Supporting information

Influence of organic ligands on the stoichiometry of magnetite nanoparticles

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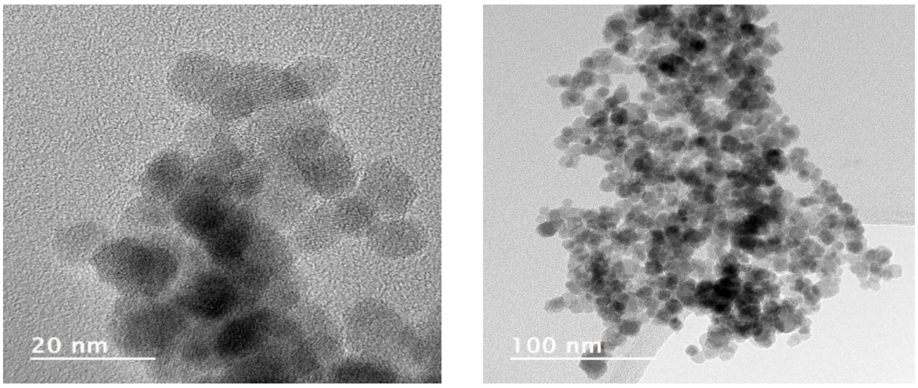
Table S1. Effective Fe(II)/Fe(III) ratio (R_{eff}) obtained from chemical analysis and average particle size by TEM for stoichiometric nanomagnetite (R0.5) and oxidized products (R0.1), equilibrated at pH 8 during 20 days, in presence of citrate and EDTA at pH 8.

Sample	R_{eff} in solid phase	Particle size by TEM (nm)	References
R0.1	0.1 ± 0.01	9.6 ± 2.3	(Jungcharoen et al., 2022)
R0.1 + citrate	0.1 ± 0.03	9.2 ± 1.4	Present work
R0.1 + EDTA	0.1 ± 0.03	9.5 ± 1.4	Present work
R0.5	0.5 ± 0.01	11.5 ± 1.5	(Jungcharoen et al., 2022)
R0.5 + citrate	0.5 ± 0.03	10.3 ±1.3	Present work
R0.5 + EDTA	0.2 ± 0.03	9.9 ± 1.6	Present work

Table S2. Chemical reactions and corresponding equilibrium constants, which are absent from the “Minteq.v4” database of PHREEQC, but required for thermodynamic calculations. (1) calculated constants for 10 nm-sized magnetites according to Jungcharoen et al.[1]. (2) Silva et al.[2]. (3) Vukosav et al.[3]. (4) The reaction was omitted because it gave inconsistent results with the present experimental data. (Complete references are provided in the main text).

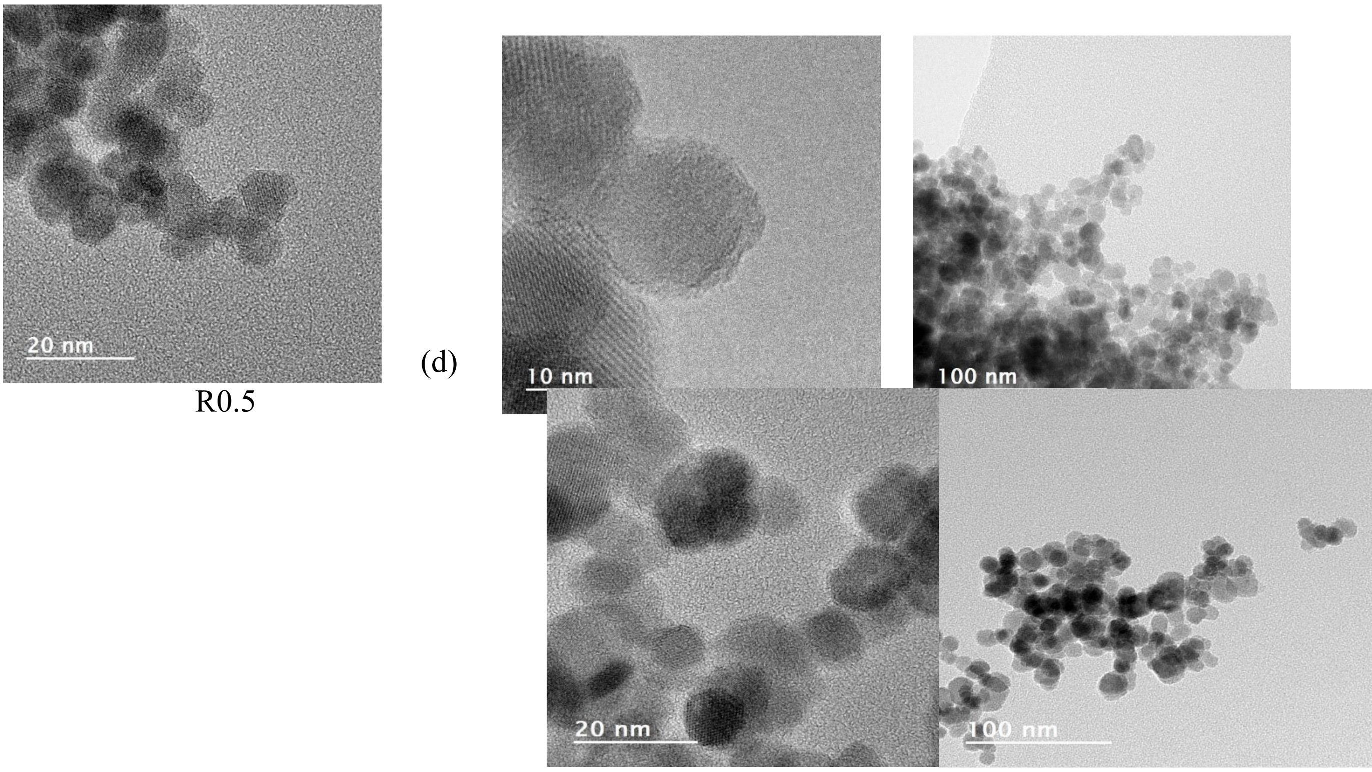
Reaction	**log K**
$Fe_8O_{12} + 24\ H^+ \rightleftharpoons 8\ Fe^{3+} + 12\ H_2O$	15.49(1)
$Fe_9O_{12} + 24\ H^+ \rightleftharpoons 6\ Fe^{3+} + 3\ Fe^{2+} + 12\ H_2O$	35.23(1)
$Citrate^{4-} + H^+ \rightleftharpoons CitrateH^{3-}$	14.40(2)
$CitrateH^{3-} + H^+ \rightleftharpoons CitrateH_2^{2-}$	6.40(2)
$CitrateH_2^{2-} + H^+ \rightleftharpoons CitrateH_3^-$	4.76(2)
$CitrateH_3^- + H^+ \rightleftharpoons CitrateH4$	3.13(2)
$Fe^{3+} + H^+ + Citrate^- \rightleftharpoons Fe(III)HCitrate$	25.69(3)
$Fe^{3+} + 2\ Citrate^- \rightleftharpoons Fe(III)Citrate_2^{5-}$	36.27(3)
$Fe^{3+} + H^+ + 2\ Citrate^- \rightleftharpoons Fe(III)HCitrate_2^{4-}$	41.4(3)
$Fe^{3+} + 2\ H^+ + 2\ Citrate^- \rightleftharpoons Fe(III)H_2Citrate_2^{3-}$	47.46(3)
$Fe^{2+} + H^+ + Citrate^- \rightleftharpoons Fe(II)HCitrate^-$	19.43(3)
$Fe^{2+} + Citrate^- \rightleftharpoons Fe(II)Citrate_2^{6-}$	Not used(4)

(a) R0.1



(b) R0.1 + Citrate

(c) R0.1 + EDTA



(d) R0.5

(e) R0.5 + Citrate

(f) R0.5 + EDTA

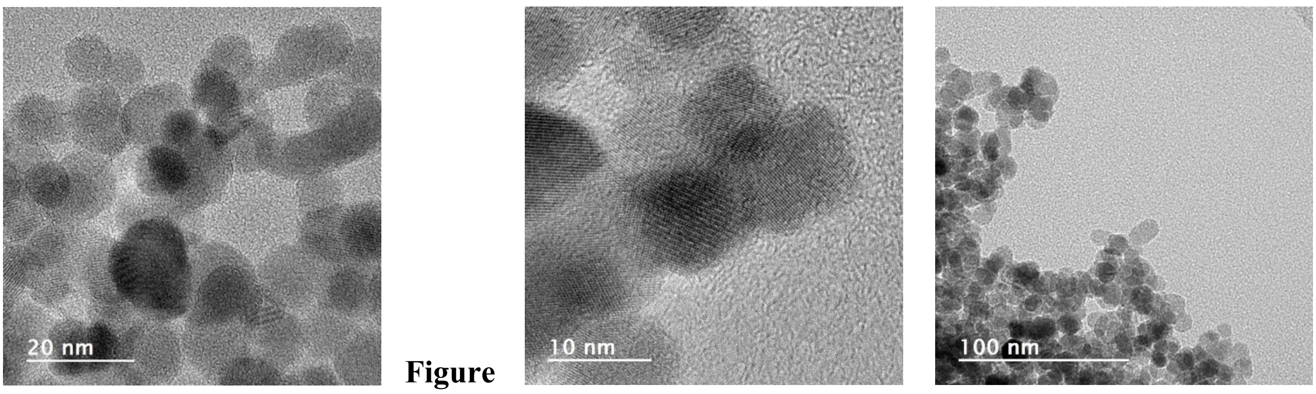


Figure S1. TEM images of oxidized products (R0.1) in absence (a) and presence of (b) citrate and (c) EDTA and stoichiometric nanomagnetite (R0.5) in absence (d) and presence of (e) citrate and (f) EDTA.

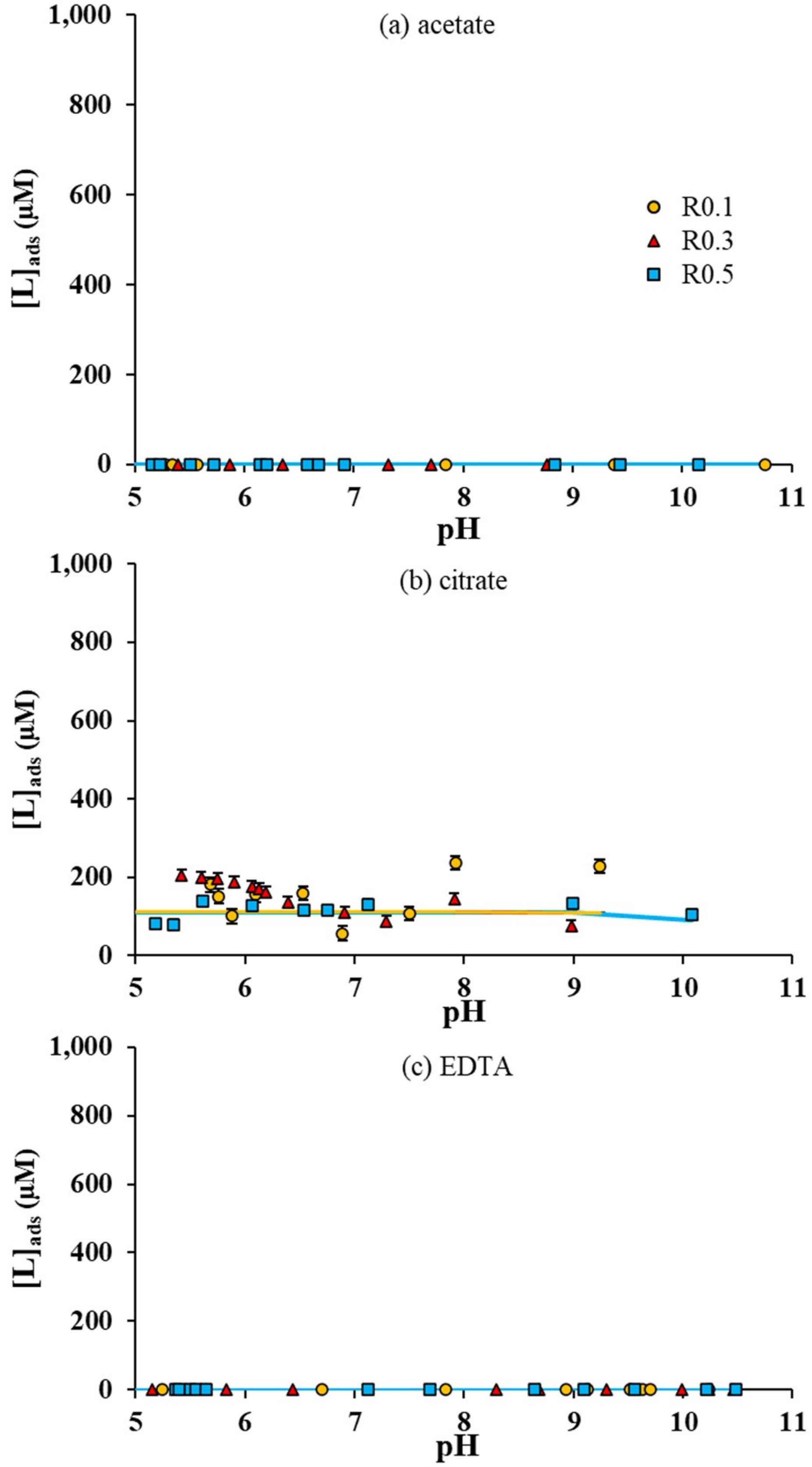


Figure S2. Adsorption of ligands ($[L]_{ads}$) (a) acetate, (b) citrate and (c) EDTA on magnetite nanoparticles as a function of pH for R0.1, R0.3, and R0.5 in presence of 1 mM of (a) acetate,

(b) citrate, and (c) EDTA in 10 mM NaCl. Lines correspond to surface complexation modelling results (only for citrate).

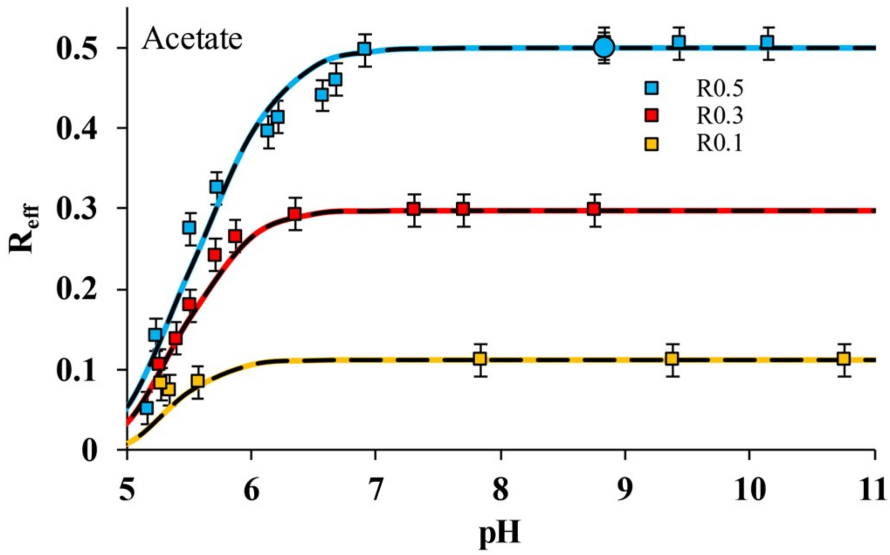


Figure S3. R_{eff} versus pH in the absence (black dashed line) and presence of acetate and magnetites with different initial stoichiometries (R0.1, R0.3 and R0.5) in 10 mM NaCl (symbols). The data represented by a large cycle symbol was determined by XMCD. Colored lines correspond to magnetite-maghemite solid solution modelling results.

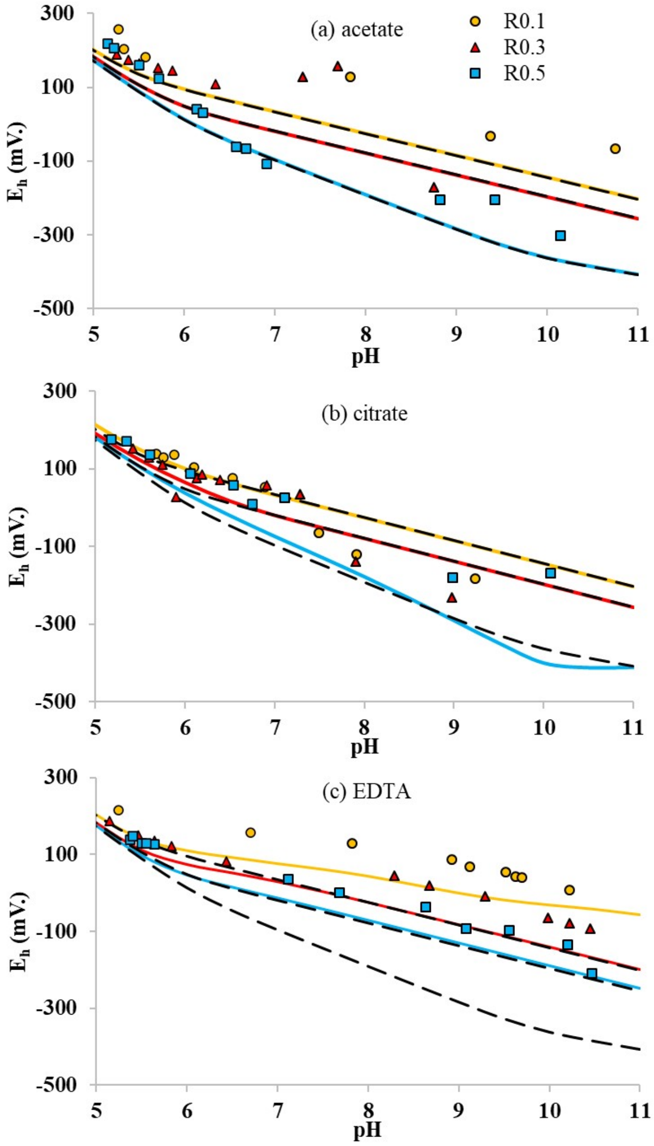


Figure S4. E_h as a function of pH for R0.1, R0.3, and R0.5 in absence (black dashed line) and presence of 1 mM of acetate, citrate, and EDTA in 10 mM NaCl (symbols). Colored lines correspond to magnetite-maghemite solid solution modelling results.

References

(1) Jungcharoen, P.; Pédrot, M.; Heberling, F.; Hanna, K.; Choueikani, F.; Catrouillet, C.; Dia, A.; Marsac, R. Prediction of Nanomagnetite Stoichiometry (Fe(II)/Fe(III)) under Contrasting PH and Redox Conditions. *Environ. Sci.: Nano* **2022**, *9* (7), 2363–2371. https://doi.org/10.1039/D2EN00112H.

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(3) Vukosav, P.; Mlakar, M.; Tomišić, V. Revision of Iron(III)–Citrate Speciation in Aqueous Solution. Voltammetric and Spectrophotometric Studies. *Analytica Chimica Acta* **2012**, *745*, 85–91. https://doi.org/10.1016/j.aca.2012.07.036.