Supporting Information

Exploring the influence of operational parameters on the reactivity of elemental iron materials

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- Iron dissolution as function of initial EDTA concentration (Table SI 3).
- Discussion on the effect of EDTA initial concentration on iron dissolution (Figure SI 1a and 1b).

Table SI 1: Main characteristics and iron content of tested Fe^0 materials.

origin	original denotation	code	form	∅ (μm)	Fe (%)
MAZ, mbH	Sorte 69[(a)]	ZVI0	fillings	100-2000	92.8
G. Maier GmbH	FG 0000/0080	ZVI1	powder	≤ 80	92[(c)]
G. Maier GmbH	FG 0000/0200	ZVI2	powder	≤ 200	92[(c)]
G. Maier GmbH	FG 0000/0500	ZVI3	powder	≤ 500	92[(c)]
G. Maier GmbH	FG 0300/2000	ZVI4	fillings	200-2000	92[(c)]
G. Maier GmbH	FG 1000/3000	ZVI5	fillings	1000-3000	92[(c)]
G. Maier GmbH	FG 0350/1200	ZVI6	fillings	100-2000	92[(c)]
MAZ, mbH	Zünder [(a)]	ZVI7	fillings	100-2000	n.d.[(b)]
Würth	Hartgußstrahlmittel	ZVI8	spherical	1200	91.5
Hermens	Hartgußgranulat	ZVI9	flat	1500	91.5
G. Maier GmbH	Graugußgranulat	ZVI10	chips	700-1500	96.7
ISPAT GmbH	Schwammeisen	ZVI11	spherical	9000	86.3
Aldrich	Fe, powder	ZVI12	powder	10	>99[(c)]
ACROS	Fe, powder, 99%	ZVI13	powder	45	99[(c)]
J. T. Baker	Fe	ZVI14	fillings		>99[(c)]
Connelly-GPM	CC-1200	ZVI15	powder	<850	89.82[(c)]
Connelly-GPM	CC-1190	ZVI16	fillings	<2360	89.82[(c)]
Connelly-GPM	CC-1004	ZVI17	fillings	<4750	89.82[(c)]

(a) Scrap iron material; [(b)] n.d.; [(c)] average values from material supplier.

Table SI 2: Elemental composition of iron materials used in this study.

ZVI	elemental composition (%)								
	C	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Ni**	**Fe**
ZVI 0	3.52	2.12	0.93	n.d. (*)	n.d.	0.66	n.d.	n.d.	92.8
ZVI 1 – 6(**)	3.20	1.95	n.d.	0.22	n.d.	0.23	n.d.	0.18	92
ZVI 7	3.13	2.12	0.36	n.d.	n.d.	0.077	n.d.	0.056	96.7
ZVI 8	3.39	0.41	1.10	n.d.	0.105	0.34	n.d.	0.088	91.5
ZVI 9	3.13	0.17	0.42	0.053	0.065	0.16	n.d.	0.23	n.d.
ZVI 10	3.13	2.17	0.36	0.022	0.029	0.077	n.d.	0.056	n.d.
ZVI 11	1.96	0.12	0.09	0.027	0.14	0.003	n.d. (*)	<0.001	98.2
ZVI 12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	99
ZVI 13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	99
ZVI 14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	99
ZVI 15-17(**)	2.85	1.85	0.60	0.132	0.107	0.1	0.15	0.13	89.82

(*) n.d. = not determined and (**) average values from material supplier

Discussion on the effect of EDTA initial concentration

The effect of initial EDTA concentrations between 2.5 and 20.0 mM (prepared from commercial Na_2-EDTA and Milli-Q purified water) was evaluated for ZVI0 (2 g L^{-1}) and the deduced characteristic parameters are given in Table SI3. Figure SI 1a summarizes the evolution of iron concentration as function of time and Figure SI 1b gives the variation of the deduced dissolution rate (k_{EDTA} values) as function of EDTA concentration.

The results in Table SI3 showed that the iron dissolution rates (k_{EDTA}) increased from 45 to 500 μg h^{-1} when the EDTA concentration increased from 2.5 to 20.0 mM. This foreseeable observation attests the ability of EDTA to characterize Fe^0 reactivity at pH values >5 and validates the chosen experimental protocol. It is interesting to note that b values decreased with increasing EDTA concentrations and reached a negative value for 20.0 mM ETDA. This trend was attributed to the increased solution corrosiveness for Fe^0. Aggressive solutions also cause too rapid dissolution of fines (atmospheric corrosion products). Based on this observation a 20.0 mM EDTA solution was used as washing fluid in pre-treatment procedures. Note that at low EDTA concentration b values are primarily a reflect of the amount of atmospheric corrosion products on Fe^0 [1]. For EDTA >15 mM (see below), b-values were meaningless. This results shows clearly that the 50 mM EDTA used by Chen et al [2] was too aggressive for washing purposes. On the other hand while using EDTA to avoid iron precipitation, Abdelouas et al. [3] did not specified used concentrations. Finally, the values of τ_{EDTA} suggest that, apart from the system with 20.0 mM, all systems need more than six days to reach iron saturation. Due to numerous interferences (discussed in the article) only a limited number of experimental points (here, $4 \leq n \leq 6$) yielding actual linearity was used. k_{EDTA} and b valued were derived by regression. τ_{EDTA} was obtained by resolving the equation $k_{EDTA}*t + b = 112$.

Figure SI 1b shows that k_{EDTA} was a linear function of time only for [EDTA] ≤15 mM. A jump can be seen between the curve for 15.0 mM and that for 20.0 mM (Figure SI 1a). As the

EDTA concentration varies from 15.0 to 20.0 mM the dissolution rate varies from 200 to 500 $\mu g\ h^{-1}$ (Table SI3).

References

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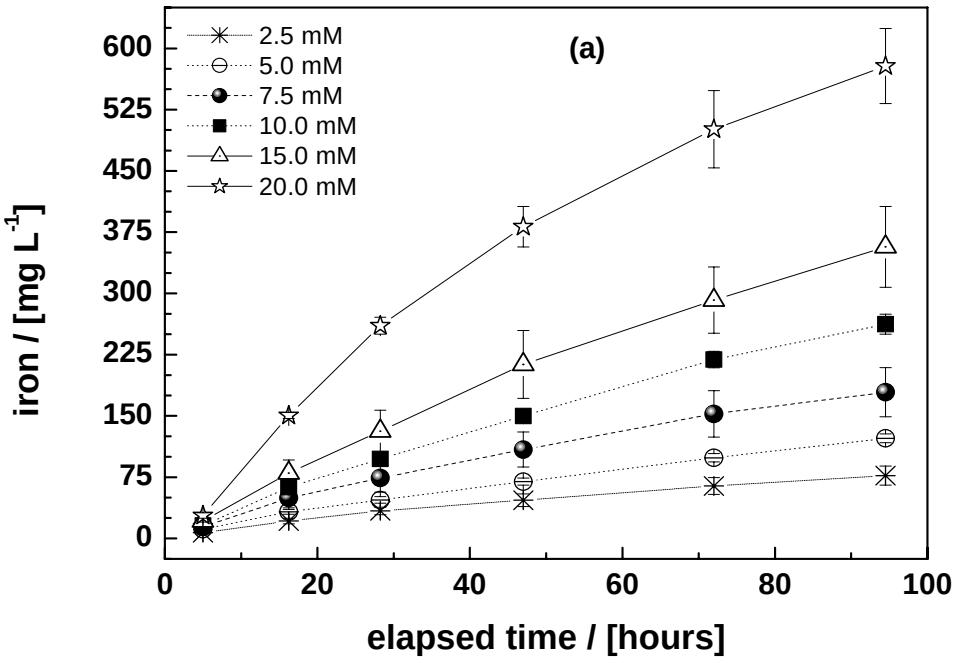
[2] J.-L. Chen, S.R. Al-Abed, J.A. Ryan, Z. Li, Effects of pH on dechlorination of trichloroethylene by zero-valent iron, J. Hazard. Mater B83 (2001), 243-254.

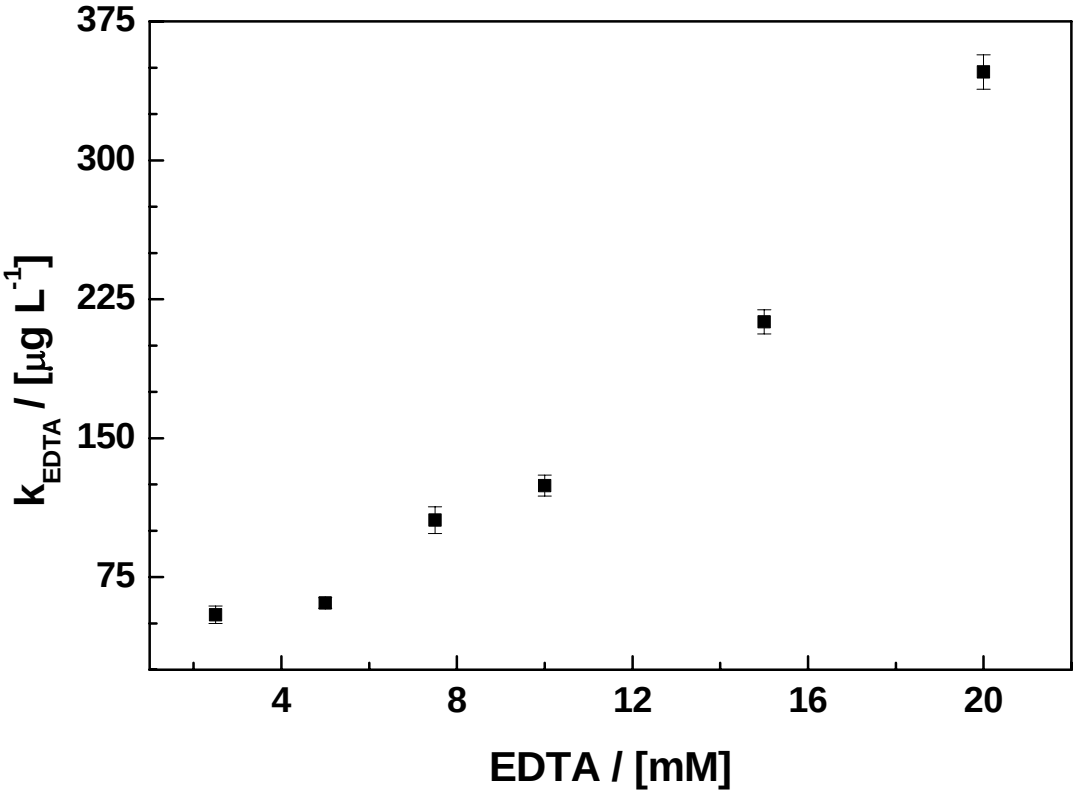
[3] A. Abdelouas, W. Lutze, H.E. Nutall, W. Gong, Réduction de l'U(VI) par le fer métallique: application à la dépollution des eaux. C. R. Acad. Sci. Paris Earth Planetary Sci. 328 (1999), 315-319.

Table SI 3: Corresponding correlation parameters (k_{EDTA}, b, R) and τ_{EDTA} of iron dissolution under various EDTA initial concentrations. General conditions: initial pH 5.2, room temperature 23 ± 2 °C, and Fe^0 (ZVI0) mass loading 2 g L^{-1}. n is the number of experimental points for which the curve iron vs. time is linear. a and b-values were calculated in Origin 6.0.

Parameter (mM)	n	R	k_{EDTA} (μg h^{-1})	b (μg)	τ_{EDTA} (d)
2.5	6	0.983	43 ± 4	257 ± 106	6.5
5.0	6	0.996	65 ± 3	300 ± 83	8.8
7.5	6	0.989	104 ± 8	204 ± 94	8.3
10.0	6	0.992	158 ± 10	14 ± 79	7.4
15.0	6	0.994	206 ± 11	33 ± 68	8.5
20.0	4	0.994	498 ± 39	-897 ± 536	4.8

Figure SI 1: Characterization of the iron dissolution from ZVI0 as a function of the EDTA concentration: (a) kinetics of iron dissolution for various initial concentrations; (b). variation of the rate of iron dissolution (k_{EDTA}) as a function of the EDTA concentration. Table SI 3 shows that for [EDTA] = 20 mg L^{-1}, only 4 experimental points (n = 4) were used for regression.




375
300
225
150
75
k_{EDTA} / [µg L^{-1}]
4
8
12
16
20
EDTA / [mM]