

*Electronic supplementary information*

**Phosphate and Phytate Adsorption and Precipitation on Ferrihydrite Surfaces**

Xiaoming Wang,<sup>a</sup> Yongfeng Hu,<sup>b</sup> Yadong Tang,<sup>c</sup> Peng Yang,<sup>a</sup> Xionghan Feng,<sup>c</sup> Wenqian

Xu,<sup>d</sup> Mengqiang Zhu\*<sup>a</sup>

*<sup>a</sup> Department of Ecosystem Science and Management, University of Wyoming, Laramie, Wyoming 82071, United States*

*<sup>b</sup> Canadian Light Source, University of Saskatchewan, Saskatoon, Saskatchewan S7N 2V3, Canada*

*<sup>c</sup> Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze River), Ministry of Agriculture, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China*

*<sup>d</sup> X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL60439, United States*

\*Corresponding author: Mengqiang Zhu

Tel: +1 307-766-5523

Email: [mzhu6@uwyo.edu](mailto:mzhu6@uwyo.edu)

### **SI-1. Syntheses of Ferrihydrite, Amorphous FePO<sub>4</sub> (AFP), and Amorphous Fe-phytate (AFIHP)**

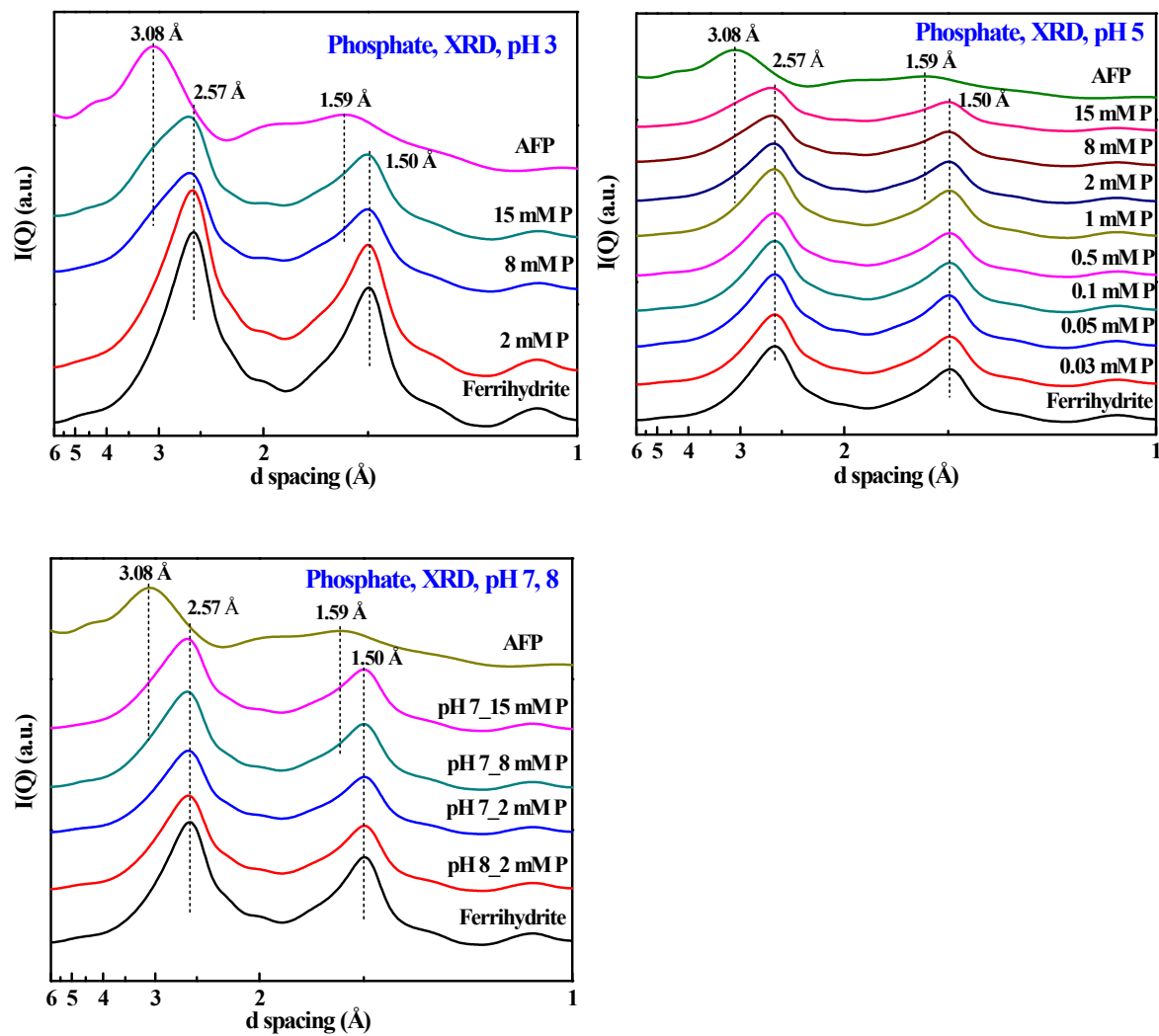
Ferrihydrite was synthesized by adding dropwise 1 M NaOH in 500 mL of 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub> until pH 7 by stirring at room temperature (RT, 20 ± 0.5 °C).<sup>1</sup> The precipitate was washed with deionized (DI) water until a conductivity of 20 μs cm<sup>-1</sup> or below was achieved. Then the solid was re-suspended in DI water and its concentration, 16.7 g/L, was measured by drying 1 mL suspension at 60 °C overnight. The Fe content in the dried ferrihydrite is 9.71 mmol/g.

Amorphous FePO<sub>4</sub> was prepared at RT by rapid mixing of 250 mL of 0.2 M Fe(NO<sub>3</sub>)<sub>3</sub> with equal volumes of 0.3 M H<sub>3</sub>PO<sub>4</sub> pre-adjusted to pH 8.8 with 1 M NaOH.<sup>2</sup> The precipitate formed was further equilibrated for 3 h in the mother liquid without pH control. For the preparation of amorphous Fe-IHP, 30 mL of 0.05 M IHP was mixed with 100 mL of 0.2 M HCl. Then, 30 mL of 0.3 M FeCl<sub>3</sub> was added dropwise to the IHP solution under stirring condition, and the pH of the mixed solution was adjusted to 2 with 1 M NaOH.<sup>3</sup> The obtained amorphous FePO<sub>4</sub> and Fe-IHP solids were both washed, air-dried, ground, and stored in a refrigerator.

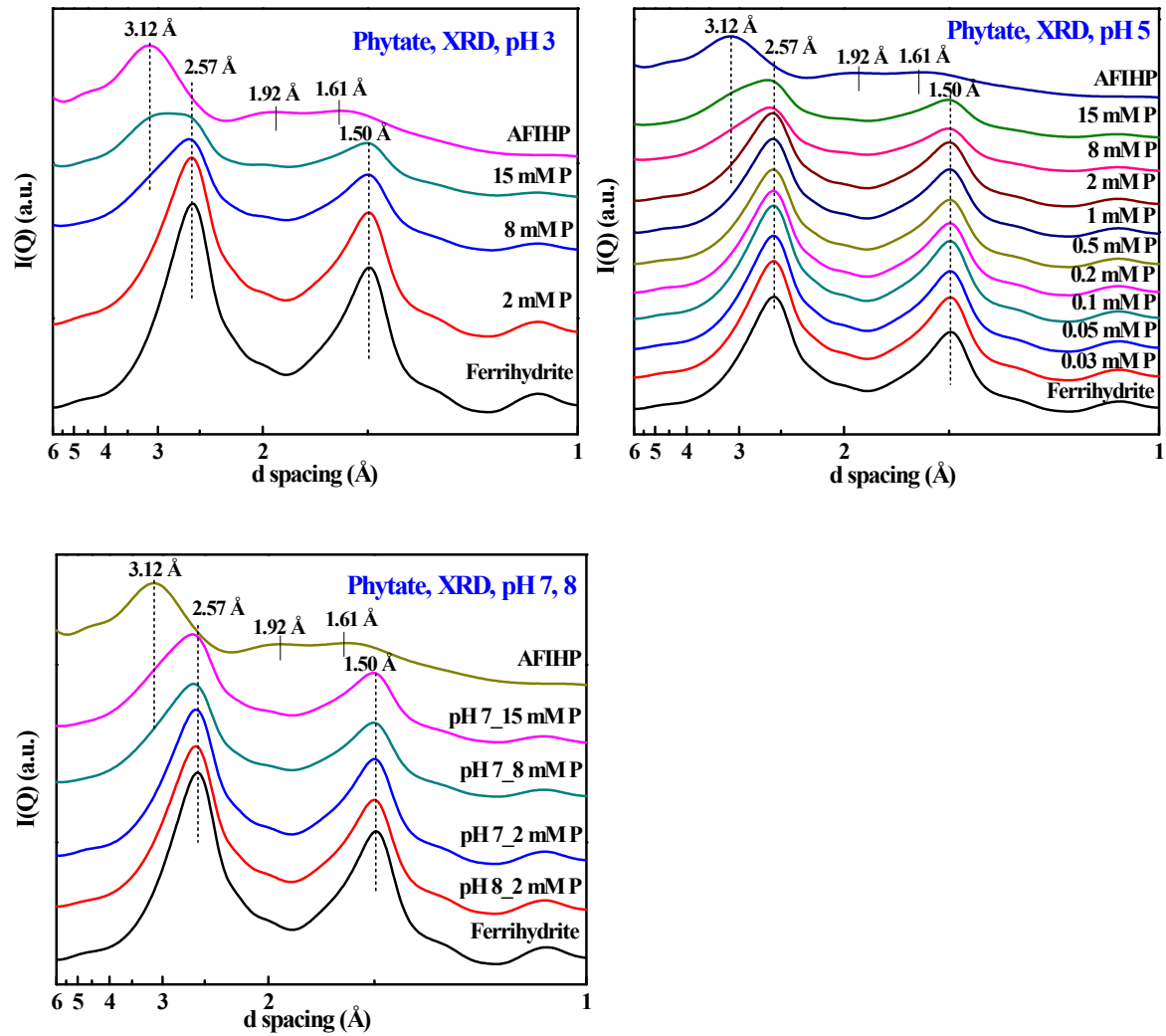
### **SI-2. Synchrotron X-ray diffraction of the wet isotherm samples**

The wet samples were loaded into polyimide tubing (Cole Parmer) with an inner diameter of 1 mm. The two ends of the tubing were immediately sealed with Epoxy gel (Devcon). An empty or DI-water loaded (18.2 MΩ·cm) tubing were also prepared for background correction. XRD data of the wet samples were collected using synchrotron radiation X-rays ( $\lambda = 0.2413 \text{ \AA}$ ) with a sample-to-detector distance of 65 cm and a PerkinElmer amorphous silicon flat panel detector at beamline 17-BM-B at the Advanced Photon Source (APS), Argonne National Laboratory. The exposure time for each sample was 10 s. Two-dimensional images were collected with the QXRD program and integrated into one-dimensional diffraction patterns by GSAS-II package.<sup>4</sup>

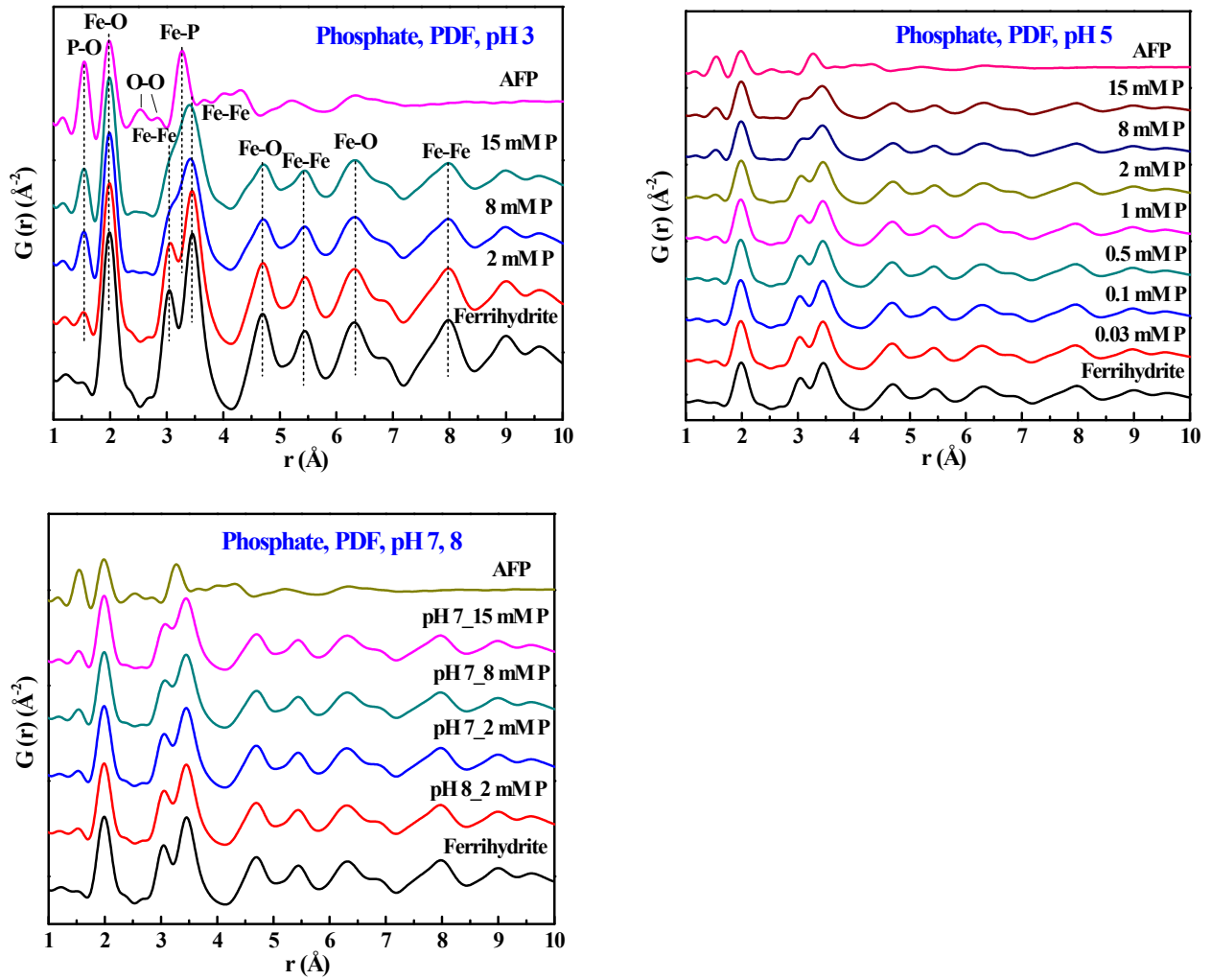
The diffraction data of water-loaded tubing were subtracted by the data of the empty tubing, which generated the XRD data of water. The XRD data of the wet samples were background corrected by subtracting the XRD data of the empty tubing and 87% of the water background.



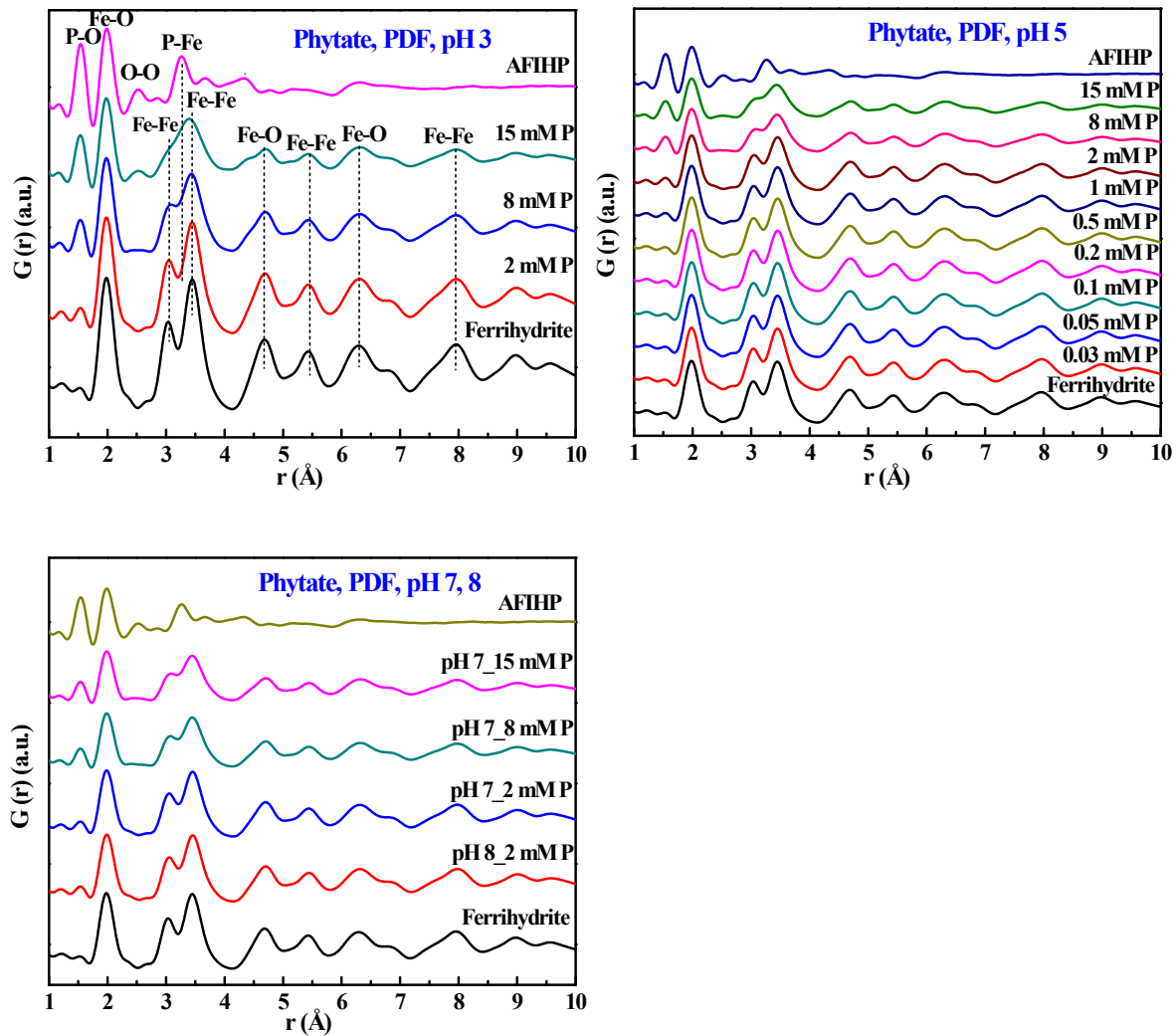
**Fig. S1.** X-ray diffraction patterns of phosphate sorption isotherm samples (dry) in the d spacing of 1 – 6 Å. The XRD patterns of ferrihydrite and AFP are included as references.



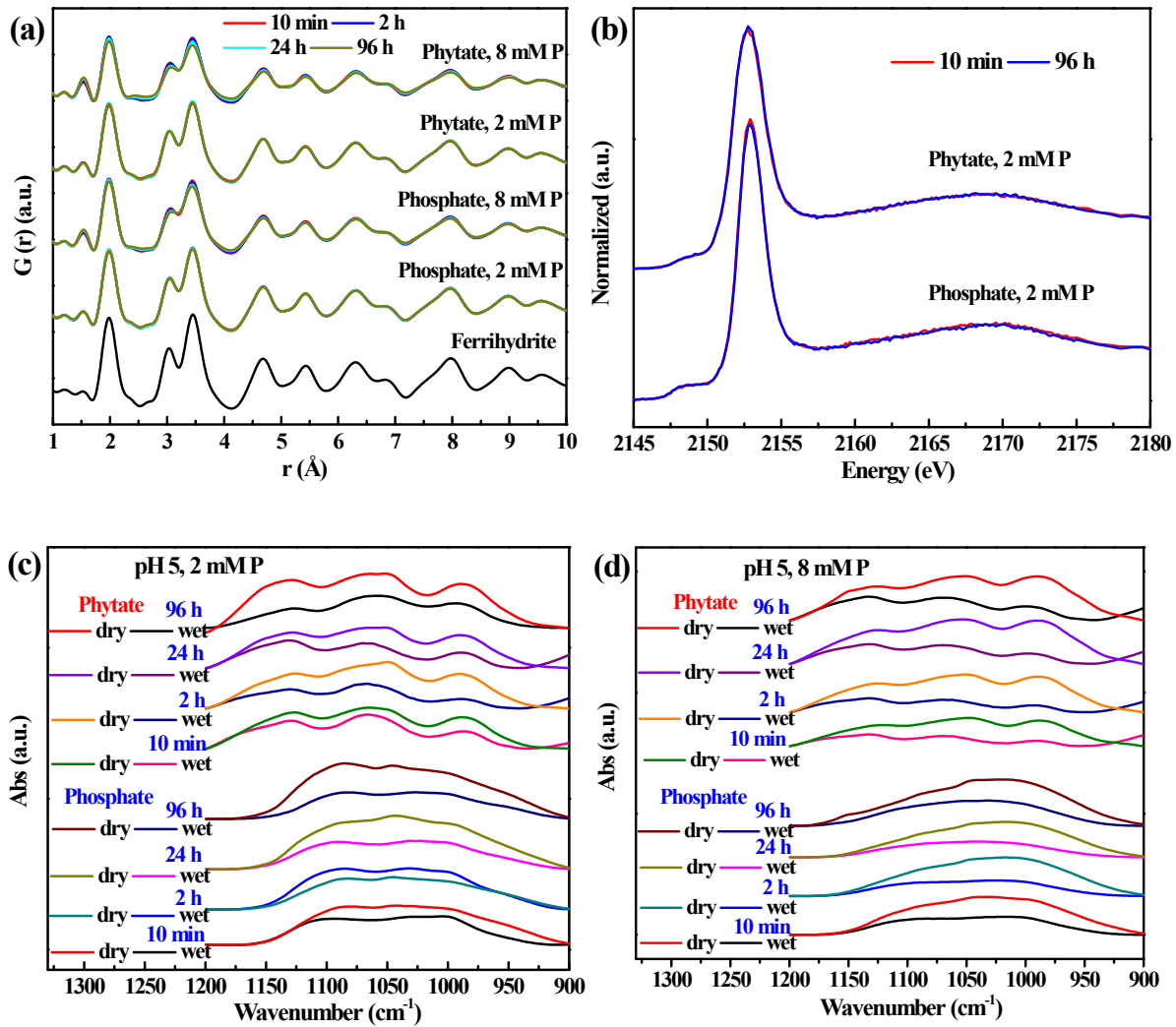
**Fig. S2.** X-ray diffraction patterns of phytate sorption isotherm samples (dry) in the d spacing of 1 – 6 Å. The XRD patterns of ferrihydrite and AFIHP are included as references.



**Fig. S3.** Pair distribution functions of phosphate sorption isotherm samples (dry) in the  $r$  range of 1–10 Å. The PDFs of ferrihydrite and AFP are included as references.

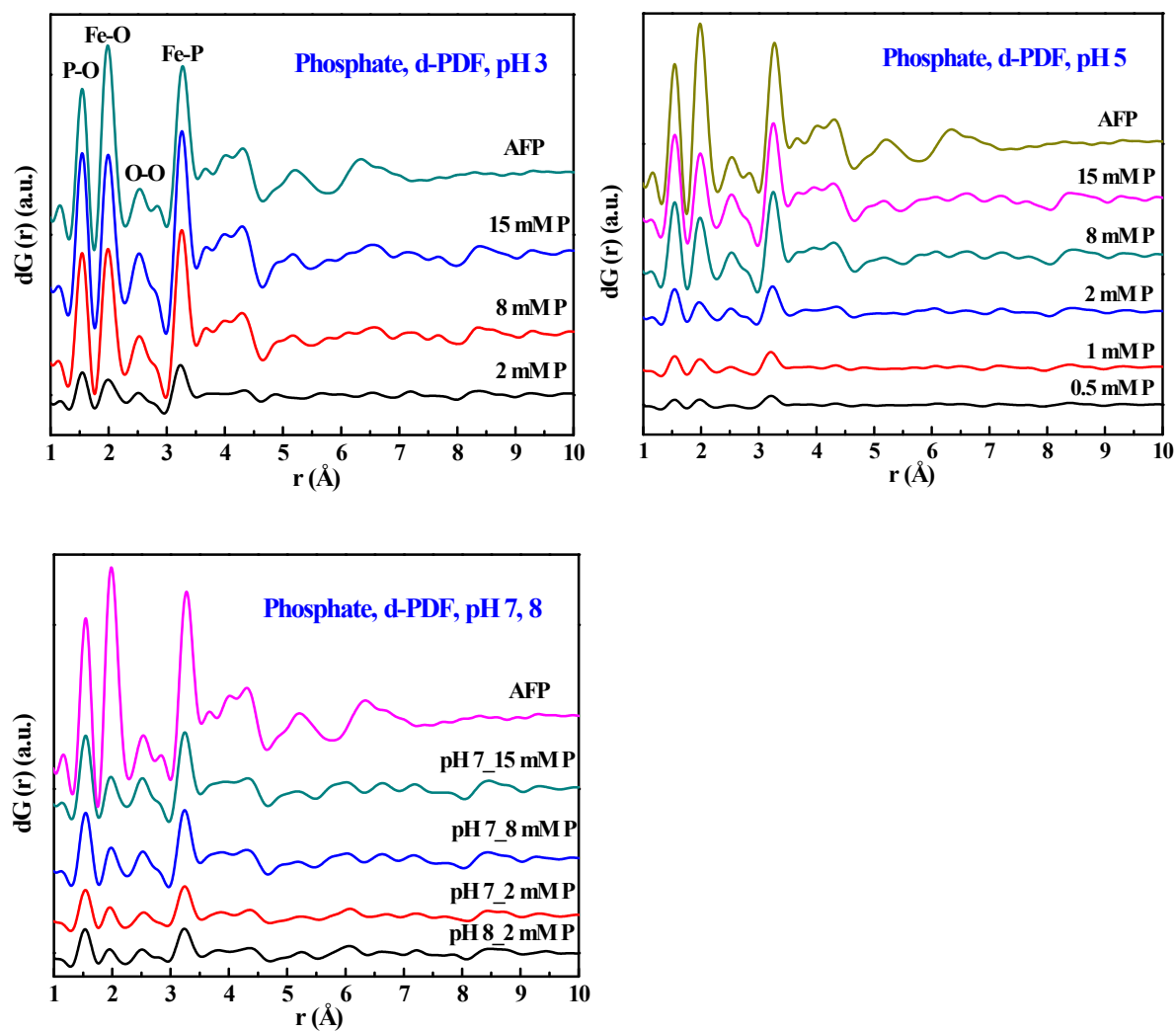


**Fig. S4.** Pair distribution functions of phytate sorption isotherm samples (dry) in the  $r$  range of 1–10 Å. The PDFs of ferrihydrite and AFIHP are included as references.

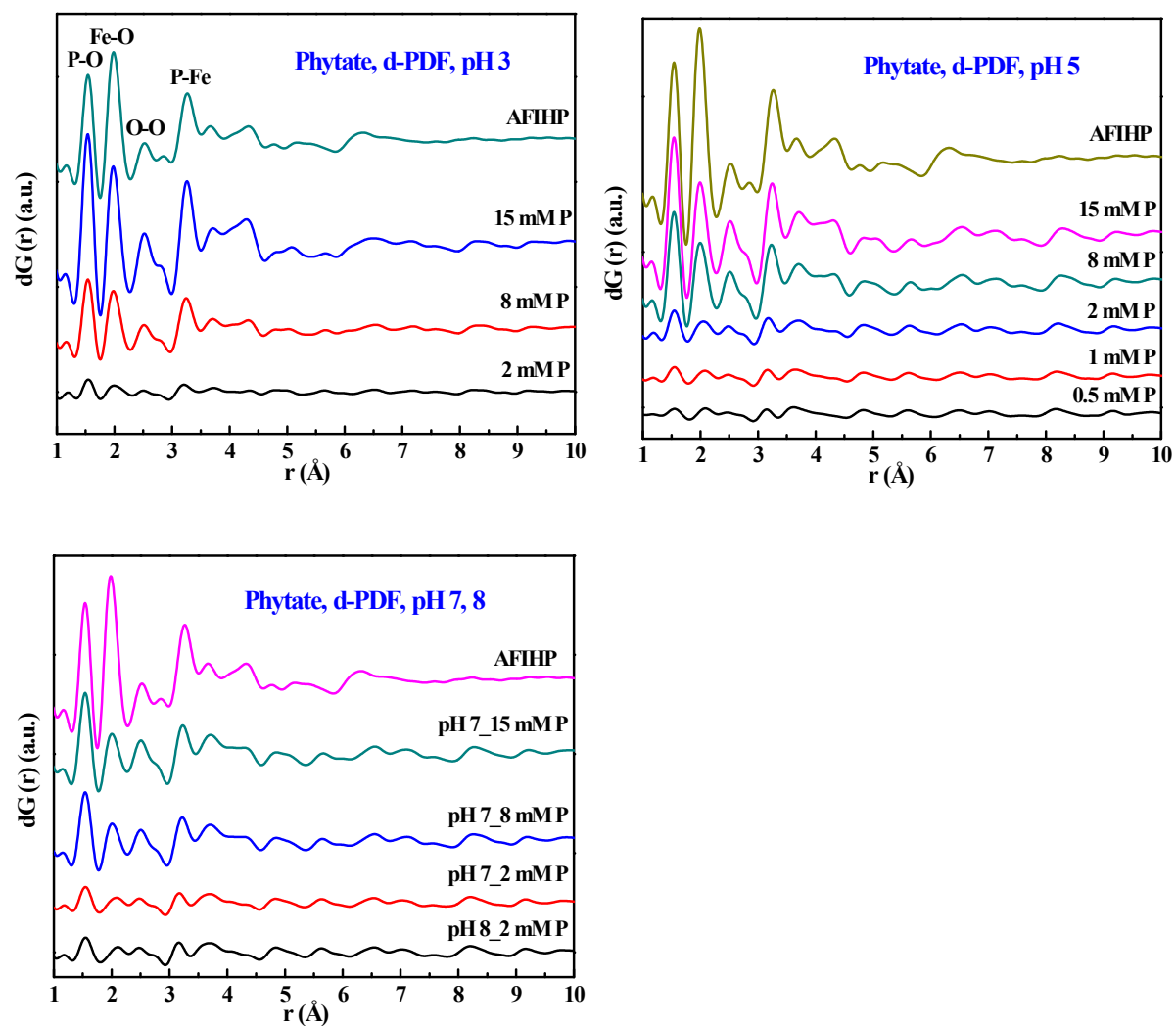


**Fig. S5.** Pair distribution functions (a, dry sample), P K-edge XANES spectra (b, dry sample), and ATR-FTIR spectra of 2 mM P (c) and 8 mM P (d) (dry and wet samples) for the selected phosphate and phytate sorption kinetic samples at pH 5.

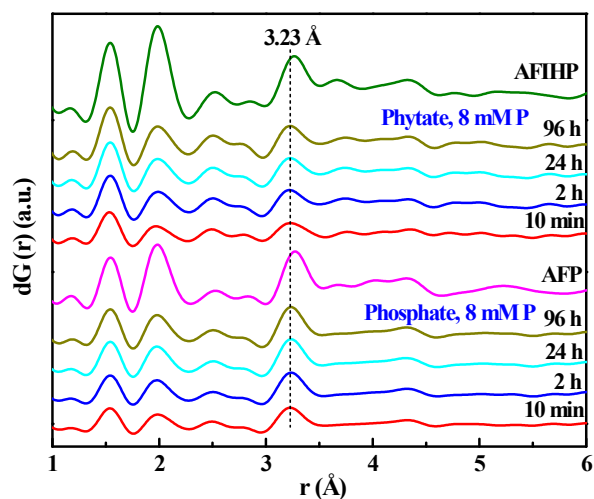




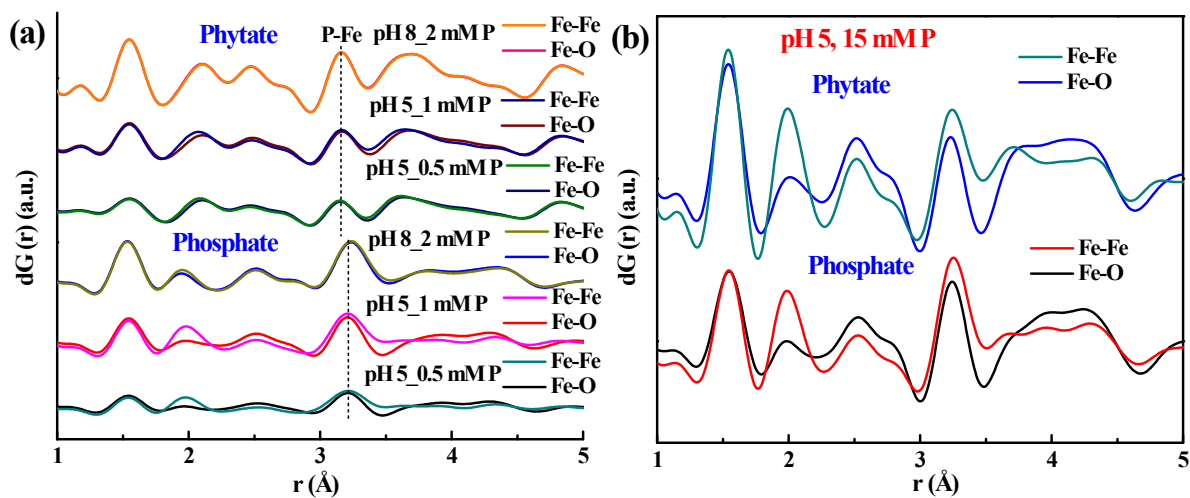
**Fig. S6.** Differential pair distribution functions of phosphate sorption isotherm samples (dry) in the  $r$  range of 1 – 10 Å by minimizing the Fe–Fe peak at 3.45 Å. The PDF of AFP is included as a reference.



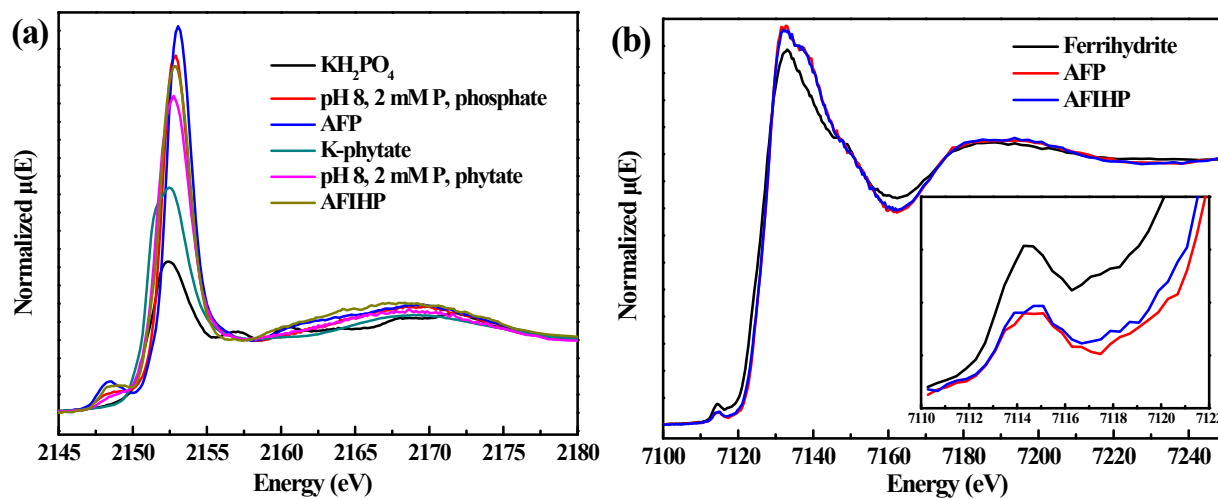
**Fig. S7.** Differential pair distribution functions of the phytate sorption isotherm samples (dry) in the  $r$  range of 1 – 10 Å by minimizing the Fe–Fe peak at 3.45 Å. The PDF of AFIHP is included as a reference.



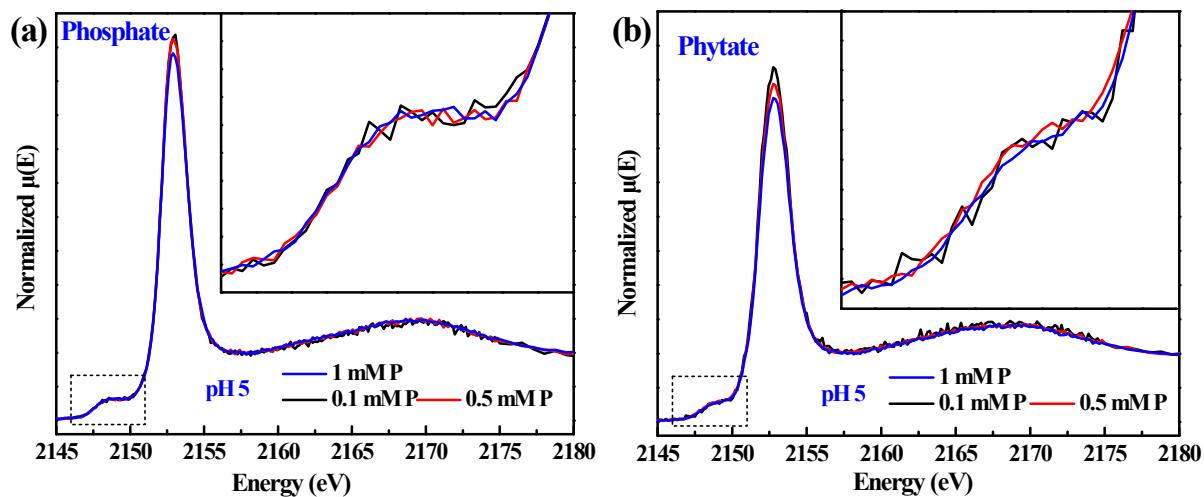
**Fig. S8.** The d-PDFs obtained by minimizing the Fe–Fe peak at 3.45 Å for the selected phosphate and phytate sorption kinetic samples prepared with 8 mM P at pH 5.



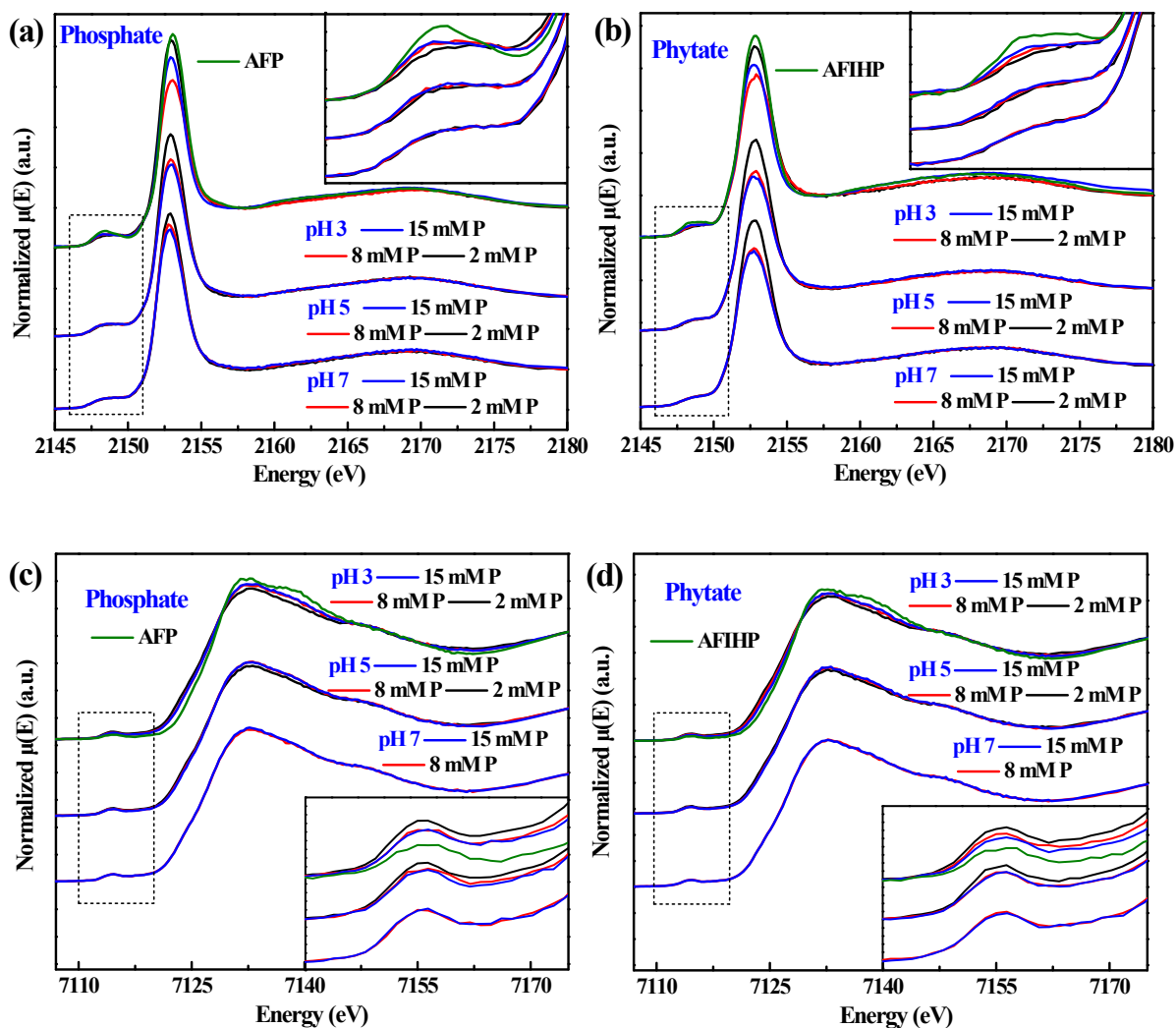
**Fig. S9.** Comparison of differential pair distribution functions of the sample (pH 8 with 2 mM P) with only adsorbed P (a) and the samples that include some precipitates (b) in the  $r$  range of 1 – 5 Å by minimizing the Fe–O or Fe–Fe peak.



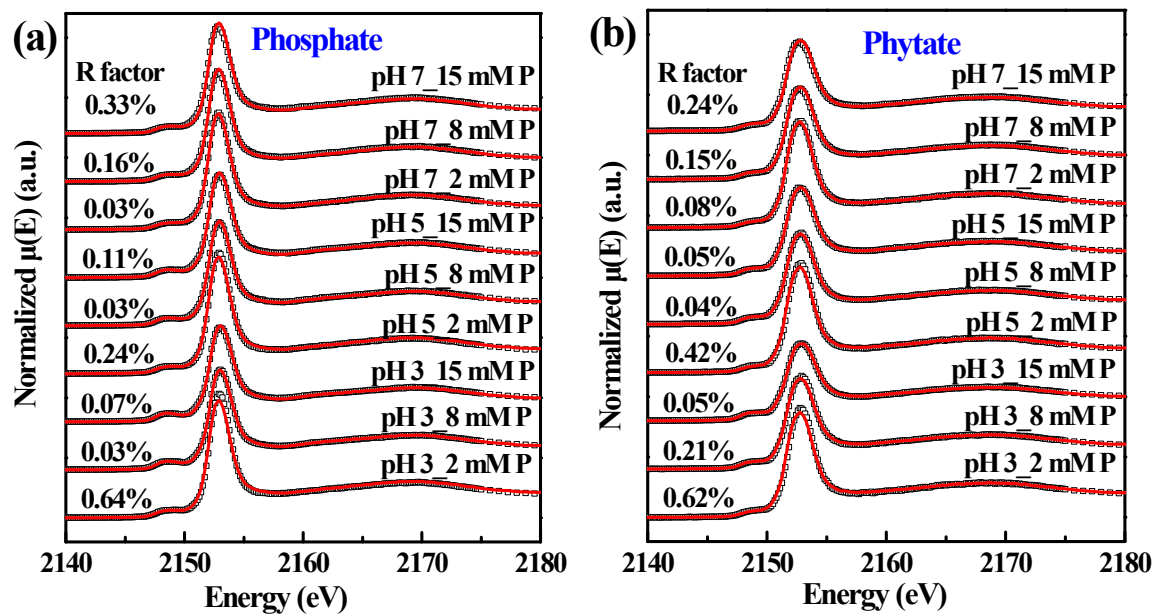
**Fig. S10.** Phosphorous K-edge XANES spectra of the end members used in linear combination fitting analysis and of potassium phosphate and phytate references (a), and Fe K-edge XANES spectra of the end members used in linear combination fitting analysis (b).



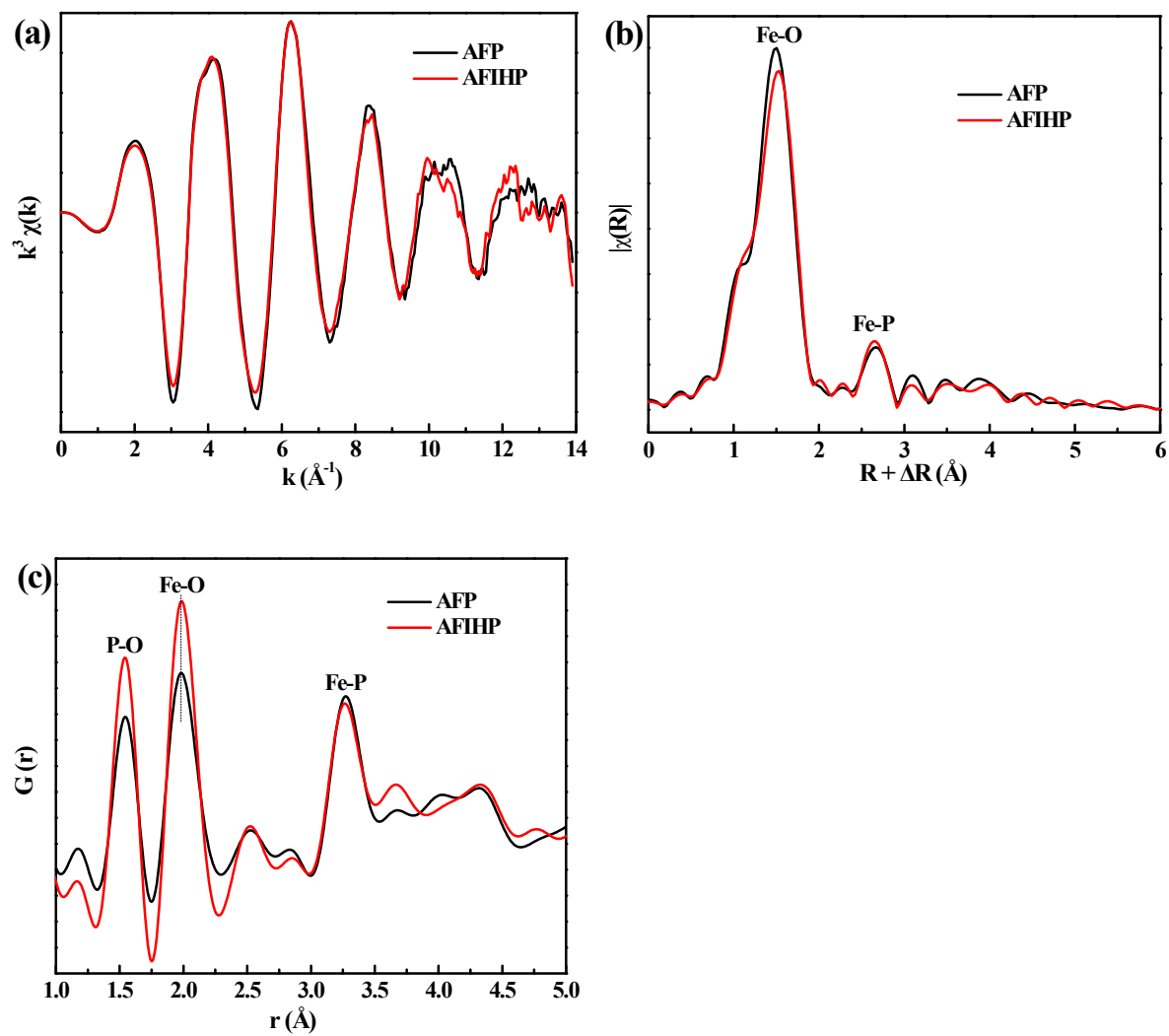
**Fig. S11.** Phosphorus K-edge XANES spectra of phosphate (a) and phytate (b) sorbed on ferrihydrite surfaces at pH 5 and 0.1 – 1 mM P for 24 h. The insets show the enlarged spectral range of 2146 – 2151 eV.



**Fig. S12.** Phosphorus (a, b) and Fe (c, d) K-edge XANES spectra for the phosphate and phytate sorption isotherm samples prepared at different pHs and initial P loadings. The spectra of AFP and AFIHP are included as the references. The insets show the enlarged pre-edge region.

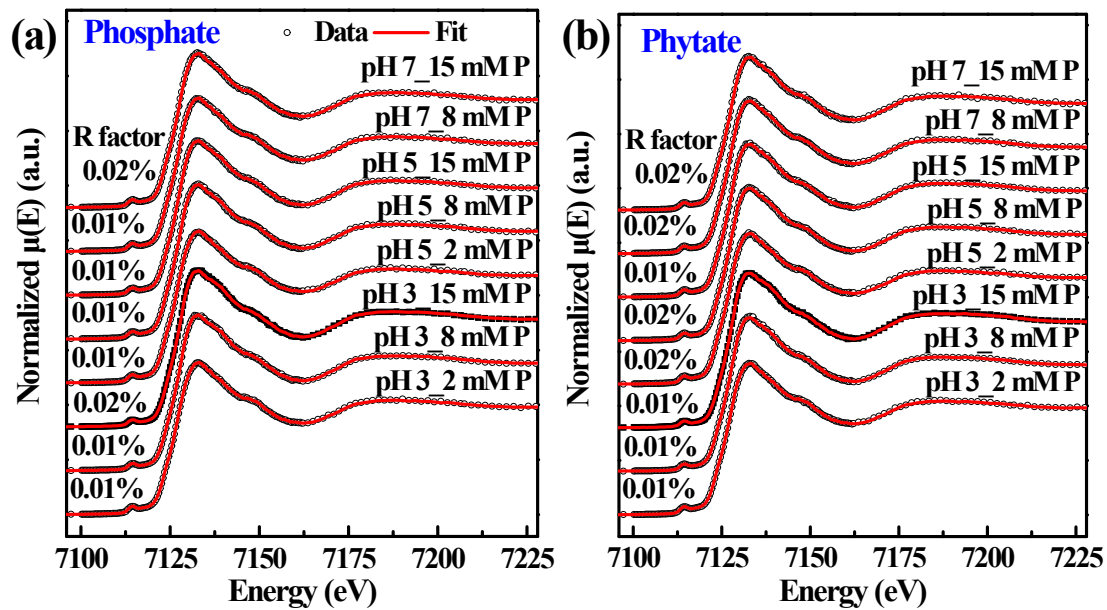


**Fig. S13.** Comparison of the P K-edge XANES spectra (black dot) and their linear combination fits (red line) for determining the relative fractions of precipitated and adsorbed P for the sorption isotherm samples.

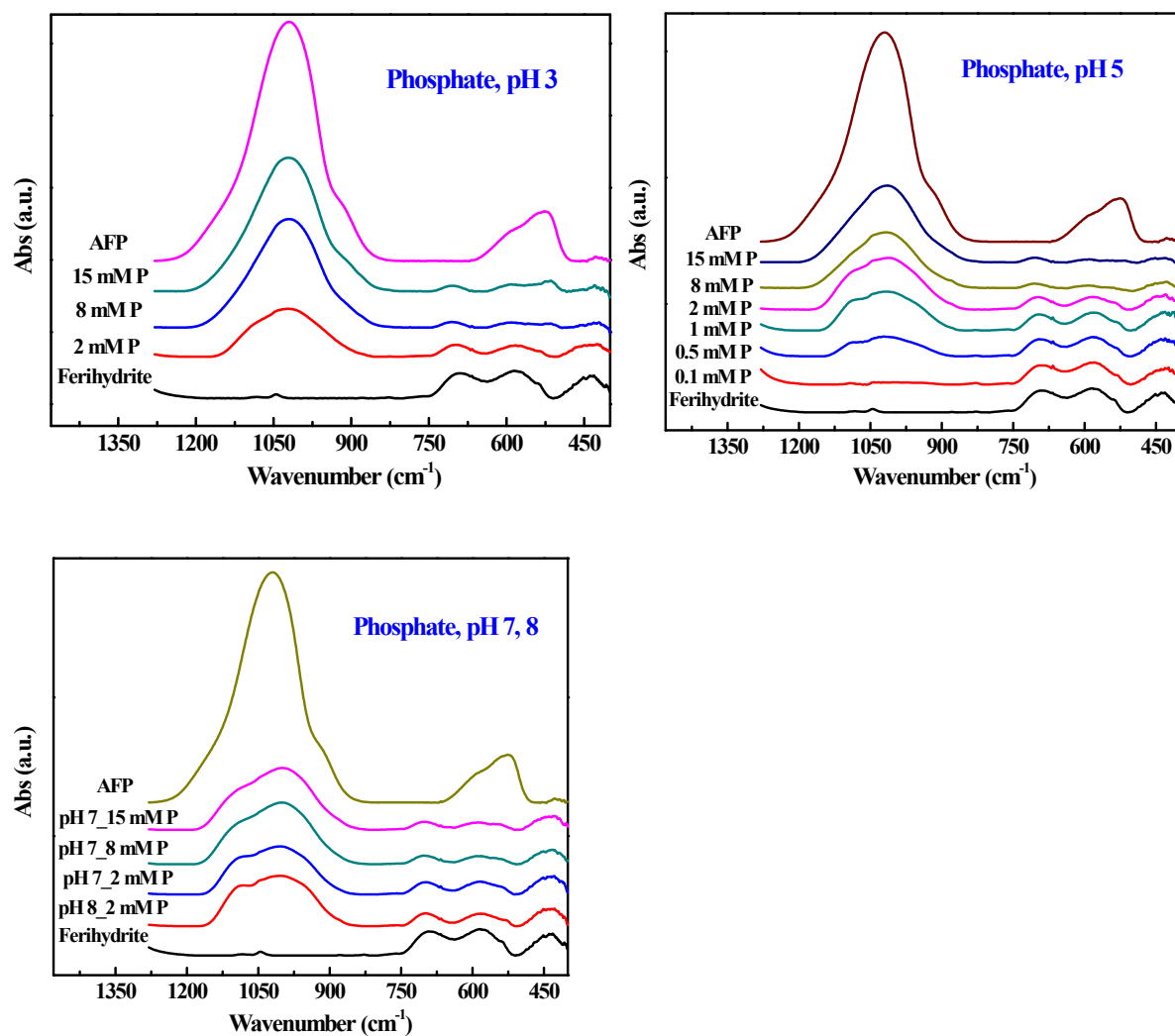


**Fig. S14.** Comparisons of Fe K-edge EXAFS spectra for AFP and AFIHP in  $k$  space (a) and  $R$  space (b), and their PDF data (c).

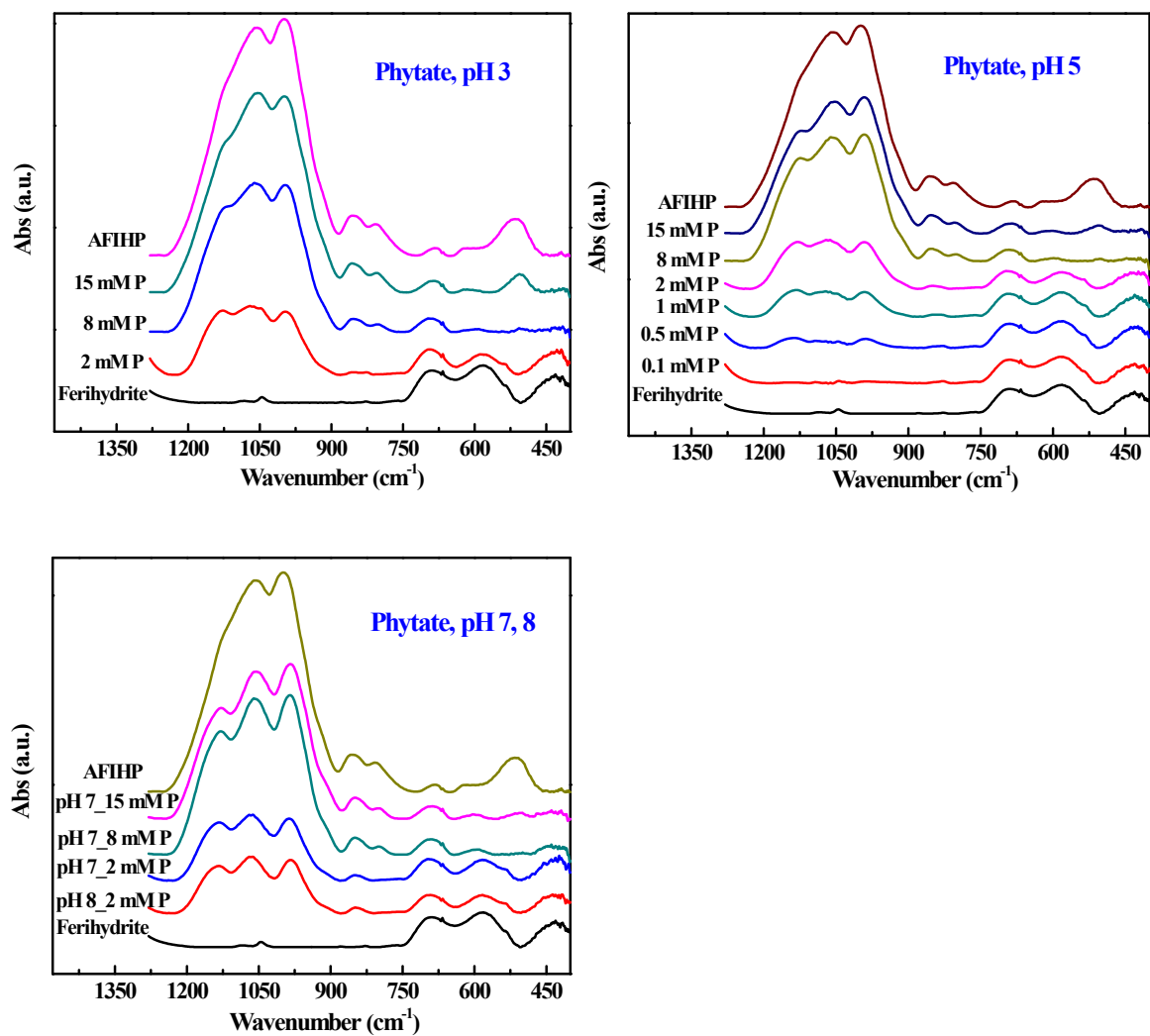




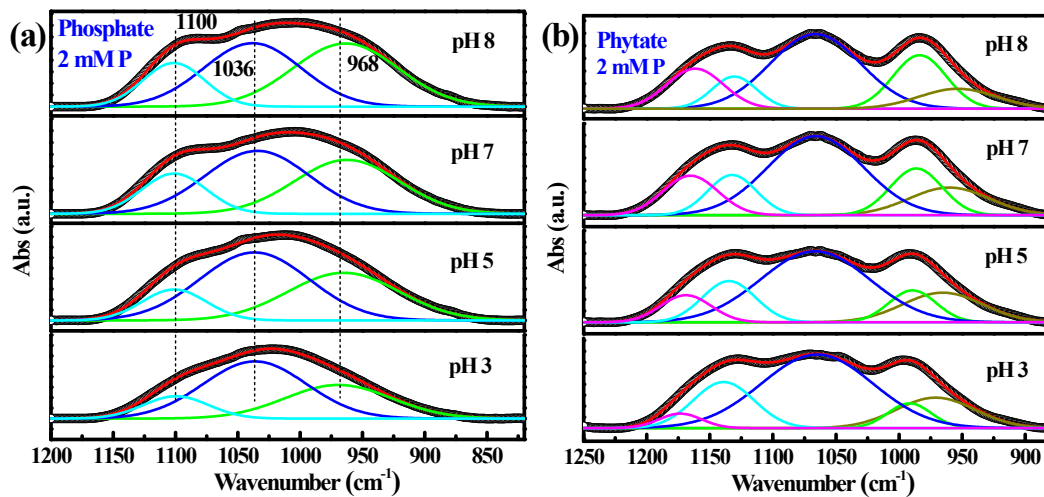
**Fig. S15.** Comparison of the Fe K-edge XANES spectra (black dot) and their linear combination fits (red line) for determining surface precipitation proportion of P sorption isotherm samples in Fe.



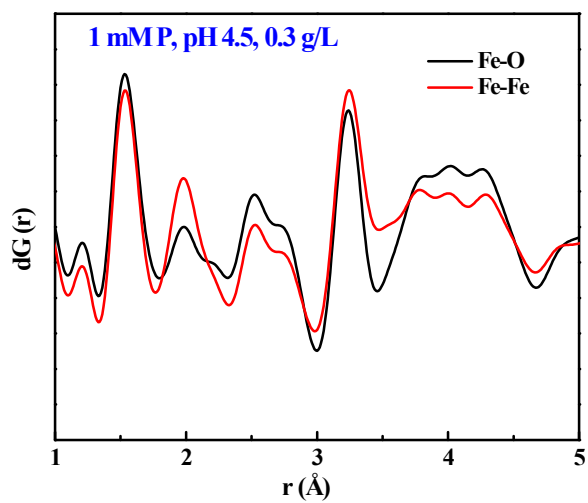
**Fig. S16.** ATR-FTIR spectra of phosphate sorption isotherm samples (dry) in the range of 1280 – 400  $\text{cm}^{-1}$ . The spectra of AFP are included as a reference.



**Fig. S17.** ATR-FTIR spectra of the IHP sorption isotherm samples (dry) in the range of 1300 – 400 cm<sup>-1</sup>. The spectra of AFIHP are included as a reference.



**Fig. S18.** A comparison of the spectra of 2 mM P of phosphate (a) or phytate (b) sorption isotherm samples (dry) at different pHs after drying. The spectra were fit with Gaussian profiles.



**Fig. S19.** Comparison of differential pair distribution functions of the two-line ferrihydrite samples with P sorbed in Wang et al.<sup>1</sup> in the  $r$  range of 1–5 Å by minimizing the Fe–O or Fe–Fe peak.

**Table S1.** The peak deconvolution parameters of 2 mM P of phosphate sorption isotherm samples at different pHs in the range of 1200 – 820 cm<sup>-1</sup> of the ATR-FTIR spectra.

	<b>Peak1</b>		<b>Peak2</b>		<b>Peak3</b>	
	Position (cm <sup>-1</sup> )	Area (%)	Position (cm <sup>-1</sup> )	Area (%)	Position (cm <sup>-1</sup> )	Area (%)
<b>pH 3</b>	969	32.8	1036	53.9	1100	13.3
<b>pH 5</b>	965	35.9	1037	50.6	1102	13.5
<b>pH 7</b>	962	38.1	1034	44.3	1101	17.5
<b>pH 8</b>	963	42.8	1038	39.9	1101	17.3

**Table S2.** The peak deconvolution parameters of 2 mM P of phytate sorption isotherm samples at different pHs in the range of 1250 – 880 cm<sup>-1</sup> of the ATR-FTIR spectra.

	<b>Peak1</b>		<b>Peak2</b>		<b>Peak3</b>		<b>Peak4</b>		<b>Peak5</b>	
	Position (cm <sup>-1</sup> )	Area (%)	Position (cm <sup>-1</sup> )	Area (%)	Position (cm <sup>-1</sup> )	Area (%)	Position (cm <sup>-1</sup> )	Area (%)	Position (cm <sup>-1</sup> )	Area (%)
<b>pH 3</b>	971	15.9	992	7.1	1065	54.3	1139	18.5	1173	4.1
<b>pH 5</b>	965	15.6	989	10.0	1066	51.0	1134	14.4	1168	9.0
<b>pH 7</b>	960	13.5	986	14.8	1066	46.5	1132	11.9	1165	13.3
<b>pH 8</b>	953	10.4	983	19.3	1066	45.5	1131	9.7	1162	15.2
Assignment <sup>5</sup>	v <sub>as</sub> (P–O–C)		v <sub>s</sub> (P–O in PO <sub>3</sub> <sup>2-</sup> )		v <sub>s</sub> (P–O in HPO <sub>3</sub> <sup>-</sup> )		v <sub>as</sub> (P–O in PO <sub>3</sub> <sup>2-</sup> )		v <sub>as</sub> (P–O in HPO <sub>3</sub> <sup>-</sup> )	

## References

1. X. Wang, W. Li, R. Harrington, F. Liu, J. B. Parise, X. Feng and D. L. Sparks, *Environ. Sci. Technol.*, 2013, **47**, 10322-10331.
2. C. Mikutta, C. Schroder and F. M. Michel, *Geochim. Cosmochim. Acta*, 2014, **140**, 708-719.
3. Z. He, C. W. Honeycutt, T. Q. Zhang and P. M. Bertsch, *J. Environ. Qual.*, 2006, **35**, 1319-1328.
4. V. D. R. Toby BH, *J Appl Cryst*, 2013, **46**, 544-549.
5. X. Guan, C. Shang, J. Zhu and G. Chen, *J. Colloid Interface Sci.*, 2006, **293**, 296-302.