieved by the co-adsorption and precipitation of phosphate with Fe^{3+} from photoreductive dissolution of ferrihydrite, without changing the valence of iron.

Photoreductive dissolution reactions can happen on other minerals as well. The photoreductive dissolution processes of iron (hydr)oxides have been widely studied, during which photoelectrons can be generated in iron (hydr)oxides (especially for those of low crystallinity) to reduce Fe (III), thanks to their semiconductor characteristics and/or photolysis characteristics (Sherman, 2005; Wells et al., 1991; Xu et al., 2021). In addition to various iron (hydr)oxides, a number of studies have shown that light irradiation can cause the reduction of manganese (hydr)oxides and the release of Mn(II) (Lu et al., 2021; Luther, 2005; Sakai et al., 2005). Theoretically, this photoreductive dissolution-induced immobilization process may also operate for the adsorption of oxyanions on minerals (e.g., iron (hydr)oxides, manganese (hydr)oxides).

4. Conclusion

This work showed a widely occurring but previously overlooked process that the immobilization of phosphate on Fh was enhanced by light irradiation. In this process, photoreductive dissolution accelerated the release of Fe ions from Fh, which can co-adsorb with phosphate back to Fh surface to form ternary complexes/precipitation, making the K_d value of phosphate on Fh under light irradiation (21 L/g) evidently larger than that in the dark (13 L/g). Besides, the desorption ratio of adsorbed phosphate from the light irradiated Fh was also evidently reduced, which can help the long-term immobilization of phosphate on Fh. Considering the prevalent of iron (hydr)oxides in the nature and the widespread photoreductive dissolution, this process should play an important role in immobilizing oxyanions on iron (hydr)oxides.

CRediT authorship contribution statement

Ying Lv: Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Visualization. **Jing Liu:** Data curation, Writing – review & editing, Supervision, Software. **Chaorong Chen:** Data curation, Resources, Writing – review & editing. **Xiaoju Lin:** Methodology, Software, Formal analysis, Data curation. **Xiao Wu:** Data curation, Writing – review & editing. **Qingze Chen:** Resources, Funding acquisition. **Hongping He:** Supervision, Project administration, Funding acquisition. **Runliang Zhu:** Data curation, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank Dr. Yunfei Xi from Queensland University of Technology for his linguistic assistance during the revision of this manuscript. This work was financially supported by the National Natural Science Foundation of China (No. 41872044, 41902040), Queensland-Chinese Academy of Sciences Collaborative Science Fund (No. 132744KYSB20200001_o), Science and Technology Planning Project of Guangdong Province (2020B1212060055), and Youth Innovation Promotion Association CAS (No. 2020347). This is contribution No. IS-3191 from GIGCAS.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.155835>.

References

- Abdala, D.B., Northrup, P.A., Arai, Y., Sparks, D.L., 2015. Surface loading effects on orthophosphate surface complexation at the goethite/water interface as examined by extended X-ray absorption fine structure (EXAFS) spectroscopy. *J. Colloid Interface Sci.* 437, 297–303. <https://doi.org/10.1016/j.jcis.2014.09.057>.
- Antelo, J., Fiol, S., Pérez, C., Mariño, S., Arce, F., Gondar, D., López, R., 2010. Analysis of phosphate adsorption onto ferrihydrite using the CD-MUSIC model. *J. Colloid Interface Sci.* 347, 112–119. <https://doi.org/10.1016/j.jcis.2010.03.020>.
- Appelo, C.A.J., Van Der Weiden, M.J.J., Tournassat, C., Charlet, L., 2002. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* 36, 3096–3103. <https://doi.org/10.1021/es010130n>.
- Arai, Y., Sparks, D.L., 2001. ATR-FTIR spectroscopic investigation on phosphate adsorption mechanisms at the ferrihydrite–water interface. *J. Colloid Interface Sci.* 241, 317–326. <https://doi.org/10.1006/jcis.2001.7773>.
- Arai, Y., Sparks, D.L., 2007. Phosphate reaction dynamics in soils and soil components: a multiscale approach. *Advances in Agronomy*. Elsevier, pp. 135–179. [https://doi.org/10.1016/S0065-2113\(06\)94003-6](https://doi.org/10.1016/S0065-2113(06)94003-6).
- Barrón, V., Torrent, J., 2013. Iron, manganese and aluminium oxides and oxyhydroxides. *Eur. Mineral. Union Notes Mineral.* 14, 297–336. <https://doi.org/10.1180/EMU-notes.14.9>.
- Bhandari, N., Hausner, D.B., Kubicki, J.D., Strongin, D.R., 2010. Photodissolution of ferrihydrite in the presence of oxalic acid: an in situ ATR-FTIR/DFT study. *Langmuir* 26, 16246–16253. <https://doi.org/10.1021/la101357y>.
- Bhandari, N., Reeder, R.J., Strongin, D.R., 2011. Photoinduced oxidation of arsenite to arsenate on ferrihydrite. *Environ. Sci. Technol.* 45, 2783–2789. <https://doi.org/10.1021/es103793y>.
- Bhandari, N., Reeder, R.J., Strongin, D.R., 2012. Photoinduced oxidation of arsenite to arsenate in the presence of goethite. *Environ. Sci. Technol.* 46, 8044–8051. <https://doi.org/10.1021/es300988p>.
- Borer, P., Sulzberger, B., Hug, S.J., Kraemer, S.M., Kretzschmar, R., 2009. Photoreductive dissolution of iron(III) (hydr)oxides in the absence and presence of organic ligands: experimental studies and kinetic modeling. *Environ. Sci. Technol.* 43, 1864–1870. <https://doi.org/10.1021/es801352k>.
- Boxall, C., Kelsall, G., Zhang, Z., 1996. Photoelectrophoresis of colloidal iron oxides. Part 2.—Magnetite (Fe_3O_4). *J. Chem. Soc. Faraday Trans.* 92, 791–802. <https://doi.org/10.1039/FT9969200791>.
- Cai, R., Du, Y., Zhang, W., Tan, H., Zeng, T., Huang, X., Yang, H., Chen, C., Liu, H., Zhu, J., Peng, S., Chen, J., Zhao, Y., Wu, H., Huang, Y., Xu, R., Lim, T.M., Zhang, Q., Zhang, H., Yan, Q., 2013. Synthesis of porous amorphous FePO_4 nanotubes and their lithium storage properties. *Chem. Eur. J.* 19, 1568–1572. <https://doi.org/10.1002/chem.201203935>.
- Compton, J., Mallinson, D., Glenn, C.R., Filippelli, G., Zanin, G.Y., 2000. Variations in the Global Phosphorus Cycle. <https://doi.org/10.2110/pec.00.66.0021>.
- Cornell, R.M., Schwertmann, U., 2003. The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses. 1st ed. Wiley <https://doi.org/10.1002/3527602097>.
- Das, S., Hendry, M.J., Essilfie-Dughan, J., 2011. Transformation of two-line ferrihydrite to goethite and hematite as a function of pH and temperature. *Environ. Sci. Technol.* 45, 268–275. <https://doi.org/10.1021/es101903y>.
- Elzinga, E.J., Sparks, D.L., 2007. Phosphate adsorption onto hematite: an in situ ATR-FTIR investigation of the effects of pH and loading level on the mode of phosphate surface complexation. *J. Colloid Interface Sci.* 308, 53–70. <https://doi.org/10.1016/j.jcis.2006.12.061>.
- Fang, L., Liu, R., Li, J., Xu, C., Huang, L.Z., Wang, D., 2018. Magnetite/Lanthanum hydroxide for phosphate sequestration and recovery from lake and the attenuation effects of sediment particles. *Water Res.* 130, 243–254. <https://doi.org/10.1016/j.watres.2017.12.008>.
- Fang, L., Zeng, W., Xu, L., Huang, L.Z., 2020. Green rusts as a new solution to sequester and stabilize phosphate in sediments under anoxic conditions and their implication for eutrophication control. *Chem. Eng. J.* 388, 124198. <https://doi.org/10.1016/j.cej.2020.124198>.
- Fang, L., Xu, L., Deng, J., Gao, S., Huang, L.Z., 2021. Induced generation of hydroxyl radicals from green rust under oxic conditions by iron-phosphate complexes. *Chem. Eng. J.* 414, 128780. <https://doi.org/10.1016/j.cej.2021.128780>.
- Fei, Y., Hua, J., Liu, C., Li, F., Zhu, Z., Xiao, T., Chen, M., Gao, T., Wei, Z., Hao, L., 2018. Aqueous Fe(II)-induced phase transformation of ferrihydrite coupled adsorption/immobilization of rare earth elements. *Minerals* 8, 357. <https://doi.org/10.3390/min8080357>.
- Fu, H., Yang, Y., Zhu, R., Liu, J., Usman, M., Chen, Q., He, H., 2018. Superior adsorption of phosphate by ferrihydrite-coated and lanthanum-decorated magnetite. *J. Colloid Interface Sci.* 530, 704–713. <https://doi.org/10.1016/j.jcis.2018.07.025>.
- Hayes, K.F., Papelis, C., Leckie, J.O., 1988. Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces. *J. Colloid Interface Sci.* 125, 717–726. [https://doi.org/10.1016/0021-9797\(88\)90039-2](https://doi.org/10.1016/0021-9797(88)90039-2).
- Hochella, M.F., Lower, S.K., Maurice, P.A., Penn, R.L., Sahai, N., Sparks, D.L., Twining, B.S., 2008. Nanominerals, mineral nanoparticles, and earth systems. *Science* 319, 1631–1635. <https://doi.org/10.1126/science.1141134>.
- Hochella, M.F., Mogk, D.W., Ranville, J., Allen, I.C., Luther, G.W., Marr, L.C., McGrail, B.P., Murayama, M., Qafoku, N.P., Rosso, K.M., Sahai, N., Schroeder, P.A., Vikesland, P., Westerhoff, P., Yang, Y., 2019. Natural, incidental, and engineered nanomaterials and their impacts on the earth system. *Science* 363, eaau8299. <https://doi.org/10.1126/science.aau8299>.
- Hunter, R.J., 1981. Charge and potential distribution at interfaces. Zeta Potential in Colloid Science. Elsevier, pp. 11–58. <https://doi.org/10.1016/B978-0-12-361961-7.50006-7>.
- Jain, T.K., Varshney, M., Maitra, A., 1989. Structural studies of aerosol OT reverse micellar aggregates by FT-IR spectroscopy. *J. Phys. Chem.* 93, 7409–7416. <https://doi.org/10.1021/j100358a032>.
- Jambor, J.L., Dutrizac, J.E., 1998. Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. *Chem. Rev.* 98, 2549–2586. <https://doi.org/10.1021/cr970105t>.

- Jiang, D., Li, Y., Wu, Y., Zhou, P., Lan, Y., Zhou, L., 2012. Photocatalytic reduction of Cr(VI) by small molecular weight organic acids over schwertmannite. *Chemosphere* 89, 832–837. <https://doi.org/10.1016/j.chemosphere.2012.05.001>.
- Johnston, C.P., Chrysoschoou, M., 2014. Mechanisms of chromate adsorption on hematite. *Geochim. Cosmochim. Acta* 138, 146–157. <https://doi.org/10.1016/j.gca.2014.04.030>.
- Junta, J., Hochella, M., 1994. Manganese(II) oxidation at mineral surfaces - a microscopic and spectroscopic study. *Geochim. Cosmochim. Acta* 58, 4985–4999. [https://doi.org/10.1016/0016-7037\(94\)90226-7](https://doi.org/10.1016/0016-7037(94)90226-7).
- Klyukin, K., Rosso, K.M., Alexandrov, V., 2018. Iron dissolution from goethite (α -FeOOH) surfaces in water by ab initio enhanced free-energy simulations. *J. Phys. Chem. C* 122, 16086–16091. <https://doi.org/10.1021/acs.jpcc.8b03743>.
- Kong, L., He, M., Hu, X., 2016. Rapid photooxidation of Sb(III) in the presence of different Fe (III) species. *Geochim. Cosmochim. Acta* 180, 214–226. <https://doi.org/10.1016/j.gca.2016.02.022>.
- Lan, S., Wang, X., Xiang, Q., Yin, H., Tan, W., Qiu, G., Liu, F., Zhang, J., Feng, X., 2017. Mechanisms of Mn(II) catalytic oxidation on ferrihydrite surfaces and the formation of manganese (oxyhydr)oxides. *Geochim. Cosmochim. Acta* 211, 79–96. <https://doi.org/10.1016/j.gca.2017.04.044>.
- Ler, A., Stanforth, R., 2003. Evidence for surface precipitation of phosphate on goethite. *Environ. Sci. Technol.* 37, 2694–2700. <https://doi.org/10.1021/es020773i>.
- Li, L., Stanforth, R., 2000. Distinguishing adsorption and surface precipitation of phosphate on goethite (α -FeOOH). *J. Colloid Interface Sci.* 230, 12–21. <https://doi.org/10.1006/jcis.2000.7072>.
- Li, Z., Sheng, Y., Yang, J., Burton, E.D., 2016. Phosphorus release from coastal sediments: impacts of the oxidation-reduction potential and sulfide. *Mar. Pollut. Bull.* 113, 176–181. <https://doi.org/10.1016/j.marpolbul.2016.09.007>.
- Li, T., Dong, W., Zhang, Q., Xing, D., Ai, W., Liu, T., 2020. Phosphate removal from industrial wastewater through in-situ Fe²⁺ oxidation induced homogenous precipitation: different oxidation approaches at wide-ranged pH. *J. Environ. Manag.* 255, 109849. <https://doi.org/10.1016/j.jenvman.2019.109849>.
- Lin, S.Y., Chen, K.S., Liang, R.C., 1999. Thermal micro ATR/FT-IR spectroscopic system for quantitative study of the molecular structure of poly(N-isopropylacrylamide) in water. *Polymer* 40, 2619–2624. [https://doi.org/10.1016/S0032-3861\(98\)00512-6](https://doi.org/10.1016/S0032-3861(98)00512-6).
- Liu, J., Zhu, R., Xu, T., Xu, Y., Ge, F., Xi, Y., Zhu, J., He, H., 2016. Co-adsorption of phosphate and zinc(II) on the surface of ferrihydrite. *Chemosphere* 144, 1148–1155. <https://doi.org/10.1016/j.chemosphere.2015.09.083>.
- Liu, J., Zhu, R., Liang, X., Ma, L., Lin, X., Zhu, J., He, H., Parker, S.C., Molinari, M., 2018. Synergistic adsorption of Cd(II) with sulfate/phosphate on ferrihydrite: an in situ ATR-FTIR/2D-COS study. *Chem. Geol.* 477, 12–21. <https://doi.org/10.1016/j.chemgeo.2017.12.004>.
- Liu, J., Zhu, R., Chen, Q., Zhou, H., Liang, X., Ma, L., Parker, S.C., 2019. The significant effect of photo-catalyzed redox reactions on the immobilization of chromium by hematite. *Chem. Geol.* 524, 228–236. <https://doi.org/10.1016/j.chemgeo.2019.06.005>.
- Liu, J., Inoue, S., Zhu, R., He, H., Hochella, M.F., 2021a. Facet-specific oxidation of Mn(II) and heterogeneous growth of manganese (oxyhydr)oxides on hematite nanoparticles. *Geochim. Cosmochim. Acta* 307, 151–167. <https://doi.org/10.1016/j.gca.2021.05.043>.
- Liu, J., Zhu, R., Ma, L., Fu, H., Lin, X., Parker, S.C., Molinari, M., 2021b. Adsorption of phosphate and cadmium on iron (oxyhydr)oxides: a comparative study on ferrihydrite, goethite, and hematite. *Geoderma* 383, 114799. <https://doi.org/10.1016/j.geoderma.2020.114799>.
- Lu, Y., Hu, S., Liang, Z., Zhu, M., Wang, Z., Wang, X., Liang, Y., Dang, Z., Shi, Z., 2020. Incorporation of Pb(II) into hematite during ferrihydrite transformation. *Environ. Sci.-Nano* 7, 829–841. <https://doi.org/10.1039/c9en01355e>.
- Lu, A., Li, Yan, Liu, F., Liu, Y., Ye, H., Zhuang, Z., Li, Yanzhang, Ding, H., Wang, C., 2021. The photochemical cycle of Mn oxides on the Earth's surface. *Min. Mag.* 85, 22–38. <https://doi.org/10.1180/mgm.2021.10>.
- Luengo, C., Brigante, M., Antelo, J., Avena, M., 2006. Kinetics of phosphate adsorption on goethite: comparing batch adsorption and ATR-IR measurements. *J. Colloid Interface Sci.* 300, 511–518. <https://doi.org/10.1016/j.jcis.2006.04.015>.
- Luther, G.W., 2005. Manganese(II) oxidation and Mn(IV) reduction in the environment—two one-electron transfer steps versus a single two-electron step. *Geomicrobiol. J.* 22, 195–203. <https://doi.org/10.1080/014904505090946022>.
- Mallet, M., Barthélémy, K., Ruby, C., Renard, A., Naille, S., 2013. Investigation of phosphate adsorption onto ferrihydrite by X-ray photoelectron spectroscopy. *J. Colloid Interface Sci.* 407, 95–101. <https://doi.org/10.1016/j.jcis.2013.06.049>.
- Martin, R.R., Smart, R., St, C., Tazaki, K., 1988. Direct observation of phosphate precipitation in the goethite/phosphate system. *Soil Sci. Soc. Am. J.* 52, 1492–1500. <https://doi.org/10.2136/sssaj1988.03615995005200050054x>.
- Mikutta, C., Schröder, C., Marc Michel, F., 2014. Total X-ray scattering, EXAFS, and Mössbauer spectroscopy analyses of amorphous ferric arsenate and amorphous ferric phosphate. *Geochim. Cosmochim. Acta* 140, 708–719. <https://doi.org/10.1016/j.gca.2014.05.040>.
- Mills, P., Sullivan, J.L., 1983. A study of the core level electrons in iron and its three oxides by means of X-ray photoelectron spectroscopy. *J. Phys. D. Appl. Phys.* 16, 723–732. <https://doi.org/10.1088/0022-3727/16/5/005>.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36. [https://doi.org/10.1016/S0003-2670\(00\)88444-5](https://doi.org/10.1016/S0003-2670(00)88444-5).
- Pedersen, H.D., Postma, D., Jakobsen, R., Larsen, O., 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim. Cosmochim. Acta* 69, 3967–3977. <https://doi.org/10.1016/j.gca.2005.03.016>.
- Ren, H.T., Ji, Z.Y., Wu, S.H., Han, X., Liu, Z.M., Jia, S.Y., 2018. Photoreductive dissolution of schwertmannite induced by oxalate and the mobilization of adsorbed As(V). *Chemosphere* 208, 294–302. <https://doi.org/10.1016/j.chemosphere.2018.05.187>.
- Ren, H.T., Han, J., Li, T.T., Lin, Q., Lin, J.H., Lou, C.W., 2019. Oxalic acid-induced photodissolution of ferrihydrite and the fate of loaded As(V): kinetics and mechanism. *Nanomaterials* 9, 1143. <https://doi.org/10.3390/nano9081143>.
- Ruttenberg, K.C., 2019. Phosphorus cycle. *Encyclopedia of Ocean Sciences*. Elsevier, pp. 447–460. <https://doi.org/10.1016/B978-0-12-409548-9.10807-3>.
- Ruttenberg, K.C., Sulak, D.J., 2011. Sorption and desorption of dissolved organic phosphorus onto iron (oxyhydr)oxides in seawater. *Geochim. Cosmochim. Acta* 75, 4095–4112. <https://doi.org/10.1016/j.gca.2010.10.033>.
- Sakai, N., Ebina, Y., Takada, K., Sasaki, T., 2005. Photocurrent generation from semiconducting manganese oxide nanosheets in response to visible light. *J. Phys. Chem. B* 109, 9651–9655. <https://doi.org/10.1021/jp0500485>.
- Schuttlefield, J.D., Sambur, J.B., Gelwicks, M., Eggleston, C.M., Parkinson, B.A., 2011. Photo-oxidation of chloride by oxide minerals: implications for perchlorate on mars. *J. Am. Chem. Soc.* 133, 17521–17523. <https://doi.org/10.1021/ja2064878>.
- Sherman, D.M., 2005. Electronic structures of iron(III) and manganese(IV) (hydr)oxide minerals: thermodynamics of photochemical reductive dissolution in aquatic environments. *Geochim. Cosmochim. Acta* 69, 3249–3255. <https://doi.org/10.1016/j.gca.2005.01.023>.
- Shi, M., Min, X., Ke, Y., Lin, Z., Yang, Z., Wang, S., Peng, N., Yan, X., Luo, S., Wu, J., Wei, Y., 2021. Recent progress in understanding the mechanism of heavy metals retention by iron (oxyhydr)oxides. *Sci. Total Environ.* 752, 141930. <https://doi.org/10.1016/j.scitotenv.2020.141930>.
- Shi, Y., Zhong, R., Zhou, L., Lan, Y., Guo, J., 2021. Photoreductive dissolution of schwertmannite loaded with Cr(VI) induced by tartaric acid. *Chemosphere* 276, 130127. <https://doi.org/10.1016/j.chemosphere.2021.130127>.
- Stucki, J.W., 1981. The quantitative assay of minerals for Fe²⁺ and Fe³⁺ using 1,10-phenanthroline: II. A photochemical method. *Soil Sci. Soc. Am. J.* 45, 638–641. <https://doi.org/10.2136/sssaj1981.03615995004500030040x>.
- Sulzberger, B., Laubscher, H., 1995. Reactivity of various types of iron(III) (hydr)oxides towards light-induced dissolution. *Mar. Chem.* 50, 103–115. [https://doi.org/10.1016/0304-4203\(95\)00030-U](https://doi.org/10.1016/0304-4203(95)00030-U).
- Sun, G., Fu, F., Yu, G., Yu, P., Tang, B., 2021. Migration behavior of Cr(VI) during the transformation of ferrihydrite-Cr(VI) co-precipitates: the interaction between surfactants and co-precipitates. *Sci. Total Environ.* 767, 145429. <https://doi.org/10.1016/j.scitotenv.2021.145429>.
- Sverjensky, D.A., Fukushi, K., 2006. Anion adsorption on oxide surfaces: inclusion of the water dipole in modeling the electrostatics of ligand exchange. *Environ. Sci. Technol.* 40, 263–271. <https://doi.org/10.1021/es051521v>.
- Torrent, J., Schwertmann, U., Barrón, V., 1992. Fast and slow phosphate sorption by goethite-rich natural materials. *Clay Clay Miner.* 40, 14–21. <https://doi.org/10.1346/CCMN.1992.0400103>.
- Wang, X., Hu, Y., Tang, Y., Yang, P., Feng, X., Xu, W., Zhu, M., 2017. Phosphate and phytate adsorption and precipitation on ferrihydrite surfaces. *Environ. Sci. Nano* 4, 2193–2204. <https://doi.org/10.1039/c7en00705a>.
- Wells, M.L., Mayer, L.M., Donard, O.F.X., de Souza Sierra, M.M., Ackelson, S.G., 1991. The photolysis of colloidal iron in the oceans. *Nature* 353, 248–250. <https://doi.org/10.1038/353248a0>.
- Xing, G., Garg, S., Waite, T.D., 2019. Is superoxide-mediated Fe(III) reduction important in sunlit surface waters? *Environ. Sci. Technol.* 53, 13179–13190. <https://doi.org/10.1021/acs.est.9b04718>.
- Xu, T., Zhu, R., Shang, H., Xia, Y., Liu, X., Zhang, L., 2019. Photochemical behavior of ferrihydrite-oxalate system: interfacial reaction mechanism and charge transfer process. *Water Res.* 159, 10–19. <https://doi.org/10.1016/j.watres.2019.04.055>.
- Xu, T., Fang, Y., Tong, T., Xia, Y., Liu, X., Zhang, L., 2021. Environmental photochemistry in hematite-oxalate system: Fe(III)-oxalate complex photolysis and ROS generation. *Appl. Catal. B-Environ.* 283, 119645. <https://doi.org/10.1016/j.apcatb.2020.119645>.
- Yee, N., Shaw, S., Benning, L.G., Nguyen, T.H., 2006. The rate of ferrihydrite transformation to goethite via the Fe(II) pathway. *Am. Mineral.* 91, 92–96. <https://doi.org/10.2138/am.2006.1860>.
- Yu, H.Y., Li, F.B., Liu, C.S., Huang, W., Liu, T.X., Yu, W.M., 2016. Iron redox cycling coupled to transformation and immobilization of heavy metals: implications for paddy rice safety in the red soil of South China. *Advances in Agronomy*. Elsevier, pp. 279–317. <https://doi.org/10.1016/b.s.agron.2015.12.006>.
- Yu, P., Fu, F., Sun, G., Tang, B., 2021. Effects of oxalate and citrate on the behavior and redistribution of Cr(VI) during ferrihydrite-Cr(VI) co-precipitates transformation. *Chemosphere* 266, 128977. <https://doi.org/10.1016/j.chemosphere.2020.128977>.
- Zarzycki, P., Rosso, K.M., 2019. Energetics and the role of defects in Fe(II)-catalyzed goethite recrystallization from molecular simulations. *ACS Earth Space Chem.* 3, 262–272. <https://doi.org/10.1021/acsearthspacechem.8b00175>.
- Zeng, H., Fisher, B., Giammar, D.E., 2008. Individual and competitive adsorption of arsenate and phosphate to a high-surface-area iron oxide-based sorbent. *Environ. Sci. Technol.* 42, 147–152. <https://doi.org/10.1021/es071553d>.
- Zeng, G., Wan, J., Huang, D., Hu, L., Huang, C., Cheng, M., Xue, W., Gong, X., Wang, R., Jiang, D., 2017. Precipitation, adsorption and rhizosphere effect: the mechanisms for phosphate-induced pb immobilization in soils-a review. *J. Hazard. Mater.* 339, 354–367. <https://doi.org/10.1016/j.jhazmat.2017.05.038>.
- Zhang, Z., Boxall, C., Kelsall, G.H., 1993. Photoelectrophoresis of colloidal iron oxides 1. Hematite (α -Fe₂O₃). In: Tadros, Th.F., Gregory, J. (Eds.), *Colloids in the Aquatic Environment*. Elsevier, Oxford, pp. 145–163. <https://doi.org/10.1016/B978-1-85861-038-2.50014-0>.
- Zhang, X., Chen, Y., Zhao, N., Liu, H., Wei, Y., 2014. Citrate modified ferrihydrite microstructures: facile synthesis, strong adsorption and excellent Fenton-like catalytic properties. *RSC Adv.* 4, 21575–21583. <https://doi.org/10.1039/C4RA00978A>.
- Zhu, Y., Zhu, R., Yan, L., Fu, H., Xi, Y., Zhou, H., Zhu, G., Zhu, J., He, H., 2018. Visible-light Ag/AgBr/ferrihydrite catalyst with enhanced heterogeneous photo-Fenton reactivity via electron transfer from Ag/AgBr to ferrihydrite. *Appl. Catal. B Environ.* 239, 280–289. <https://doi.org/10.1016/j.apcatb.2018.08.025>.
- Zhu, L., Fu, F., Tang, B., 2019. Three-dimensional transfer of Cr(VI) co-precipitated with ferrihydrite containing silicate and its redistribution and retention during aging. *Sci. Total Environ.* 696, 133966. <https://doi.org/10.1016/j.scitotenv.2019.133966>.