Supplementary Information

Dissolved selenium(VI) removal by zero-valent iron under oxic conditions: Influence of sulfate and nitrate

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Reacted ZVI

Reacted solids particles appeared more uniform than the unreacted ZVI in all batch reactions. The solid particles also appeared to be more magnetic (sticking to the stir bar) than the unreacted samples. After few hours of reaction time, a yellow precipitate developed on the surface batch reactor and persisted to the end of the aging test for three ZVI tested.

SEM images of reacted ZVI reveal distinctive morphological changes of the particle sizes and shapes. For example, unreacted ZVI had very irregular particle shapes and a poorly crystalline appearance, evident in the nature of the fractured surfaces (conchiodal fractures) (Fig. 1a, b, c). At the end of the experiments, flakes or scale-like structures and granular crystals developed, reflecting the formation of lepidocrocite and magnetite (Fig. S1). SEM images also show unaltered poorly crystalline products similar to pristine ZVI suggesting that the ZVI had not fully oxidized to either magnetite or lepidocrocite even after 194 h of reaction time (Fig.S1). These results are in keeping with previous studies (Liu et al., 2016; Yoon et al., 2011; Olegario et al., 2010) that identified similar morphological and mineralogical changes during aging of ZVI under oxic conditions.

Table S1: Se K-edge absorption energy values of the first inflection point (E_0) and the white line (most intense) peak for the reference standards used in the XANES analysis. The E_0 of the spectrum for the Se foil [Se(0)], collected simultaneously with the spectrum of each Se standard, was calibrated to the theoretical value of 12,658 eV and the E_0 of the associated Se standard spectrum was calibrated accordingly.

This Study				Other studies			
Se standards	Oxidation state	E_0 (eV)	White line (eV)	Se standards	Oxidation state	E_0 (eV)	White line (eV)
Iron (II) Selenide	-II	12656.9	12664.9	Copper Selenide	-II	12657.1[1]	12664.8[1]
Elemental Se	0	12658.0	12659.9	Elemental Se	0	12658.0[1] 12658.0[2]	12660.2[1] 12659.5[3]
Selenite adsorbed on Ferrihydrite	IV	12662.8	12664.0	Sodium Selenite	IV	12662.3[1] 12663.0[2]	12663.9[1] 12663.9[3]
Sodium Selenate	VI	12665.8	12667.6	Sodium Selenate	VI	12665.4[1] 12666.0[2]	12667.7[1] 12667.3[3]

a [1], b [2] and c [3]

(1) Matamoros-Veloza, A.; Peacock, C. L.; Benning, L. G. Selenium speciation in framboidal and euhedral pyrites in shales. *Environ. Sci. Technol.* **2014**, *48* (16), 8972–8979.

(2) Gibson, B. D.; Blowes, D. W.; Lindsay, M. B. J.; Ptacek, C. J. Mechanistic investigations of Se(VI) treatment in anoxic groundwater using granular iron and organic carbon: An EXAFS study. *J. Hazard. Mater.* **2012**, *241–242*, 92–100.

(3) Yang, S. I. Biotransformation and Interactions of Selenium with Mixed and Pure Culture Biofilms, University of Saskatchewan, 2011.

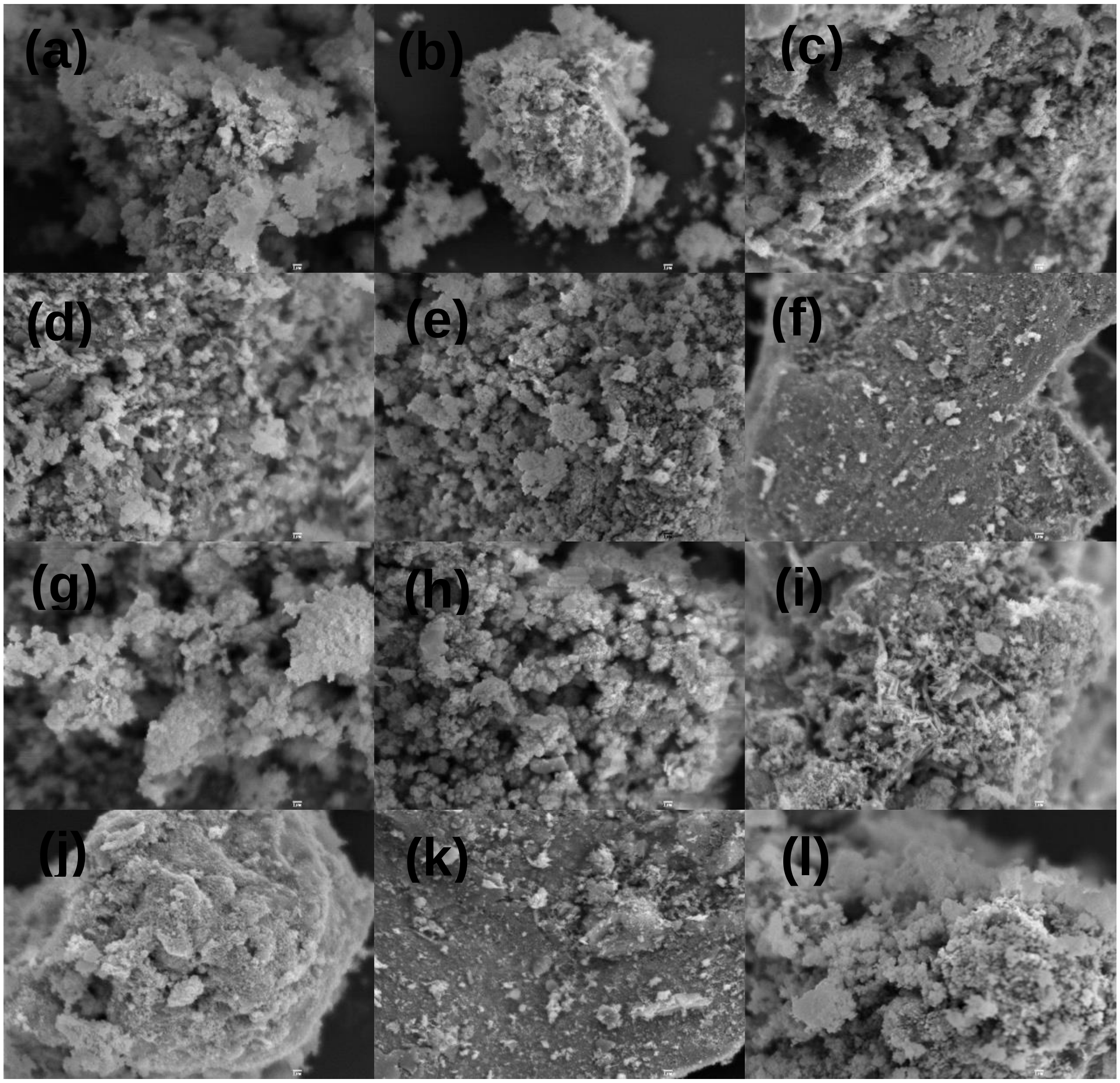
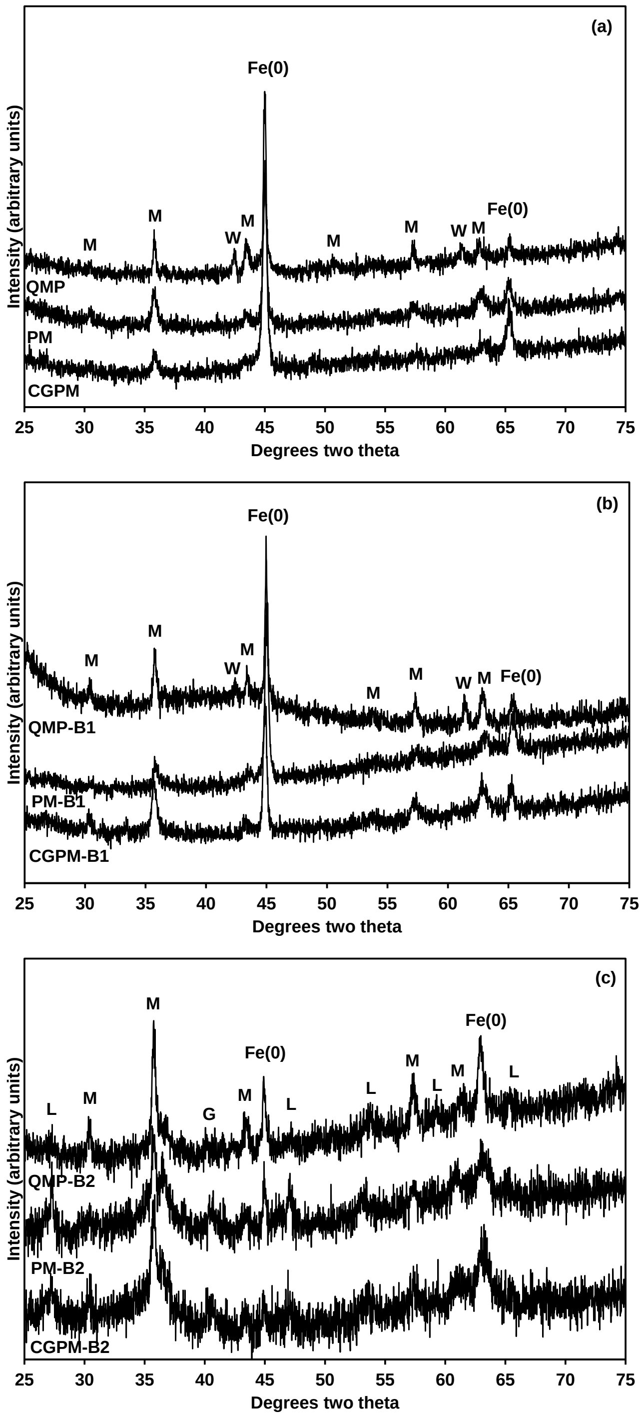


Figure S1: SEM images of reacted (a) CGPM-B1 (1 μm), (b) CGPM-B2 (1 μm), (c) CGPM-B3 (1 μm), (d) CGPM-B4 (1 μm), (e) PM-B1(1 μm), (f) PM-B2 (1 μm), (g) PM-B3 (1 μm), (h) PM-B4 (1 μm), (i) QMP-B1(1 μm), (j) QMP-B2 (1 μm), (k) QMP-B3 (1 μm), and (l) QMP-B4 (1 μm).


(a)
Fe(0)
M
M
W
M
M
M
W
M
Fe(0)
QMP
PM
CGPM
Intensity (arbitrary units)
25
30
35
40
45
50
55
60
65
70
75
Degrees two theta
(b)
Fe(0)
M
M
W
M
M
M
W
M
Fe(0)
QMP-B1
PM-B1
CGPM-B1
Intensity (arbitrary units)
Degrees two theta
(c)
M
Fe(0)
Fe(0)
L
M
G
M
L
L
M
L
M
L
QMP-B2
PM-B2
CGPM-B2
Intensity (arbitrary units)
Degrees two theta

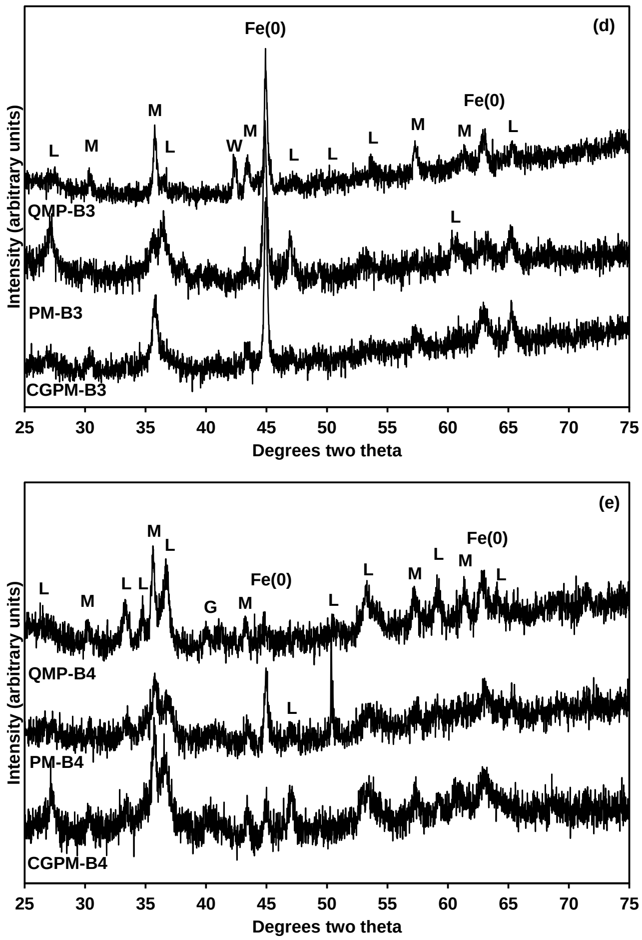
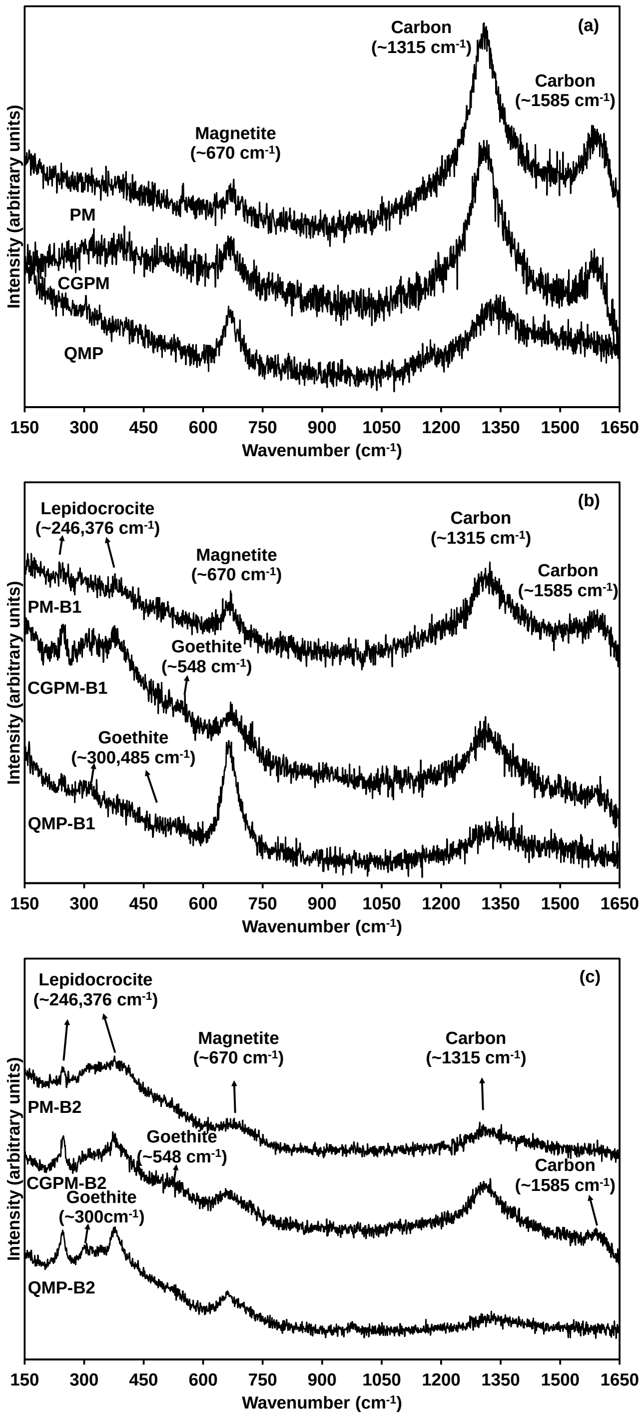


Figure S2: X-ray diffraction patterns for non-reacted ZVI (a) and ZVI from B1 (b), B2 (c), B3 (d), and B4 (e) batches. Characteristic peaks for Fe(0), goethite (G), lepidocrocite (L), magnetite (M), and wüstite (w) are labelled.


(a)
Carbon
(~1315 cm-1)
Carbon
(~1585 cm-1)
Magnetite
(~670 cm-1)
PM
CGPM
QMP
Intensity (arbitrary units)
150 300 450 600 750 900 1050 1200 1350 1500 1650
Wavenumber (cm-1)
(b)
Lepidocrocite
(~246,376 cm-1)
Magnetite
(~670 cm-1)
Carbon
(~1315 cm-1)
Carbon
(~1585 cm-1)
PM-B1
Goethite
(~548 cm-1)
CGPM-B1
Goethite
(~300,485 cm-1)
QMP-B1
Intensity (arbitrary units)
150 300 450 600 750 900 1050 1200 1350 1500 1650
Wavenumber (cm-1)
(c)
Lepidocrocite
(~246,376 cm-1)
Magnetite
(~670 cm-1)
Carbon
(~1315 cm-1)
PM-B2
Goethite
(~548 cm-1)
Carbon
(~1585 cm-1)
CGPM-B2
Goethite
(~300cm-1)
QMP-B2
Intensity (arbitrary units)
150 300 450 600 750 900 1050 1200 1350 1500 1650
Wavenumber (cm-1)

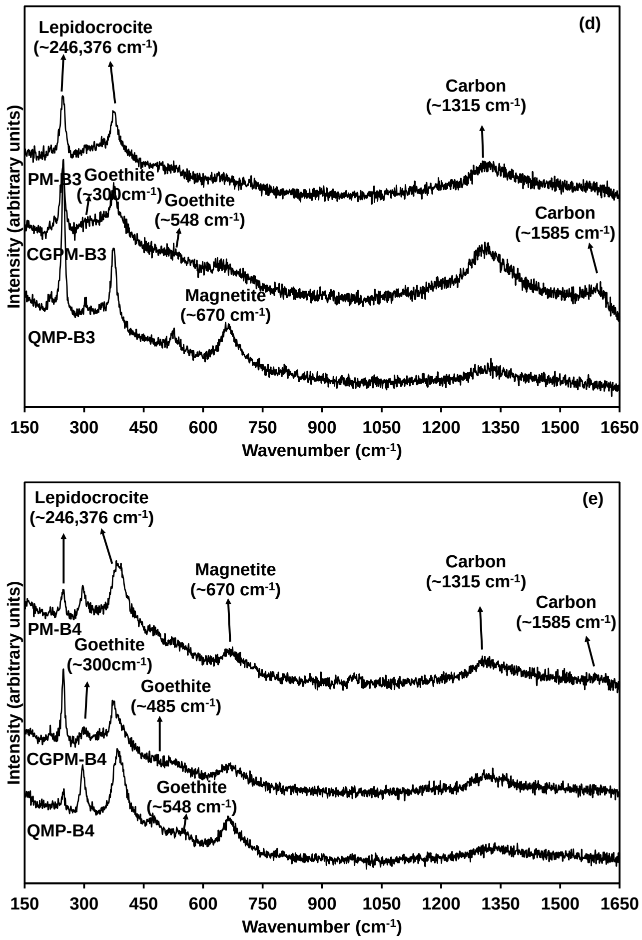


Figure S3: Raman spectra for non-reacted ZVI (a) and ZVI from B1 (b), B2 (c), B3 (d), and B4 (e) batches.

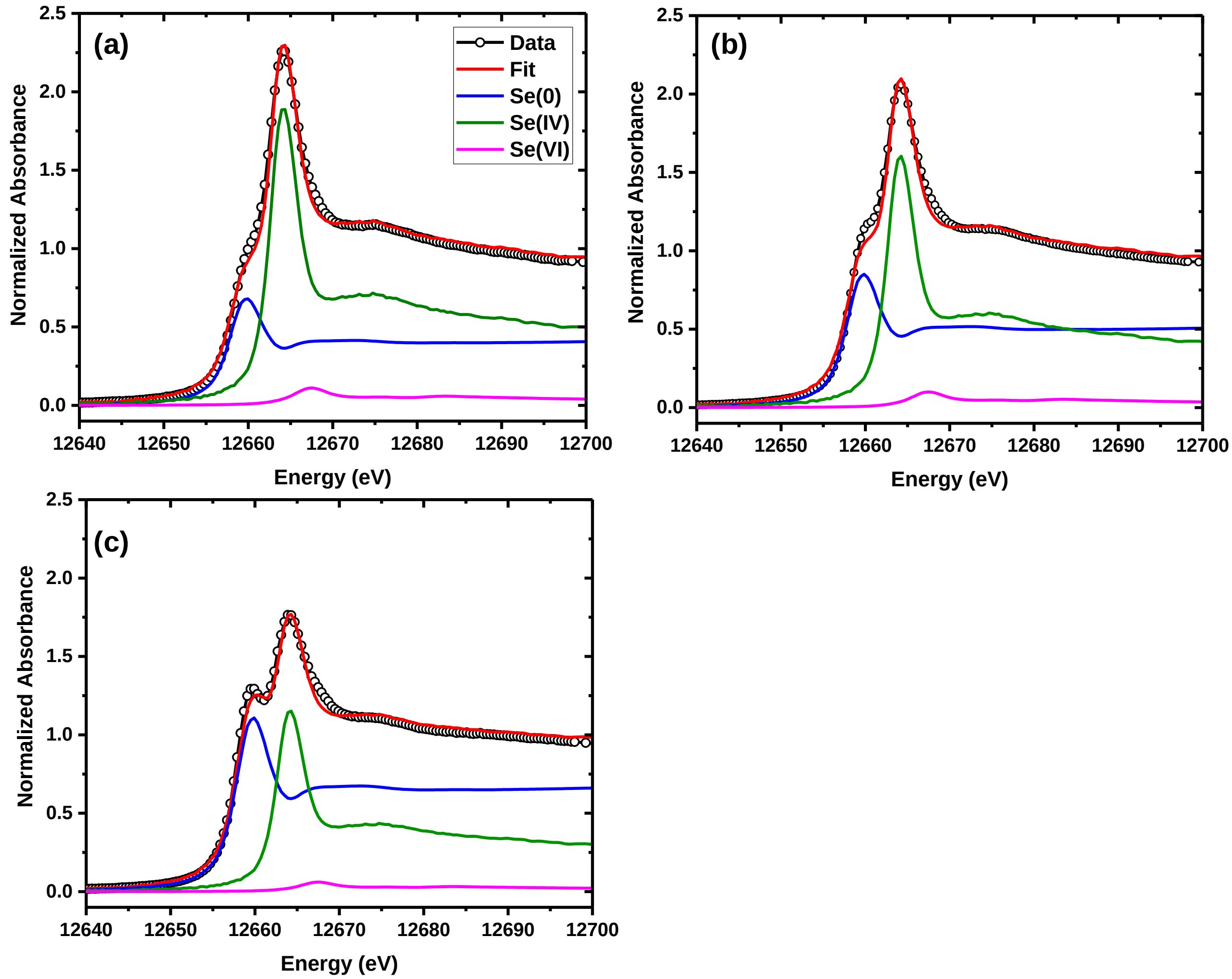


Figure S4: Experimental and linear combination fits of Se K-edge XANES spectra from reacted (a) CGPM, (b) PM and (c) QMP for B3 batches, denoting the fractional contributions of reference compounds spectra used to generate the fitted spectra.