

27 removal is yet to be elucidated. Despite a broad consensus on reductive transformations [1],
28 quantitative contaminant removal by other mechanisms has been reported. Currently, it is
29 assumed that $\text{Fe}^0/\text{H}_2\text{O}$ systems may remove chlorinated organics by reductive degradation,
30 whereas metals, metalloids and radionuclides may be removed via reductive precipitation,
31 surface adsorption or complexation, or co-precipitation with the Fe oxyhydroxides that are
32 generated in the system [2-4]. The validity of this concept is progressively questioned [6-12].
33 In fact, some of the enumerated processes must be fundamental and valid for all possible
34 pollutants while others will be valid only in particular situations (e.g., the contaminant is
35 reducible). In addition to the diversity of successfully removed contaminants in $\text{Fe}^0/\text{H}_2\text{O}$
36 systems, there is diversity among Fe^0 sources (intrinsic properties) and thus diversity in the
37 chemical reactivity of used materials.

38 Over the past 20 years Fe^0 materials used in laboratory and field $\text{Fe}^0/\text{H}_2\text{O}$ systems was
39 available from a variety of commercial sources including [13-15]: (i) chemical reagents (e.g.
40 Merck, Across, Aldrich), (ii) untreated scrap iron and by-products [15, 16], and (iii) Fe^0
41 materials manufactured for environmental remediation (e.g. Connelly-GPM Inc., G. Maier
42 GmbH, ISPAT GmbH, Peerless Metal Powders & Abrasive). The results of experiments
43 using such different materials have been compared to each other with little care on the
44 intrinsic material reactivity (see next section). To date there is no standard parameter to
45 evaluate the intrinsic reactivity of Fe^0 materials [17]. However, it is well known that, the
46 metal type and method of manufacture are as important as the environment (solution
47 corrosiveness) for corrosion processes [18]. Clearly, the presence and amount of alloying and
48 other foreign elements, the size of the material, and whether the metal is cast, forged, wrought
49 or welded are critical to material intrinsic reactivity (corrodibility). A further problem with the
50 majority of commercially available Fe^0 is that the materials are produced from scrap iron and
51 steel obtained from a number of primary industries using iron in the production of automotive
52 and related industrial parts [13]. Therefore, the “feedstock” for commercially available Fe^0 is

53 a mixture including scrap iron and steel. The mixture is heated at 700 to 1200°C in rotary
54 kilns to burn off the non-metallic materials, especially the cutting oils [13]. Accordingly, the
55 real manufacturing history of commercially available Fe⁰ is not traceable. This is the major
56 reason why materials should be characterized “as received”.

57 Factors affecting Fe⁰ reactivity in laboratory experiments can be divided into three subgroups:
58 (i) material-dependent factors (intrinsic reactivity - mostly not directly accessible to
59 researchers), (ii) environment-dependent factors (investigable at individual relevant sites), and
60 (iii) operational experimental parameters (should be designated to mimic environment-
61 dependent factors). Environment-dependent factors and operational experimental parameters
62 are not addressed in the present work. As concerning material-dependent factors, they
63 include: Fe⁰ manufacturing history, Fe⁰ elemental composition, Fe⁰ particle size (nm, μm,
64 mm), Fe⁰ surface area and surface property (also of generated oxides). A decade of
65 investigations on Fe⁰ have not clarified the relative importance of the individual factors of this
66 subgroup [15, 19, 20]. However, an unjustified importance was attributed to one of these
67 parameters: the surface area [19, 21] and kinetic rate constant (k_{obs}) are usually normalized to
68 the surface area [22, 23]. To characterize the Fe⁰ intrinsic reactivity, most of the tested
69 materials were used without any pre-treatment (“as received”). Only one material was crushed
70 and sieved to yield particle size relevant for field applications (≤ 2 mm). Their chemical
71 reactivity is evaluated as the extent of iron dissolution in the presence of
72 Ethylenediaminetetraacetate (EDTA available as Na₂-EDTA).

73 The ability of EDTA to sustain iron oxidative dissolution is well documented in the corrosion
74 science [24-26] and has been used to avoid the formation of oxide-film on Fe⁰ in experiments
75 investigating contaminant removal in Fe⁰/H₂O systems [27-29]. A comprehensive discussion
76 on the chemistry of the Fe⁰/EDTA/H₂O system is given by Pierce et al. [30]. Previous works
77 characterizing the reactivity of Fe⁰ in the presence of EDTA (2 mM) showed that the kinetic
78 rate constant of iron dissolution (termed k_{EDTA}) is a useful parameter to differentiate the

79 reactivity of Fe⁰ materials in batch systems [15]. To further characterize the reactivity of Fe⁰
80 in batch experiments, a parameter τ_{EDTA} was introduced [31, 32]. Per definition, τ_{EDTA} is the
81 time necessary to reach aqueous Fe saturation under given experimental condition assuming
82 1:1 Fe/EDTA complexation ([Fe] = 2 mM or 112 mg/L).

83 The objective of the present work was to investigate the feasibility of using EDTA to
84 characterize the reactivity of Fe⁰ materials in column studies. For this purpose a series of nine
85 pre-selected Fe⁰ materials are used. Their chemical reactivity in a 2 mM EDTA solution is
86 comparatively examined. The extent of iron dissolution in individual columns is used to
87 assess Fe⁰ reactivity. For the sake of clarity the definition of chemical reactivity will be
88 recalled.

89 **2. Electrochemical reactivity of Fe⁰**

90 In discussing the suitability of Fe⁰ for environmental remediation one has to properly
91 distinguish between the corrodibility of Fe⁰ and the corrosiveness of the aqueous
92 environment. Fe⁰ corrodibility is the material's susceptibility to corrosion or the material's
93 intrinsic chemical reactivity. Because iron corrosion is primarily an electrochemical process,
94 Fe⁰ intrinsic reactivity can be regarded as Fe⁰ electrochemical reactivity. The corrosiveness of
95 the environment refers to the aggressiveness of the aqueous solution toward Fe⁰ oxidative
96 dissolution. Consequently, Fe⁰ corrodibility and solution corrosiveness are not objective
97 parameters but subjective tendencies. Accordingly, the Fe⁰ electrochemical reactivity is its
98 tendency to undergo an oxidative dissolution. Similarly, the corrosiveness of a contaminant
99 for a given Fe⁰ material is its ability to induce oxidative dissolution of the material. Efforts to
100 characterize electrochemical reactivity of Fe⁰ in neutral and close-to-neutral solutions are
101 complicated by two major parameters: (i) the formation of oxide layers on Fe⁰, and (ii) the
102 interactions of dissolved species within the oxide layers. Therefore, efforts has been made to
103 characterize iron-corrosion-related processes in the absence of oxide layers [15, 26, 30, 31].
104 One of these efforts is used in this study. It consists in using EDTA as chelating agent to

105 avoid the formation of oxide layers on Fe^0 and thus, to sustain Fe^0 oxidative dissolution by
106 molecular O_2 (and H_2O).

107 The presentation above shows clearly that each Fe^0 material is characterized by its
108 electrochemical reactivity and each contaminant by its corrosiveness for a given Fe^0 . More
109 precisely, a given concentration of a contaminant (in a given solution – ionic strength, pH
110 value) exhibits a certain corrosiveness for a given Fe^0 . The difficulty arises when one has to
111 compare data obtained by various investigators under different experimental conditions even
112 when the experiments would have used the same mass loading of a given Fe^0 material [32].
113 To take these weaknesses into account, the present study comparatively investigates the
114 kinetics and the extent of Fe^0 oxidative dissolution by molecular O_2 (and H_2O) in the presence
115 of EDTA for nine materials in column experiments.

116 **3. Materials and Methods**

117 **3.1 Solutions**

118 Based on previous works, a working EDTA-solution of 0.002 M was used [15, 31, 32].
119 Working EDTA solutions (0.02 M or 2 mM) was obtained by a one step dilution (1:20) of a
120 stock solution prepared from an analytical grade chemical (ethylenediaminetetraacetic acid di-
121 sodium salt - ACROS Organics). A standard iron solution (1000 mg/L) from Baker JT[®] was
122 used to calibrate the Spectrophotometer. The reducing reagent for Fe^{III} -EDTA was ascorbic
123 acid. The ascorbic buffer was used to keep the pH <4.0. 1,10 orthophenanthroline (ACROS
124 Organics) was used as reagent for Fe^{II} complexation. Used L(+)-ascorbic acid and L-ascorbic
125 acid sodium salt were of analytical grade. All solutions were prepared using deionised water.

126 **3.2 Fe^0 materials**

127 One laboratory grade iron powder (ACROS Organics - ZVI9), one scrap iron (ZVI7), and
128 seven commercially available iron materials have been tested. Table 1 summarizes the main
129 characteristics of these materials together with their iron content. Before used ZVI3 was
130 crushed and sieved; the size fraction 1.0-2.0 mm was used without any further pretreatment.

131 The specific surface area of the materials varies between 0.043 and 1.8 m² g⁻¹. These data
132 were compiled from the literature (Tab. 1). The objective of this study is to compare the
133 materials in the form in which they could be used in field applications. Accordingly, the
134 materials were compared mostly on the basis of the extent of iron dissolution from the same
135 initial mass of Fe⁰ (1.0 g) by the same volume of 2 mM EDTA. Apart from ZVI3, all other
136 materials were used as obtained. Crushing and sieving ZVI3 aimed at working with materials
137 of particle size relevant for field applications. The materials differ regarding their
138 characteristics such as iron content, nature and proportion of alloying elements, and shape. No
139 information about the manufacture process (e.g. raw material, heat treatment) was available.

140 A survey of the elemental composition (Table 1) shows that the tested materials primarily
141 differ in their carbon (and silicon) contents. Thereafter the tested materials can be divided into
142 three classes: (i) ZVI1, ZVI2, ZVI4, ZVI5, ZVI6 and ZVI7 containing more than 3% carbon
143 (cast irons), (ii) ZVI8 and ZVI9 containing less than 3% C are mild steels, and (iii) ZVI3,
144 direct reduced iron, containing 1.96 % C belongs to the third class because of the particularity
145 of his manufacturing technology, yielding to porous materials.

146 Apart from ZVI5 with a regular spherical shape, homogeneous size (d = 1.2 mm) and smooth
147 surface [34], all other materials were irregular in shape (filings and shavings) with a rough
148 surface. ZVI3 was of very rough surface and even porous. ZVI1, ZVI4, ZVI5, ZVI6 and ZVI9
149 were visibly covered with rust whereas all other samples retained their metallic glaze.

150 The nine used materials were selected from eighteen Fe⁰ materials after characterization in
151 batch experiments using the EDTA-test [15]. The results are presented elsewhere [32]. The
152 results suggested that the batch EDTA-test may not be suitable for characterizing powdered
153 Fe⁰ and Fe⁰ filings with high proportion of fines [32]. To test the validity of this assumption
154 one powdered material (from six tested in [32]) was incorporated in this study together with
155 eight materials representative for the variability of the reactivity obtained for the twelve other
156 granular materials (chips, filings, shavings).

157 **3.3 Iron dissolution studies**

158 Laboratory scale glass columns were operated in up-flow mode. Nine glass columns (40 cm
159 long, 2.6 cm inner diameter) were used. The columns were packed with sand. Each column
160 contains 1.0 g of a different Fe⁰ material in its most upper part. The effective length, the bulk
161 density and the porosity of the packed columns were not characterized as they were not
162 necessary for the discussion of the results. The kinetics and the extent of iron oxidative
163 dissolution by EDTA were the sole targets. The influent solution contained 2 mM EDTA and
164 was pumped upwards from PE bottles using a peristaltic pump (Ismatec, ICP 24). Tygon
165 tubes were used to connect inlet reservoir, pump, column and outlet. The experiment was
166 performed at room temperature (21-25 °C). A stable flow rate of about 11.0 mLh⁻¹ was
167 maintained throughout the experiment. Samples for analysis were collected in flow through
168 bottles at periodic intervals. The experiments were stopped after 62 days.

169 **3.4 Analytical methods**

170 The aqueous iron concentration was determined with a Varian Cary 50 UV-VIS
171 spectrophotometer, using a wavelength of 510 nm for iron determination and following the
172 1,10 orthophenanthroline method [38, 39]. The instrument was calibrated for iron
173 concentration ≤ 10 mg.L⁻¹. The pH value was measured by combined glass electrodes (WTW
174 Co., Germany). Electrodes were calibrated with five standards following a multi-point
175 calibration protocol in agreement with the current IUPAC recommendation [40].

176 **4. Results and discussion**

177 **4.1 Expression of experimental results**

178 The amounts of Fe dissolved during 62 d are expressed as a percentage, on a mass basis, of
179 the total mass (1 g) of the used materials and summarized in Table 2. Although the Fe content
180 of individual materials was available, the leaching percentage was referenced to the initial
181 mass of material (1.0 g). This choice is justified by the fact that materials are characterized on
182 the weight basis for their capacity to be used for contaminant removal. Regardless from the

183 actual removal mechanism, the extent of contaminant mitigation is necessarily coupled with
184 the extent of Fe dissolution. Therefore, not the total Fe content is essential, but rather the
185 reactive proportion (leaching extent) and the kinetics of the leaching process. The changes in
186 pH was not recorded. The kinetics of Fe dissolution is expressed as variation of aqueous Fe
187 concentration with the cumulative volume which is directly proportional to the elapsed time.
188 The experiment was stopped after that 16.0 to 16.8 L of EDTA has flowed through the
189 columns. Potentially, 16 L of EDTA (2 mM) can dissolved 1.8 g Fe. Depending on the
190 electrochemical reactivity of the individual materials, the amount of leached Fe during the test
191 varies from 27 to 73 % of the initial weight of Fe⁰ material (1.0 g).

192 **4.2 Kinetics of Fe⁰ oxidative dissolution**

193 Figure 1a shows that two from the nine tested materials exhibited markedly increased
194 dissolution kinetics after the half time of the experiment (1 month corresponding to the date
195 where 8 L of EDTA has flowed through the columns): ZVI3 (direct reduced iron) and ZVI8
196 (powder). After 1 month all materials exhibited very similar dissolution kinetics (Fig 1a). The
197 powdered material exhibited the most rapid kinetic of iron dissolution with 77 % of the total
198 leached amount of Fe (729 mg after 62 d, Table 2) been leached after 1 month. The extent of
199 iron leaching after 1 month for all other materials, relative to the total leached amount at the
200 end of the experiment, varies between 54 and 66 %. The order of reactivity of the material
201 deduced from the extent of leached iron after 1 month (31 d) is the following:

202 $ZVI5 < ZVI7 < ZVI2 < ZVI9 < ZVI4 < ZVI6 < ZVI3 < ZVI1 < ZVI8.$

203 The order of reactivity derived from the total amount of leached iron at the end of the
204 experiment (62 d) is the following:

205 $ZVI5 < ZVI4 < ZVI6 < ZVI9 < ZVI11 < ZVI2 < ZVI7 < ZVI3 < ZVI8$

206 Either Fe⁰ material used in this study (including powdered ZVI8) might be suitable for use in
207 field reactive wall applications unless it is not affordable. The different reactivity for
208 dissolution in 2 mM EDTA would certainly influence the choice of Fe⁰ with regard of site

209 specific conditions. It is interesting to notice that ZVI9 with one of the largest surface area
210 ($1.8 \text{ m}^2 \text{ g}^{-1}$) is one of the poorest reactive materials. Also ZVI5 and ZVI6 with the largest
211 carbon content are among the less reactive materials. Given the similarities in surface area of
212 used materials due to similarity in the particle size (except for powdered ZVI8 and porous
213 ZVI3), it is definitively clear that Fe^0 manufacture history causes the observed differences in
214 reactivity. Due to lack of information on these two aspects, their importance can not be
215 accurately accessed or discussed in the remainder of the paper. Although discussing the
216 effects of Fe^0 manufacture history is over the scope of this work, a brief discussion on the
217 impact of iron content and surface area will be given bellow.

218 Figure 2 summarises the extent of iron dissolution from tested materials as function of
219 specific surface area (Fig. 2a) and the iron content (Fig. 2b) of the materials. It is obvious that
220 neither the iron content nor the SSA correlated with the extent of Fe leaching by EDTA. From
221 Fig. 2a the material with the highest surface area exhibited one of the lowest Fe leaching
222 efficiency and from Fig. 2b the material with the lowest iron content exhibited the highest Fe
223 leaching efficiency.

224 Figure 1b summarises the kinetics of iron dissolution from the seven granular materials
225 (filings, chips) with similar reactivity in fig 1a. Due to a change in the scale on the
226 concentration axe ($\leq 50 \text{ mg/L}$) a certain reactivity differentiation can be made graphically. For
227 example it can be seen that ZVI5 (cast iron having the least surface area) is the least reactive
228 material whereas ZVI1, ZVI2 and ZVI7 exhibit an increased initial dissolution kinetic. After
229 about one month ZVI7 (and to some extent ZVI2) was the sole material exhibiting an
230 increased dissolution kinetics. These results indicated that systems containing powdered and
231 granulated materials will loss their efficiency sometimes after their field implementation. For
232 systems with powdered materials the loss of efficiency is due to depletion of readily reactive
233 site at the surface. Efficiency loss for granular material is due to intrinsic properties. Note that
234 no passivation due to hydroxide/oxide precipitation is expected under flowing conditions in

235 EDTA. Considering intrinsic reactivity loss in material selection will certainly reduce the
236 probability of barrier failure. For example, Morrison et al. [41], reported on a $\text{Fe}^0/\text{H}_2\text{O}$ system
237 that showed sooner breakthrough than expected for molybdenum and uranium. Performance
238 failure was attributed to: (i) the continual build-up of mineral precipitates on the Fe^0 surface,
239 (ii) the loss of pore space, (iii) the development of preferential flow paths, and (iv) the
240 complete bypass of the $\text{Fe}^0/\text{H}_2\text{O}$ system resulting in the loss of hydraulic control. The results
241 of the present study suggest that a non purposeful material selection could have been an
242 important factor as well.

243 **4.3 Extent of Fe^0 oxidative dissolution**

244 Figure 3 summarises the evolution of the cumulative mass of leached iron as function of the
245 volume passed through the columns. As for the kinetics, a net difference is observed for ZVI8
246 and ZVI3 (Fig. 3a). All other seven materials exhibited very similar dissolution behaviour in
247 the initial phase of the experiment (4 L of EDTA passed or 2 weeks) and a clearer reactivity
248 differentiation with increasing experimental duration. Most of available experiments are
249 performed in batch systems (iron precipitation after saturation) and the experimental durations
250 are rarely greater than 2 days. In such experiments only the initial reactivity of Fe^0 materials
251 are tested. Even though tested materials are often those used for field $\text{Fe}^0/\text{H}_2\text{O}$ systems,
252 accurate long-term data are very difficult to obtain, particularly when service life in the range
253 of decades are needed. This study shows that long-term column experiments (together with
254 purposeful modelling efforts) can help to bridge the gap between field and laboratory.

255 **4.4 Discussion**

256 The results of Fe^0 oxidative dissolution by molecular O_2 in 2 mM from this study are
257 compared with that obtained by the same materials for methylene blue (MB) discoloration
258 [42] and 2 mM EDTA Fe^0 dissolution in batch systems [32]. The order of reactivity of
259 material for column studies for 1 month (initial dissolution) and 2 months (long term

260 dissolution) are given separately above. The order of reactivity for the other systems are the
261 following:

262 EDTA: $ZVI5 < ZVI2 < ZVI9 < ZVI4 < ZVI6 < ZVI7 < ZVI3 < ZVI1 < ZVI8$

263 MB: $ZVI5 < ZVI2 < ZVI7 < ZVI3 < ZVI6 < ZVI9 < ZVI4 < ZVI1 < ZVI8$

264 The comparison of the initial kinetics of Fe^0 dissolution in batch (k_{EDTA}) and column (31 d)
265 studies reveals that ZVI5 and ZVI2 are the least reactive materials whereas ZVI3, ZVI1 and
266 ZVI8 are the most reactive ones. However, ZVI1, ZVI2 and ZVI5 are all cast irons whereas
267 ZVI3 is direct reduced iron. Therefore, the relative Fe^0 reactivity can not be predicted from
268 the elemental chemical composition. Only direct reduced iron could confirm the foreseeable
269 effect of increased reactivity due to porosity or increased surface area.

270 The relative reactivity of the four other materials do not show also a net trend. This is
271 certainly due to the fact that 1 month is a too long time to be considered as time of initial
272 dissolution. Therefore, the order of reactivity considering the initial dissolution is the
273 following obtained in batch experiments:

274 $ZVI5 < ZVI2 < ZVI9 < ZVI4 < ZVI6 < ZVI7 < ZVI3 < ZVI1 < ZVI8$.

275 The order of dissolution deduced from the total mass of Fe leached after 62 days was the
276 following:

277 $ZVI5 < ZVI4 < ZVI6 < ZVI9 < ZVI1 < ZVI2 < ZVI7 < ZVI3 < ZVI8$.

278 It is very interesting to observe that only ZVI5 and ZVI8 conserved their ranking in both
279 classifications. However, it can be emphasized that for longer experimental duration ZVI8
280 (powder) will be depleted. Therefore, the selection of a material should take into account its
281 reactivity, the relative the flux of contaminant in the ground water and the volume of water to
282 be treated. In some cases it could be advantageous to work with a less reactive material like
283 ZVI5 which is reactive in the long-term. Some applications will need powdered and even
284 nano-sized Fe^0 for short-time rapid contaminant removal. Next to the iron intrinsic reactivity
285 yielding Fe^0 dissolution, the relationship between Fe^0 reactivity and contaminant removal

286 depends on the oxide-films formed as result of iron corrosion. To take this important aspect
287 into account the relative reactivity of used materials as accessed by the extent of methylene
288 blue (initial concentration 20 mg/L) discoloration for 1 month [42] was compared to the data
289 on iron dissolution in 2 mM EDTA. The results of MB removal were more comparable to that
290 of iron dissolution in batch systems than to that of columns systems. The slight differences
291 can be attributed to the surface state (roughness, oxidation state) of individual materials.

292 **5. Concluding remarks**

293 EDTA has been used for the characterization of the reactivity of Fe⁰ materials mostly of
294 similar particle size (comparable available surface area). The observed great differences in the
295 chemical reactivity could not be correlated with the surface area. This suggests that surface
296 area plays a secondary role in controlling Fe⁰ electrochemical reactivity. The carbon content
297 of the materials was not also determinant for electrochemical reactivity. Because intrinsic
298 factors determining the chemical reactivity of Fe⁰ materials are of limited accessibility,
299 available materials should be tested in a systematic holistic approach to identify trends in their
300 general reactivity. In this effort, beside batch and column study with chelating agents (e.g.
301 EDTA), long-term batch and column experiment with various contaminants are needed.
302 Given the large spectrum of contaminants that have been successfully removed in Fe⁰/H₂O
303 systems, this ambitious work can not be achieved by individuals or isolated research groups.
304 The challenge should be to move from studies proving the viability of Fe⁰ technology to
305 investigations incorporated within a broad-based understanding of process occurring in
306 Fe⁰/H₂O systems [43]. In this effort the proper characterization of used materials is a
307 fundamental issue.

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- 428
- 429

429 **Table 1:** Origin, name and main characteristics of tested Fe⁰ materials.

430

origin	original denotation	code	form	Ø (µm) ^(a)
MAZ, mbH	Sorte 69 ^(b)	ZVI6	filings	80-4000
G. Maier GmbH	FG 0300/2000	ZVI1	filings	200-2000
G. Maier GmbH	FG 1000/3000	ZVI4	filings	1000-3000
Würth	Hartgußstrahlmittel	ZVI5	spherical	1200
Hermens	Hartgußgranulat	ZVI2	granular	1500
G. Maier GmbH	Graugußgranulat	ZVI7	chips	350-1200
ISPAT GmbH	Schwammeisen	ZVI3	filings	9000
Connelly-GPM	ETC-CC-1004	ZVI9	filings	500-1000
ACROS	Fe, powder, 99%	ZVI8	powder	45

431 ^(a) Average values from material supplier; ^(b) Scrap iron material.

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433

433 **Table 2.** Elemental composition and specific surface area (SSA) of iron materials used in this
 434 study. n.a. = not available and n.d. = not determined.

435

ZVI	Elemental (%)							SSA (m ² /g)
	C	Si	Mn	Cr	Mo	Ni	Fe	
ZVI1 ^(a)	3.2	1.95	n.a.	0.023	n.a.	0.02	92.00	0.048 ^(b)
ZVI2	3.13	0.17	0.42	0.16	n.d.	0.23	96.7	0.50 ^(c)
ZVI3	1.96	0.12	0.09	0.003	n.d.	<0.001	86.3	0.63 ^(d)
ZVI4 ^(a)	3.2	1.95	n.a.	0.023	n.a.	0.02	92.00	0.048 ^(b)
ZVI5	3.39	0.41	1.10	0.34	n.d.	0.088	91.5	0.043 ^(c)
ZVI6	3.52	2.12	0.93	0.66	n.d.	n.d.	99.8	0.29 ^(e)
ZVI7 ^(a)	3.13	2.17	0.36	0.077	n.d.	0.056	96.7	0.50 ^(f)
ZVI8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	99.0	n.a.
ZVI9 ^(a)	2.85	1.85	0.60	0.10	0.15	0.13	89.82	1.8 ^(g)

436 ^(a) Data of elemental composition from supplier, ^(b) ref. [33], ^(c) ref. [34], ^(d) Data from supplier,
 437 ^(e) ref. [35]; ^(f) ref. [36], ^(g) ref. [37].

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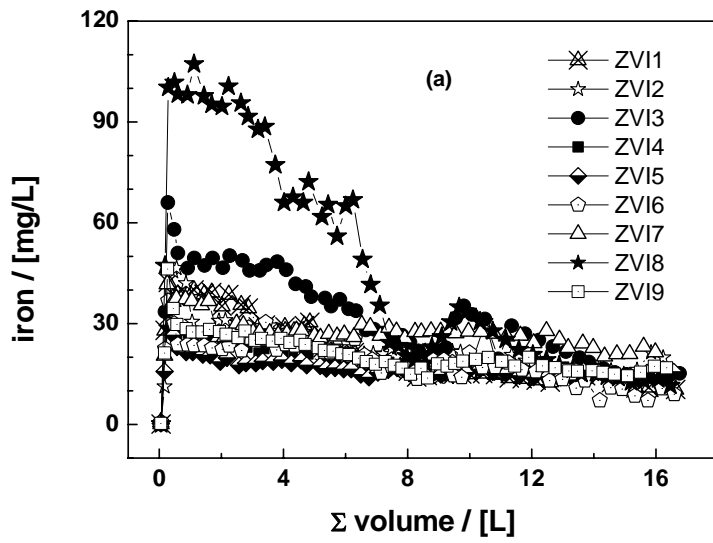
440 **Table 3:** Extent of Fe dissolution in column studies for the nine tested Fe⁰ materials. ‘V_T’ is
 441 the total volume of EDTA (2 mM) that has flowed into the individual columns.
 442 ‘m_T’ is the total mass of leached Fe from individual materials and P (%) is the
 443 corresponding percentage relative to the initial mass of 1.0 g (or 1000 mg). As a
 444 rule, the more reactive a material the bigger the m_T and P values. General
 445 conditions: pH₀ = 5.2, [EDTA]₀ = 2 mM, T = 23 ± 2 °C.

Fe⁰	form	V_T (L)	m_T (mg)	P (%)
ZVI5	spherical	16.6	272	27.2
ZVI4	filings	16.6	295	29.5
ZVI6	filings	16.6	298	29.8
ZVI9	filings	16.3	332	33.2
ZVI1	filings	16.6	340	34.0
ZVI2	granular	16.2	376	37.6
ZVI7	chips	16.0	430	43.0
ZVI3	filings	16.8	513	51.3
ZVI8	powder	16.5	729	72.9

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448 Figure 1

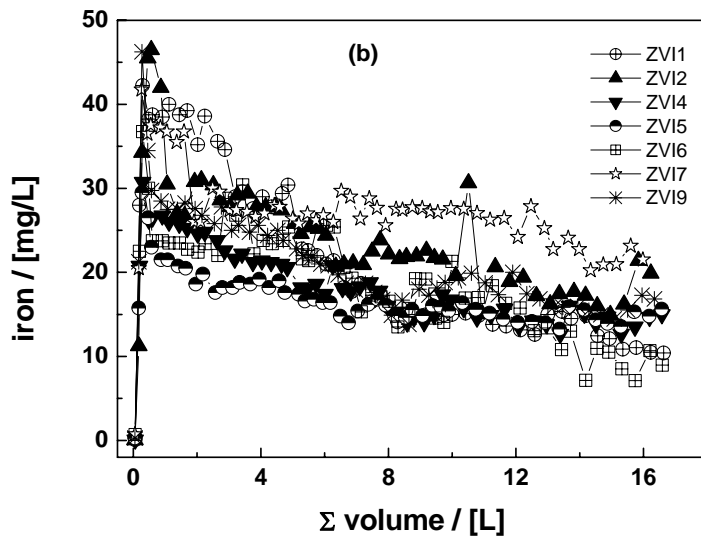
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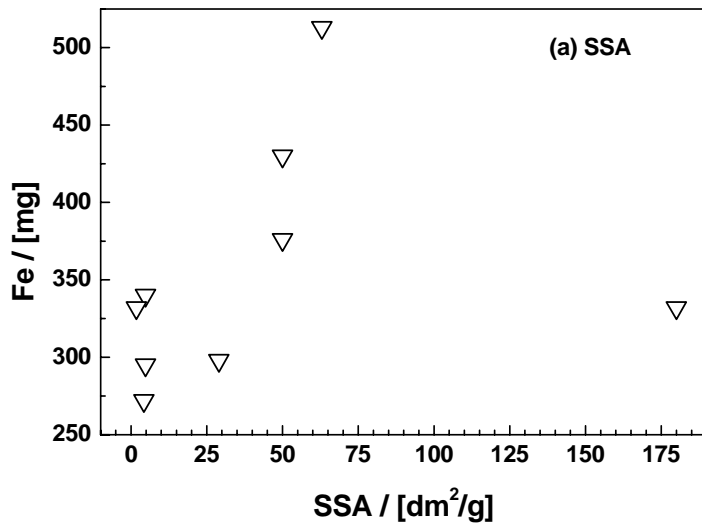
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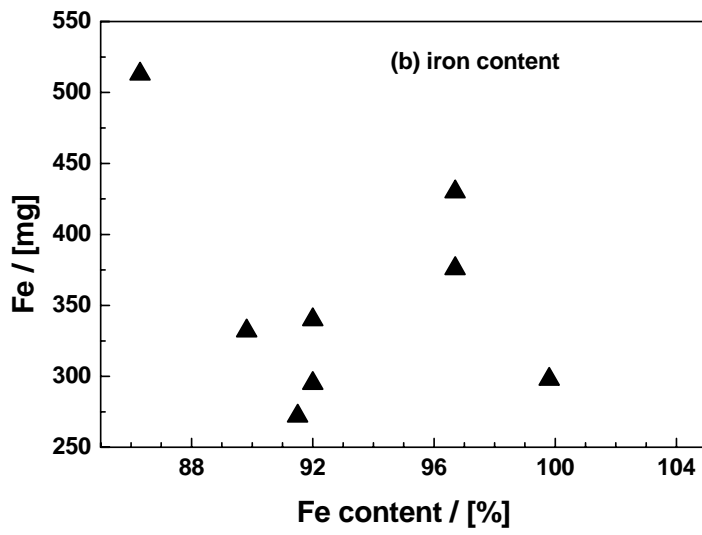
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454 **Figure 2**
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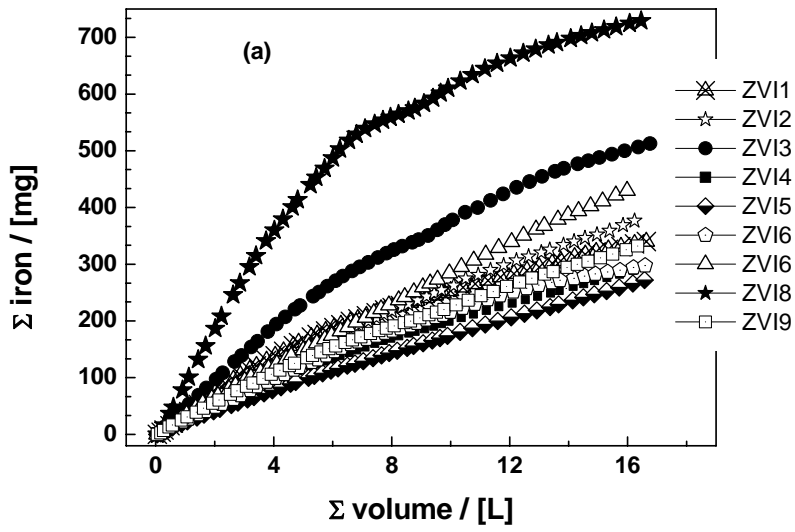


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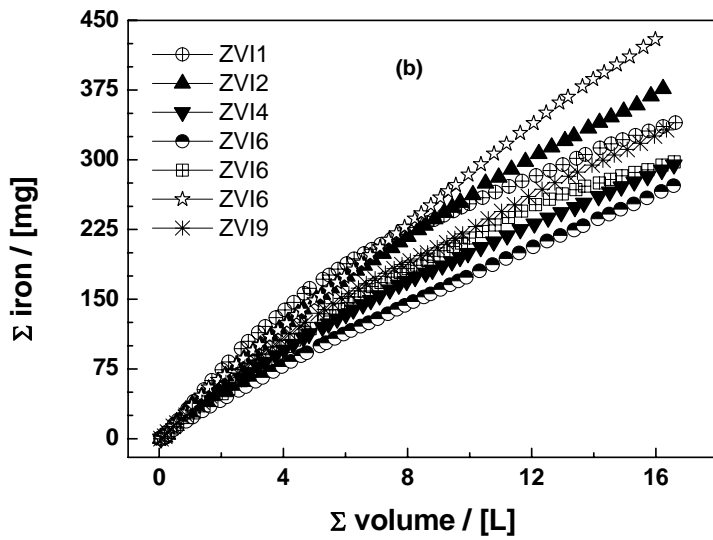


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461 Figure 2
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466 **Figure Captions**

467 **Figure 1:**

468 Iron release (mg/L) from the Fe⁰ materials by 2 mM EDTA for 62 days in column
469 experiments: (a) all tested Fe⁰ materials and (b) the seven Fe⁰ materials exhibiting similar
470 reactivity. The lines are not fitting functions, they simply connect points to facilitate
471 visualization.

472 **Figure 2:**

473 Cumulative iron release (mg) from the Fe⁰ materials as function of (a) material specific
474 surface area (SSA), and (b) material iron content. It is interesting to see that both parameters
475 play a secondary role in controlling Fe electrochemical reactivity.

476 **Figure 3:**

477 Cumulative iron release (mg) from the Fe⁰ materials as function of the total volume of 2 mM
478 EDTA passed through the columns: (a) for all tested Fe⁰ materials and (b) for the seven Fe⁰
479 materials exhibiting similar reactivity. The lines are not fitting functions, they simply connect
480 points to facilitate visualization.

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