Supplementary Text S1

Chemicals. 4-Nitrophenyl phosphate (pNPP) disodium hexahydrate and 3-(*N*-morpholino)-propanesulfonic acid (MOPS) were purchased from Sigma-Aldrich (St. Louis, USA). Ferric chloride ($FeCl_3$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2$), urea, ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), and potassium antimony tartrate hemihydrate ($KSbC_4HO_7 \cdot 0.5H_2O$) were purchased from Aladdin Co. Ltd (Shanghai, China). Sodium acetate (CH_3COONa), acetic acid (CH_3COOH), sodium hydroxide (NaOH), potassium dihydrogen phosphate (KH_2PO_4), and ethyl alcohol absolute (C_2H_5OH) were obtained from Tianjin Chemical Reagent Co. (Tianjin, China). Ultrapure water was used in all experiments. All chemicals were analytical grade and used without further purification.

Supplementary Text S2

Preparation of goethite. The goethite used in the experiment was synthesized according to a hydrothermal method [1]. Briefly, 400 mL of 2.5 mol L^{-1} NaOH solution was prepared and slowly added to 500 mL of 0.5 mol L^{-1} $FeCl_3$ solution. The resulting suspension was aged in an oven at 70 °C for 60 h. The precipitates were washed to neutral pH using ultrapure water and finally dried at 40 °C.

Preparation of akaganeite. The akaganeite was synthesized via a hydrothermal method [2]: 5.4 g of $FeCl_3 \cdot 6H_2O$ was added into a beaker containing 200 mL of deionized water with 5.0 g of urea. The reaction mixture was heated at 80 °C under water bath for 24 h. After cooling to room temperature, the brownish yellow precipitates were separated by centrifugation, washed with deionized water, and dried in an oven at 60 °C.

Preparation of lepidocrocite. The lepidocrocite was prepared through an air oxidation method[1]: initially, 0.2 mol L^{-1} $FeCl_2$ solution was titrated with 0.5 mol L^{-1} NaOH under aeration, the addition of NaOH was no longer needed until the suspension was maintained at pH 6.5−7.0. The resulting viscous solid suspension was washed with ultrapure water and absolute ethanol several times, and finally dried in an oven at 40 °C.

Supplementary Text S3

Material characterization. The shape, morphology, and particle sizes of the nanomaterials were characterized by transmission electron microscopy (TEM, JEM-2800, JEOL, Japan). The crystal structures of the nanomaterials were determined by X-ray diffraction (XRD) using a D/Max-2500 diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation. Raman spectra were collected with a RM2000 spectrometer at an excitation wavelength of 532 nm (Renishaw, London, UK). The Brunauer-Emmett-Teller (BET) specific surface area (SA_{BET}) of the nanomaterials were determined on an ASAP 2020 instrument (Micromeritics Co., Norcross, USA). The ζ-potential values of the nanomaterials in aqueous suspension were measured within a pH range from 3 to 11 with a particle size analyzer (Litesizer 500, Anton Paar, Austria).

Pyridine adsorption infrared spectroscopy (Py-IR) measurements of the materials were performed using a Tensor 27 FTIR spectrometer (Bruker, Karlsruhe, Germany). Samples were pretreated in situ, which involved preheating under vacuum (10^{-3} Pa) at 200 °C for 1 h to remove adsorbed volatile impurities in the materials, cooling to room temperature, and then equilibrating with pyridine vapor for 30 min. Subsequently, the pyridine-adsorbed sample was heated under vacuum (10^{-3} Pa) at 150 °C for 30 min, and FTIR spectra were recorded at 100 °C.

Supplementary Text S4

Hydrolysis experiments of pNPP. The pNPP hydrolysis experiments were performed both in aqueous solution as control and in suspensions of the nanomaterials at environmentally relevant conditions (pH 6.0, 7.0, and 8.0) in the dark. The electrolyte solutions were buffered to the desired pH using 5.0 mmol L^{-1} acetic acid/acetate (for pH 6.0) or MOPS/MOPS-Na (for pH 7.0 and 8.0). The pH was adjusted with CH_3COOH or NaOH. The experimental steps were as follows: 40 mL of the buffer solution was added to a 40-mL amber glass vial containing 4.0 mg of iron oxyhydroxides. The suspensions were sonicated in a water bath for 30 min and equilibrated on an orbital shaker at 25 °C and 160 rpm for 24 h. Then, 40 μL of pNPP stock solution (6.0 g L^{-1} in methanol) was added to the amber glass vial using a micro-syringe to achieve an initial pNPP concentration of 6.0 mg L^{-1}. Then, the bottles were immediately sealed and agitated on the orbital shaker at 25 °C and 160 rpm. At certain time intervals, 3.0 mL of the suspension was withdrawn and transferred to a clean amber glass vial, which contained 0.5 mL of 0.1 mol L^{-1} NaOH solution to terminate the reaction. The solution was filtered with 0.22-μm membrane filter to remove the nanomaterials. Then, the concentrations of pNPP and 4-nitrophenol (4-NP, hydrolysis product) were determined using a UV-vis spectrophotometer (Agilent Cary 300, USA) at 310 and 400 nm, respectively (After mixing with 0.1 mol L^{-1} NaOH, the solution became alkaline, and 4-nitrophenol was transformed to 4-nitrophenolate, which exhibits an absorption peak centered at 400 nm). Solution pH was also checked during sampling and was found to be essentially unchanged in all the experiments. Each experiment was run in triplicate. A blank control experiment was conducted at each pH without adding iron oxyhydroxides, following the same procedure as described above.

Supplementary Text S5

Phosphate adsorption experiments. The adsorption isotherms of inorganic phosphate ion onto the iron oxyhydroxide nanomaterials were measured as follows: Briefly, 8 mg nanomaterial was added to a series of 8-mL amber glass bottles containing 8 mL of 5 mmol L^{-1} acetic acid/acetate or MOPS buffer solution at pH 6.0, 7.0, and 8.0. After equilibrating for 24 h, a given volume of KH_2PO_4 stock solution was added to the bottles to obtain initial phosphate concentrations is 6 mg L^{-1}. The bottles were capped, sealed with parafilm, and agitated on an orbital shaker (at 25 °C and 160 rpm) for 5 days. Then the solutions were filtered through 0.22-μm membrane filter. The equilibrium phosphate concentration was determined using the ammonium molybdate method to monitor the absorbance at 880 nm on a spectrophotometer (Agilent Cary 300, USA) [3,4]. Each experiment was run in triplicate.

Supplementary Text S6

Langmuir−Hinshelwood (L−H) model. The L−H modeling of the iron oxyhydroxides hydrolysis kinetics was carried out using kinetics data involving different initial concentrations. Specified amounts of pNPP methanol stock solution were transferred using a micro-syringe into a series of amber glass vials containing 4.0 mg of iron oxyhydroxides nanomaterials and 40 mL of buffer solution, to achieve initial pNPP concentrations of 3.2, 4.3, 6.0, 9.7, 13.0, and 16 mg L^{-1}. All other procedures are the same as described above in text S4, and each experiment was run in triplicate.

The pNPP hydrolysis kinetics data was fitted to the pseudo-first-order kinetic model:

$$C/C_0 = \exp(-k_{obs}\, t) \tag{1}$$

where C_0 (mg L^{-1}) is the initial pNPP concentration, C (mg L^{-1}) is the pNPP concentration at a given time t (h), and k_{obs} (h^{-1}) is the apparent pseudo-first-order rate constant.

The Langmuir-Hinshelwood (L−H) model (Eqn. 2) was linearized (Eqn. 3) to fit the data and obtain the adsorption coefficient of pNPP on the nanomaterials, K_L (L mg^{-1}), and the reaction rate constant of adsorbed pNPP, k_r (mg L^{-1} h^{-1}).

$$r_0 = k_r K_L C_0/(1 + K_L C_0) \tag{2}$$

$$1/r_0 = 1/k_r + 1/(k_r K_L C_0) \tag{3}$$

where r_0 (mg L^{-1} h^{-1}) is the initial reaction rate, which was calculated according to Eqn. 4:

$$r_0 = k_{\mathrm{obs}} C_0 \qquad (4)$$

Supplementary Text S7

In situ attenuated total reflectance fourier transform infrared spectra (in situ ATR-FTIR) measurements of pNPP adsorption. In situ ATR-FTIR spectra were collected using a Nicolet 8700 FTIR spectrometer with a HATRPlus accessory (Thermos, U.S.A.), equipped with a purge gas generator and a liquid-nitrogen-cooled mercury cadmium telluride detector. The ATR flow cell houses a 45° ZnSe crystal as the internal reflection element measuring 80 × 10 × 4 mm.

Films of the iron oxyhydroxides nanomaterials were directly deposited onto the ZnSe crystal from slurries containing a known amount of powder material in a water/ethanol mixture. Briefly, 500 μL of a 2 g L^{-1} iron oxyhydroxides suspension was evenly spread on the ZnSe crystal and left to be air-dried overnight to form a uniform film. This film was gently rinsed with ultrapure water to flush out the loosely adhered particles and impurities, followed by preliminary equilibration with ultrapure water adjusted to pH 6.0 using 0.1 mol L^{-1} HCl or NaOH, at a flow rate of 1.0 mL min^{-1} until there was no further change observed in the spectra. All spectra were acquired with 256 scans across a wavenumber range of 900−1500 cm^{-1} with resolution of 4 cm^{-1}. A background spectrum was recorded to account for the absorbance of the ZnSe crystal, the pristine/iron oxyhydroxides film, and ultrapure water, and all subsequent spectra were obtained as ratios against this background. The solution flowing over the film was then switched to 100 mg L^{-1} pNPP solution, adjusted to the same pH. Preliminary experiments on the bare ZnSe crystal showed that the contributions from dissolved pNPP (100 mg L^{-1}) were negligible in the FTIR spectrum.

Supplementary Text S8

Theoretical Calculations. Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP 5.4.4). Surface models were constructed for three FeOOH polymorphs: a p(3×1) supercell of the goethite (α-FeOOH)_(021) surface [5,6], a p(1×3) supercell of the akaganeite (β-FeOOH)_(100)) surface [7], and a p(1×3) supercell of the lepidocrocite (γ-FeOOH)_(100) surface[8]. To minimize periodic boundary effects, a 15 Å vacuum layer was added perpendicular to each surface slab. Core-electron interactions were treated using the projector augmented-wave (PAW) method within the generalized gradient approximation (GGA) employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. A Hubbard U correction (U = 5.0 eV) was applied to Fe atoms. Brillouin zone integration used a (2 × 2 × 1) Monkhorst-Pack k-point grid, with a plane-wave cutoff energy of 450 eV. The phosphate group of pNPP molecule was set to interact with a surface Fe atom, and then the structures were optimized for potential energy without any constraints. Structural relaxations proceeded until forces on atoms were below 0.05 eV $Å^{-1}$ and energy changes were less than 10^{-6} eV. During optimization, lattice constants were held fixed, and only internal coordinates were relaxed under specific layer constraints: the lowest 5 atomic layers (of 9 total) for goethite, and the lowest 9 layers (of 15 total) for both akaganeite and lepidocrocite were fixed to simulate the bulk substrate. The DFT-D3 method was incorporated to account for van der Waals interactions and hydrogen bonding between water molecules, pNPP, and the mineral surfaces.

The adsorption energies (E_{ads}) were calculated according to Eq. (5):

$$E_{\mathrm{ads}} = E_{\mathrm{slab+H2O+pNPP}} - E_{\mathrm{slab+H2O}} - E_{\mathrm{pNPP}} \qquad (5)$$

where, $E_{\mathrm{slab+H2O+pNPP}}$ is the total energy of the optimized slab model with H_2O molecules and the pNPP complex, $E_{\mathrm{slab+H2O}}$ represents the energy of the slab model with H_2O molecules before pNPP adsorption, and E_{pNPP} is the initial energy of the pNPP alone. This approach offers a detailed molecular-level insight into the adsorption processes.

The Bader code[9] was used to analyze the Bader charge of each atom. The charge density difference was obtained by subtracting the charge densities of the individual fragments from that of the total system. For partial density of states (PDOS) analysis, Gaussian smearing was used, with the sigma set at 0.1 eV, and 2000 points were scattered. The Lobster software[10] was used to perform the crystal orbital Hamilton population (COHP) analysis[11].

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