SUPPORTING INFORMATION

Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation

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Table S1. Kinetic data used in **Figure 4C**.*

CoC type	Iron type	k_m (L/g/h) −S treatment	k_m (L/g/h) +S treatment	+/− Ratio	Refs	Sulfidation Approach
CT	***ZVI***	***2.814E-04***			***Hansson et al., 2008 [1]***	***Aqueous-Solid (Fe(0) from Sigma Aldrich)***
CT	S-ZVI		2.251E-04	0.80		Fe exposed to Na_2S for 10 days, $[S_T]$ = 10E-3 M
CT	S-ZVI		2.251E-04	0.80		Fe exposed to Na_2S for 10 days, $[S_T]$ = 10E-5 M
CT	S-ZVI		3.377E-04	1.50		Fe exposed to Na_2S for 30 days, $[S_T]$ = 10E-3 M
CT	S-ZVI		2.251E-04	1.00		Fe exposed to Na_2S for 30 days, $[S_T]$ = 10E-5 M
CT	S-ZVI		4.503E-04	2.00		Fe exposed to Na_2S for 60 days, $[S_T]$ = 10E-3 M
CT	S-ZVI		2.251E-04	1.00		Fe exposed to Na_2S for 60 days, $[S_T]$ = 10E-5 M
CT	***CMC-nZVI***	***115.000***			***Nezamabadi, 2016 [2]***	***Aqueous-Solid (t=15 min)***
CT	S-CMC-nZVI		202.000	1.76		S wt% = 0.5
CT	S-CMC-nZVI		224.000	1.95		S wt% = 1
CT	S-CMC-nZVI		160.000	1.39		S wt% = 1.5
CT	S-CMC-nZVI		146.000	1.27		S wt% = 2
CT	S-CMC-nZVI		11.200	0.10		S wt% = 3
CT	S-CMC-nZVI		2.100	0.02		S wt% = 4
CT	S-CMC-nZVI		5.840	0.05		S wt% = 5
CT	S-CMC-nZVI		7.000	0.06		S wt% = 6
CT	S-CMC-nZVI		6.800	0.06		S wt% = 8
CT	S-CMC-nZVI		2.920	0.03		S wt% = 10
CF	***CMC-nZVI***	***0.820***			***Nezamabadi, 2016 [2]***	***Aqueous-Solid (t=15 min)***
CF	S-CMC-nZVI		1.280	1.56		S wt% = 0.5
CF	S-CMC-nZVI		1.930	2.35		S wt% = 1
CF	S-CMC-nZVI		1.590	1.93		S wt% = 1.5
CF	S-CMC-nZVI		1.460	1.78		S wt% = 2
1,1,1-TCA	***CMC-nZVI***	***0.860***			***Nezamabadi, 2016***	***Aqueous-Solid (t=15 min)***
1,1,1-TCA	S-CMC-nZVI		3.490	4.06		S wt% = 0.5
1,1,1-TCA	S-CMC-nZVI		6.090	7.08		S wt% = 1

CoC type	Iron type	k_m (L/g/h) −S treatment	k_m (L/g/h) +S treatment	+/− Ratio	Refs	Sulfidation Approach
1,1,1-TCA	S-CMC-nZVI		3.150	3.66		S wt% = 1.5
TCE	***nZVI***	***0.036***			***Kim et al., 2011 [3]***	***Aqueous-Aqueous***
TCE	S-nZVI		0.315	8.84		dithionite loading 0.1 g/L
TCE	S-nZVI		0.452	12.70		dithionite loading 0.5 g/L
TCE	S-nZVI		0.530	14.88		dithionite loading 1.0 g/L
TCE	S-nZVI		0.772	21.69		dithionite loading 2.0 g/L
TCE	S-nZVI		0.593	16.66		dithionite loading 5.0 g/L
TCE	***S-nZVI***	***0.036 [3]***	***0.450***	***12.64***	***Kim et al., 2013 [4]***	***Aqueous-Aqueous***
TCE	S-nZVI		0.510	14.32		pH 7
TCE	S-nZVI		0.590	16.57		pH 8
TCE	S-nZVI		0.690	19.38		pH 9
TCE	S-nZVI		0.750	21.06		1.0 mM NaCl
TCE	S-nZVI		0.730	20.50		10 mM NaCl
TCE	S-nZVI		0.680	19.10		0.1 mM $CaCl_2$
TCE	S-nZVI		0.720	20.22		0.8 mM $CaCl_2$
TCE	S-nZVI		0.790	22.19		2.0 mM $CaCl_2$
TCE	S-nZVI		0.770	21.63		0.1 mM $MgCl_2$
TCE	S-nZVI		0.880	24.71		0.8 mM $MgCl_2$
TCE	S-nZVI		0.960	26.96		2.0 mM $MgCl_2$
TCE	S-nZVI		0.610	17.13		5.0 mg/L HA
TCE	S-nZVI		0.570	16.01		10 mg/L HA
TCE	S-nZVI		0.440	12.36		20 mg/L HA
TCE	S-nZVI		0.390	10.95		50 mg/L HA
TCE	S-nZVI		0.670	18.82		0.8 mM/20 mg/L Ca^{2+}/HA
TCE	S-nZVI		0.820	23.03		0.8 mM/20 mg/L Mg^{2+}/HA
TCE	***nZVI***	***1.380E-03***			***Han and Yan 2016 [5]***	***Aqueous-Aqueous Aqueous-Solid (t = 20 min)***
TCE	S-nZVI		0.048	34.78		thiosulfate S/Fe = 0.05
TCE	S-nZVI		0.047	33.91		dithionite S/Fe = 0.05

CoC type	Iron type	k_m (L/g/h) −S treatment	k_m (L/g/h) +S treatment	+/− Ratio	Refs	Sulfidation Approach
TCE	S-nZVI		0.062	45.22		sulfide S/Fe = 0.05
TCE	S-nZVI		0.054	39.13		thiosulfate S/Fe = 0.05
TCE	***nZVI***	***0.006***			***Rajajayavel and Ghoshal 2015 [6] Aqueous-Solid (t = 10 min)***	
TCE	S-nZVI		0.203	33.75		Fe/S = 33
TCE	S-nZVI		0.129	21.50		Fe/S = 50
TCE	S-nZVI		0.303	50.42		Fe/S = 22
TCE	S-nZVI		0.241	40.13		Fe/S = 14
TCE	S-nZVI		0.216	36.00		Agw-1 Fe/S = 22
TCE	S-nZVI		0.242	40.33		Agw-2 Fe/S = 22
TCE	S-CMC-nZVI		0.288	47.92		CMC-nZVI Fe/S = 22
HBCD	***nZVI***	***0.234***			***Li et al., 2017 [7]***	***Aqueous-Aqueous***
HBCD	S-nZVI		0.316	1.35		S-nZVI = 0.5 g/L, 30 °C, pH 7
HBCD	S-nZVI		0.050	0.21		S-nZVI = 0.5 g/L, 10 °C
HBCD	S-nZVI		0.148	0.63		S-nZVI = 0.5 g/L, 20 °C
HBCD	S-nZVI		0.526	2.25		S-nZVI = 0.5 g/L, 40 °C
HBCD	S-nZVI		0.156	0.67		S-nZVI = 0.5 g/L, pH = 3
HBCD	S-nZVI		0.352	1.50		S-nZVI = 0.5 g/L, pH = 5
HBCD	S-nZVI		0.252	1.08		S-nZVI = 0.5 g/L, pH = 9
HBCD	S-nZVI		0.164	0.70		S-nZVI = 0.5 g/L, Ionic strength = 0.01
HBCD	S-nZVI		0.122	0.52		S-nZVI = 0.5 g/L, Ionic strength = 0.05
HBCD	S-nZVI		0.090	0.39		S-nZVI = 0.5 g/L, Ionic strength = 0.1
HBCD	S-nZVI		0.052	0.22		S-nZVI = 0.5 g/L Ca^{2+}
HBCD	S-nZVI		0.084	0.36		S-nZVI = 0.5 g/L Mg^{2+}
HBCD	S-nZVI		0.164	0.70		S-nZVI = 0.5 g/L Cl^-
HBCD	S-nZVI		0.030	0.13		S-nZVI = 0.5 g/L NO_3^-
HBCD	S-nZVI		0.110	0.47		S-nZVI = 0.5 g/L HCO_3^-
HBCD	S-nZVI		0.180	0.77		S-nZVI = 0.1 g/L
HBCD	S-nZVI		0.198	0.85		S-nZVI = 1.0 g/L
HBCD	S-nZVI		0.241	1.03		S-nZVI = 2.0 g/L

CoC type	Iron type	k_m (L/g/h) −S treatment	k_m (L/g/h) +S treatment	+/− Ratio	Refs	Sulfidation Approach
						Aqueous-Solid (t=24 hr)
1,2-DCA	***CMC-nZVI***	***1.200E-05***			***Nunez Garcia et al., 2016 [8]***	*CMC 1.0 w/w%, Pd 0.5 w/w%*
1,2-DCA	CMC-S-nZVI		3.700E-05	3.08		S/Fe = 0.98, CMC 1.0 w/w%, Pd 0.5 w/w%
1,2-DCA	CMC-S-nZVI		3.600E-05	3.00		S/Fe = 0.49, CMC 1.0 w/w%, Pd 0.5 w/w%
1,2-DCA	S-nZVI		6.500E-05	5.42		S/Fe = 0.49, CMC 1.0 w/w%, Pd 0.5 w/w%
1,2-DCA	CMC-S-nZVI		7.600E-04	63.33		S/Fe = 0.98, CMC 1.0 w/w%, Pd 0.5 w/w%
						Aqueous-Solid (t=24 hr)
1,1,2-TCA	***CMC-nZVI***	***2.800E-03***			***Nunez Garcia et al., 2016 [8]***	*CMC 1.0 w/w%, Pd 0.5 w/w%*
1,1,2-TCA	CMC-S-nZVI		6.100E-05	0.02		S/Fe = 0.49, CMC 1.0 w/w%, Pd 0.5 w/w%

* Includes only literature values that report pairs of contaminant disappearance rates constants with and without (+S and –S, respectively) sulfidation, under otherwise comparable conditions; rate constants without S (–S) are in **bold**.

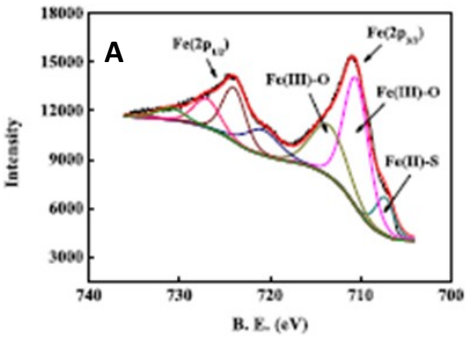
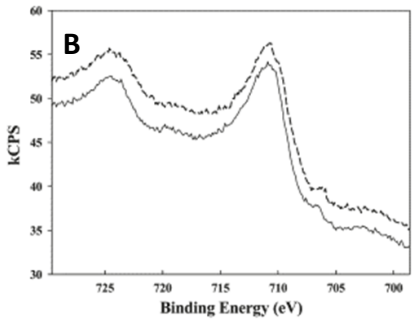
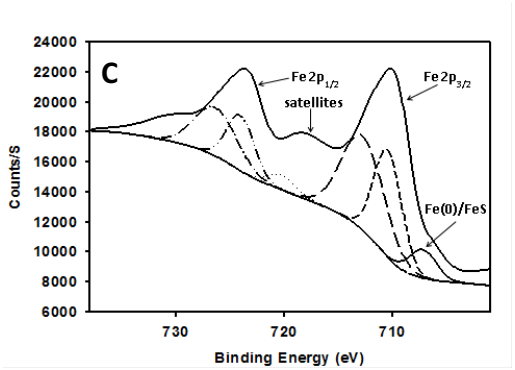
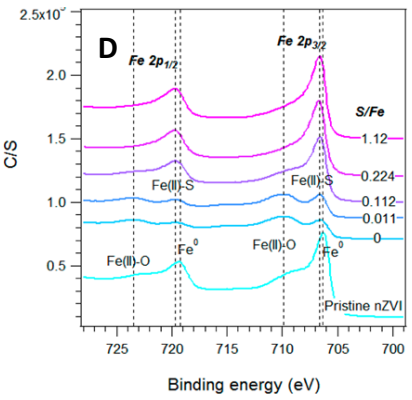
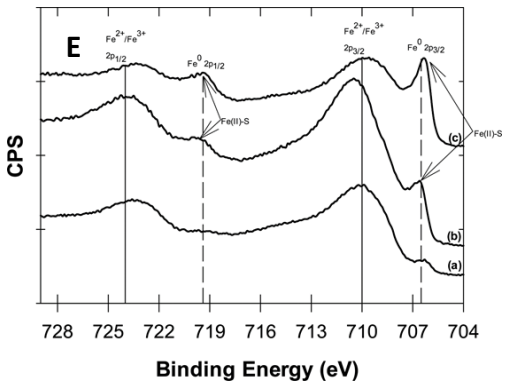
Sulfidation Approach	XPS Fe 2p Spectra	
Aqueous-Aqueous		
Aqueous-Solid (short duration)		
Aqueous-Solid (long duration)		

Figure S1. Compilation of Fe 2p XPS spectra of sulfidated nZVI reported in the literature. Two patterns observed: (*i*) absence of FeS peak near 706 eV (A [*7*], B [*3*], and C [*6*]); (*ii*) presence of FeS peak near 706 eV (D [*9*] and E [*8*]).

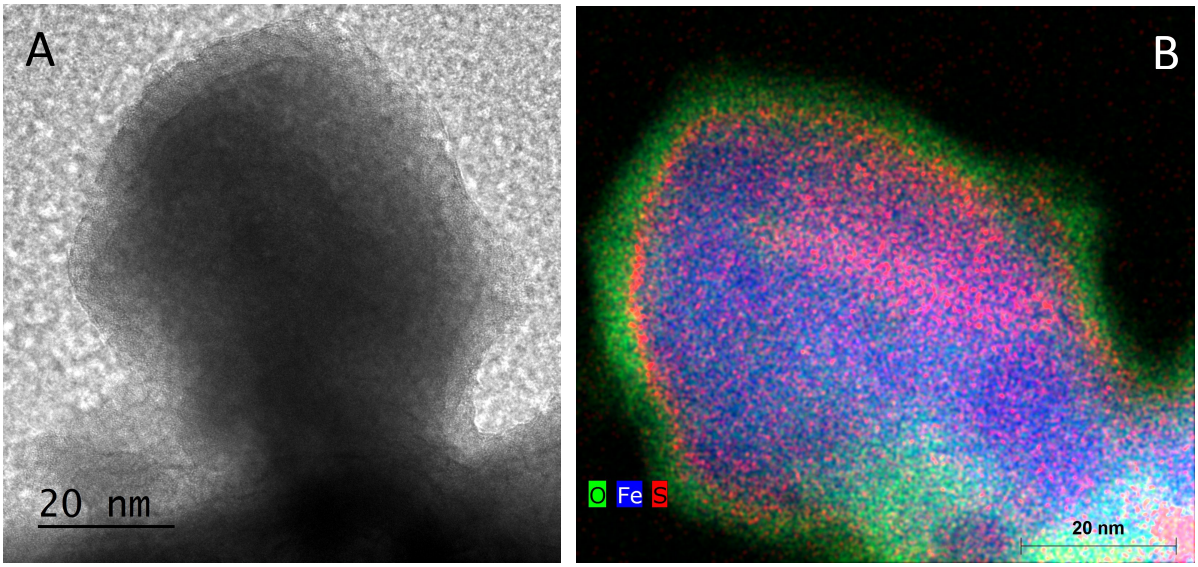


Figure S2. (A) Transmission electron micrograph and (B) the corresponding elemental mapping (note, figures are mutually rotated) of oxide-free nZVI sulfidated by aqueous-solid process (sulfide, 5 min treatment). In B, oxide layer is clearly covering a thin and mostly uniform layer of sulfur (Preliminary result).

References in Table S1

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