Electronic Supplementary Information

Reversible Fe(II) Uptake/Release by Magnetite Nanoparticles

Huan Peng[1, 2], Carolyn I. Pearce[3], Alpha T. N'Diaye[5], Zhenli Zhu[2, *], Weifeng Huang[4], Kevin M. Rosso[3], Juan Liu[1, 6, *]

[1]The Key Laboratory of Water and Sediment Sciences, Ministry of Education, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, P. R. China

[2]State Key Laboratory of Biogeology and Environmental Geology, School of Earth Sciences, China University of Geosciences, Wuhan, Hubei 430074, China

[3]Pacific Northwest National Laboratory, Richland, WA 99352, USA

[4]College of Engineering, Peking University, Beijing 100871, China

[5]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

[6]Beijing Key Laboratory
of Mineral Environmental
Function, Peking
University, Beijing
100871, China

13 Pages

---

1 Section

3 Tables

6 Figures

Section S1. Chemicals, the glovebox, and nanoparticle characterization

Disodium anthraquinone-2,6-disulfonate (>98%, oxidized form) was purchased from Tokyo Chemical Industry, Japan. Other chemical reagents were ACS reagent grade and acquired from Sigma-Aldrich. Iron(III) chloride hexahydrate (97%), iron(II) chloride tetrahydrate (98%) and ammonium hydroxide solution (28% NH_3 in H_2O, 99.99%) used for magnetite synthesis. MES (2-(N-Morpholino)ethanesulfonic acid, 99%) and HEPES(4-(2-hydroxyethyl)-1-piperazineethane-sulfonic acid, 99.5%) used as buffer solutions. Iron(II) sulfate heptahydrate (>99%) used for $Fe(II)_{aq}$ stock solution preparation. Capillaries (Charles Supper Company, 0.5mm O.D.) and capillary wax were used for micro-XRD samples preparation. Deionized water (Millipore Milli-Q system, > 18.2 MΩ cm resistivity) was boiled for at least 30 min and then degassed for 12 h in glovebox (N_2 atmosphere, residual O_2 lower than 1 ppm). Degassed and deionized water (DDW) was stored in the glovebox for preparation of all solutions and suspensions. NP synthesis and all batch experiments were conducted under ambient conditions inside an anoxic glovebox (N_2 atmosphere from liquid N_2 boil-off with lower than 1 ppm residual O_2; Innovative Technology, Inc., Massachusetts) with PureLab GP 2-HE inert gas purifier. NP suspensions and all stock solutions were prepared and stocked inside the anaerobic glovebox. All syringe filters, glassware, and plastic were degassed in the glovebox antechamber and equilibrated with the anaerobic atmosphere prior to use.

The concentrations of Fe(II) and total Fe in the suspension of synthetic NPs were measured by acid digestion. The protocol has been reported in detail in our previous studies.[1, 2] A certain volume of NP suspension was completely dissolved in N_2-sparged 5 M HCl solution inside the glovebox overnight with shaking. Then, the concentrations of dissolved Fe(II) and total Fe in the diluted acid digest solution were determined using the ferrozine assay[3] with a UV-2501PC spectrophotometer and inductively coupled plasma optical emission spectrometry (Perkin-Elmer, Optima 2100DV), respectively. The total Fe(II)/Fe(III) ratios for the synthetic NPs was determined according to the measured concentrations of dissolved Fe(II) and total Fe. All measurements were performed in triplicate.

The specific surface area (SSA) of magnetite NPs was measured via the multipoint Brunauer-Emmer-Teller (BET) method by using a quantachrome Autosorb automated gas sorption system (Quantachrome Co.) with the degassing temperature of ~423 K. Particle size and morphology of the synthetic NPs were measured by JEOL-JEM 2010 transmission electron microscope (TEM). TEM samples were prepared by placing a drop of diluted suspension on a 400 mesh copper grid coated with ultrathin carbon layer and then drying it inside the glovebox. The crystalline phase of the synthetic NPs was determined by powder X-ray diffraction (XRD) using a Philips PW 3040/00 X'pert MPD system with Cu Kα radiation (λ = 1.5406 Å). The sample for powder XRD measurement was prepared by magnetically separating NPs from the stock NP suspension and then drying the NPs in the anaerobic glovebox.

Table S1. Calculated speciation distribution of 250 - 1000 µM $Fe^{2+}_{(aq)}$ in the 30mM buffer solution at pH 6 – 8.

Initial $[Fe^{2+}_{(aq)}]$ (µM)	pH 6		pH 7		pH 8	
	Fe^{2+} (%)	$FeOH^{+}$ (%)	Fe^{2+} (%)	$FeOH^{+}$ (%)	Fe^{2+} (%)	$FeOH^{+}$ (%)
250	99.972	0.028	99.725	0.275	97.316	2.682
500	99.973	0.027	99.727	0.273	97.329	2.669
750	99.973	0.027	99.728	0.272	97.341	2.657
1000	99.973	0.027	99.729	0.271	97.354	2.644

Table S2. The slopes, intercepts, and R^2 values of the fitted lines in Figure 2†.

Initial $[Fe^{2+}_{(aq)}]$ (μM)	pH = 6	pH = 7	pH = 8
0	$y = 0.1819 x + 46.72$ $R^2 = 0.988$	$y = 0.06883 x + 40.13$ $R^2 = 0.946$	$y = -0.00003x + 0.2469$ $R^2 = 0.999$
250	$y = 0.1639 x + 29.23$ $R^2 = 0.999$	$y = 0.04677 x - 16.43$ $R^2 = 0.974$	$y = -0.04038 x - 132.3$ $R^2 = 0.930$
750	$y = 0.1455 x + 15.50$ $R^2 = 0.976$	$y = 0.04462 x - 37.14$ $R^2 = 0.979$	$y = -0.08720 x - 214.7$ $R^2 = 0.992$
1000	$y = 0.1629 x - 56.96$ $R^2 = 0.990$	$y = 0.07088 x - 187.8$ $R^2 = 0.993$	NA*

† The "Instrument" weighting method was used in the linear fitting for all samples, except the case at pH 6 without added $Fe^{2+}_{(aq)}$. "No weighting" method was used in this specific case, in order to obtain a better fitting.

*When magnetite loading was more than ~ 0.3 g L^{-1} ([Fe(II)] equivalent = 1300 μM), $\Delta[Fe^{2+}_{(aq)}]$ reached a plateau. The data cannot be fitted using a linear function.

Table S3. The slopes, intercepts, and R^2 values of the fitted lines in Figure S4.

Magnetite Concentration (μM)	pH = 6	pH = 7	pH = 8
300	$y = -0.0797x + 80.5$ $R^2 = 0.889$	$y = -0.1042x + 34.63$ $R^2 = 0.914$	$y = -0.5039x + 0.144$ $R^2 = 0.965$
800	$y = -0.1288x + 196.2$ $R^2 = 0.955$	$y = -0.1021x + 76.27$ $R^2 = 0.826$	$y = -0.4899x + 0.484$ $R^2 = 0.992$
1300	$y = -0.1291x + 299.5$ $R^2 = 0.913$	$y = -0.2012x + 138.4$ $R^2 = 0.929$	$y = -0.5973x - 0.0077$ $R^2 = 0.931$
2000	$y = -0.1268x + 425.8$ $R^2 = 0.952$	$y = -0.1694x + 160.1$ $R^2 = 0.856$	$y = -0.5559x+0.084$ $R^2 = 0.945$
3000	$y = -0.2019x + 575.2$ $R^2 = 0.974$	$y = -0.2123x + 250.5$ $R^2 = 0.964$	$y = -0.6358x + 0.155$ $R^2 = 0.999$

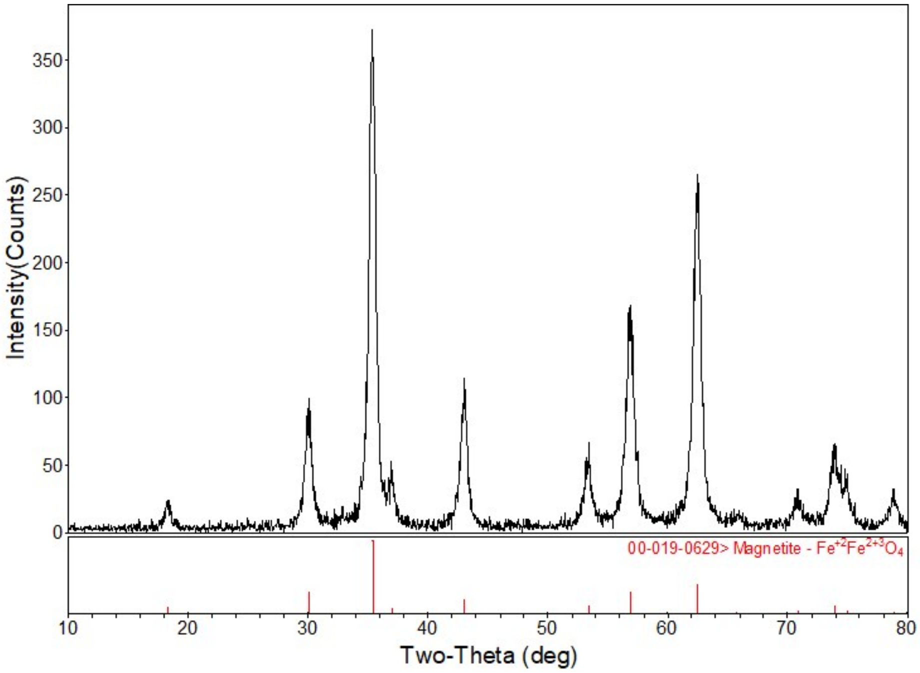

Figure S1. XRD pattern of synthetic magnetite NPs. The reference for magnetite (JCPDS card number: 00-019-0629) is shown in red at the bottom.

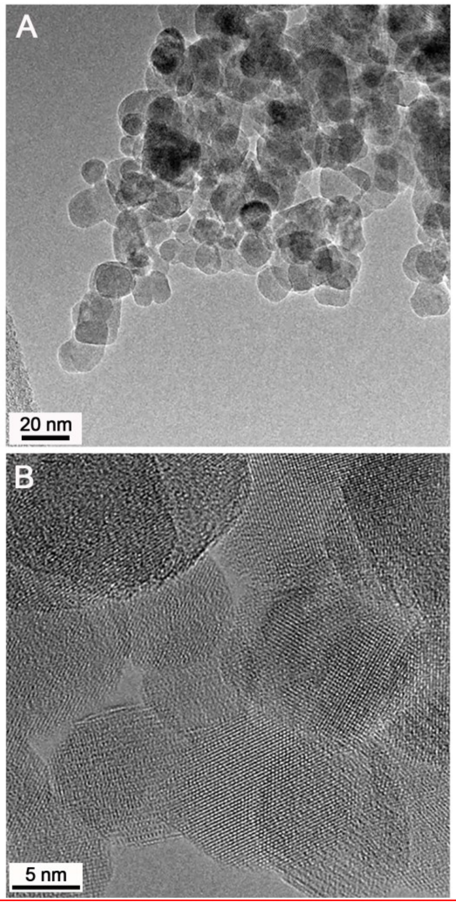

Figure S2. The low (A) and high (B) magnification TEM images of synthetic magnetite NPs.

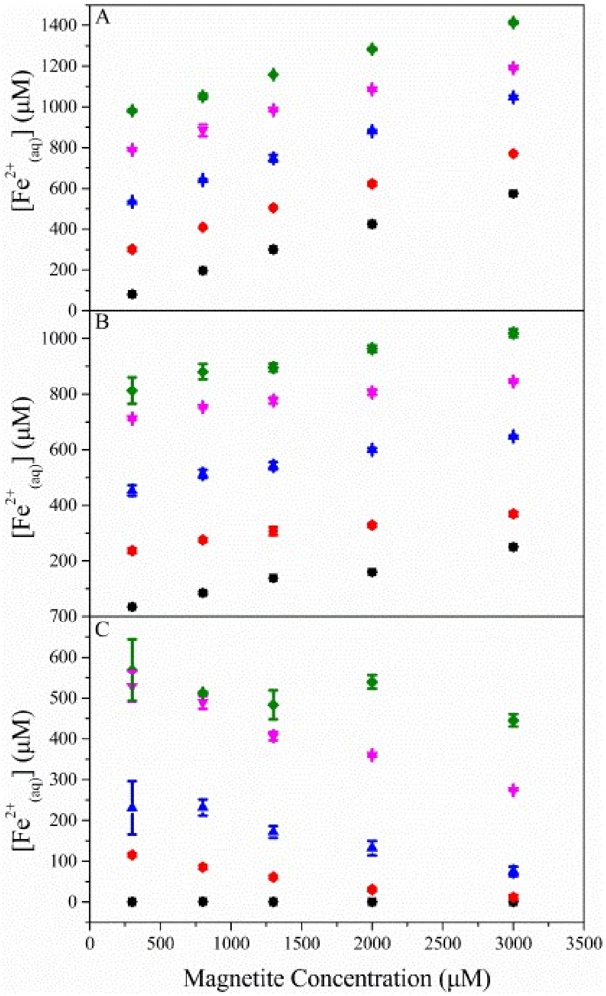

Figure S3. The equilibrium concentrations of Fe$^{2+}_{(aq)}$ after 24-hour reactions in the suspensions of 300 - 3000 μM magnetite NPs amended with 0 μM (black), 250 μM (red), 500μM (blue), 750 μM (magenta), and 1000 μM (green) Fe$^{2+}_{(aq)}$ at pH 6 (A), 7 (B), and 8 (C), respectively.

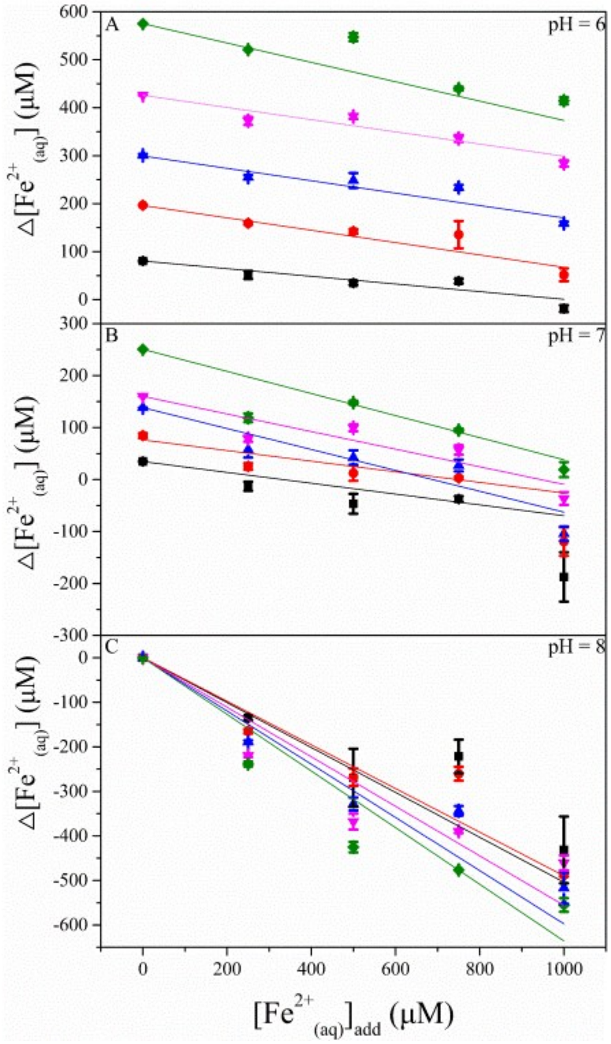

Figure S4. $\Delta[Fe^{2+}_{(aq)}]$ versus the concentration of added $Fe^{2+}_{(aq)}$ at pH 6 (A), pH 7 (B), and pH 8 (C), respectively, in the suspensions of magnetite NPs with [Fe(II)] equivalent of 300 μM (black), 800 μM (red), 1300 μM (blue), 2000 μM (magenta) and 3000 μM (green), respectively. The dots are the measured results and the corresponding lines are the fitted lines. The equations and R^2 values of the fitted lines are shown in Table S3.

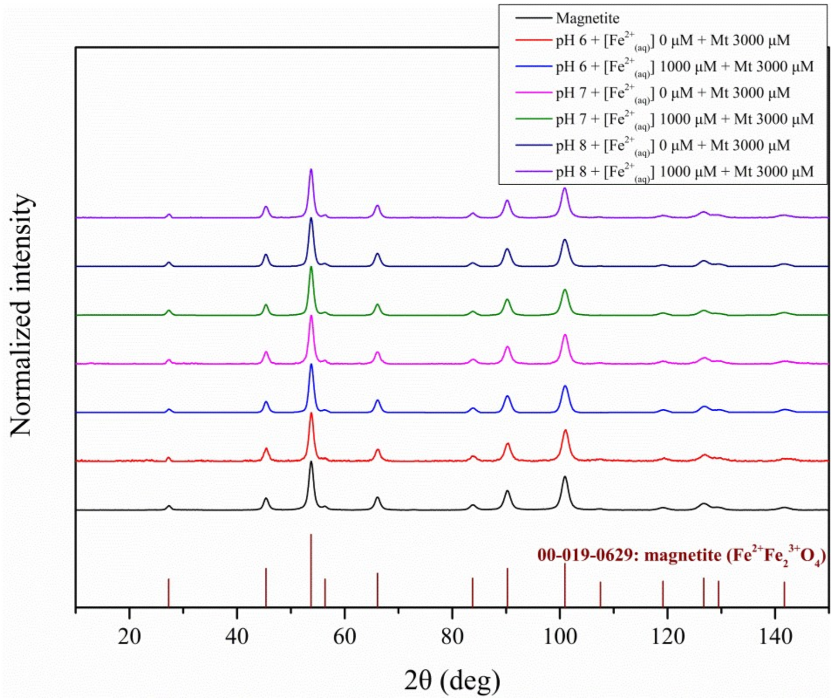

Figure S5: XRD patterns of magnetite NPs in the stock suspension (black) and in the buffer solution at pH 6 (red), pH 7 (magenta), and pH 8 (navy), respectively, as well as those of NPs after 24-hour reaction with 1000 μM $Fe^{2+}_{(aq)}$ at pH 6 (blue), pH 7 (green), and pH 8 (purple), respectively. The reference for magnetite (JCPDS card number: 00-019-0629) is shown in brown at the bottom.

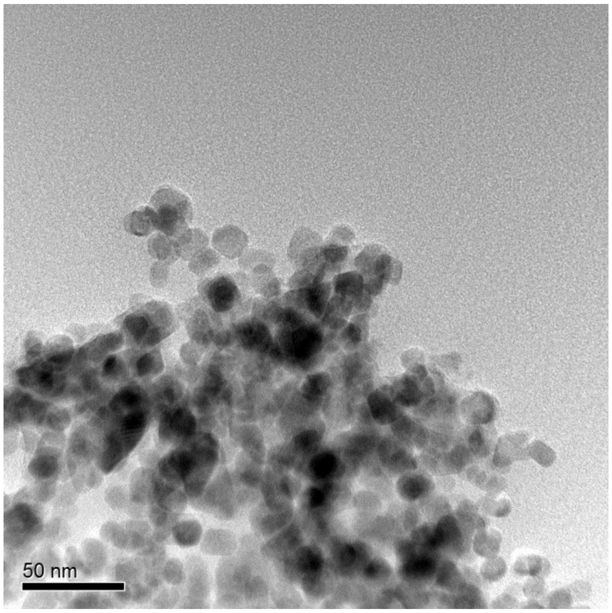

Figure S6. The representative TEM image of magnetite NPs after reaction with $Fe^{2+}_{(aq)}$ at pH 7

REFERENCES

1. J. Liu, C. I. Pearce, O. Qafoku, E. Arenholz, S. M. Heald and K. M. Rosso, Tc(VII) reduction kinetics by titanomagnetite ($Fe_{3-x}Ti_xO_4$) nanoparticles, *Geochim. Cosmochim. Acta*, 2012, **92**, 67-81.
2. C. I. Pearce, O. Qafoku, J. Liu, E. Arenholz, S. M. Heald, R. K. Kukkadapu, C. A. Gorski, C. M. B. Henderson and K. M. Rosso, Synthesis and properties of titanomagnetite ($Fe_{3-x}Ti_xO_4$) nanoparticles: A tunable solid-state Fe(II/III) redox system, *J. Colloid Interface Sci.*, 2012, **387**, 24-38.
3. L. L. Stookey, Ferrozine---a new spectrophotometric reagent for iron, *Anal. Chem.*, 1970, **42**, 779-781.