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# Sulfidation of ZVI/AC composite leads to highly corrosion-resistant nanoremediation particles with extended life-time

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9

# 10 Abstract

11 Nanoscale zero-valent iron (nZVI) is a powerful reductant for many water pollutants. The lifetime of nZVI in aqueous environments is one of its limitations. Sulfidation of the nZVI 12 surface by reduced sulfur species is known to significantly modify the particle properties. In 13 the present study we examined various post-synthesis sulfidation methods applied on 14 15 Carbo-Iron, a composite material where iron nanostructures are embedded in colloidal activated carbon (AC) particles. In such cases, where ZVI is surrounded by carbon, sulfidation 16 17 largely inhibits the anaerobic corrosion of ZVI in water whereas its dechlorination activity 18 was slightly increased. Even at a very low molar S/Fe ratio of 0.004 a strong decrease of the corrosion rate by a factor of 65 was achieved, while concurrently dechlorination of 19 tetrachloroethene (PCE) was accelerated by a factor of three compared to the untreated 20 particles. As a consequence, over 98 % of the reduction equivalents of the sulfidated ZVI 21 were utilized for the reduction of the target contaminant (33 mg L<sup>-1</sup> PCE) under simulated 22 groundwater conditions. In a long-term experiment over 160 days the extended life-time 23 and the preservation of the reduction capacity of the embedded ZVI were confirmed. 24 25 Reasons for the modified reaction behavior of Carbo-Iron after sulfidation compared to previously studied nZVI are discussed. We hypothesize that the structure of the carbon-26 embedded iron is decisive for the observed reaction behavior. In addition to reaction rates, 27 the product pattern is vastly different compared to that of sulfidated nZVI. The triple 28 combination of ZVI, AC and sulfur makes the composite particle very suitable for practical in-29 situ applications. 30

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- 32
- Keywords: Carbo-Iron, zero-valent iron, dechlorination, anaerobic corrosion, sulfidation

# 35 Highlights

- 36 Substantial decrease of anaerobic corrosion of Carbo-Iron's ZVI by sulfide treatment
- 37 Long-term study over 160 days verifies the preservation of ZVI activity by sulfidation
- 38 The ZVI/AC/S system shows a ZVI utilization towards dechlorination close to 100 %
- 39

# 40 Graphical abstract



## 46 **1. Introduction**

Iron-based materials are widely used for the reductive in-situ destruction of groundwater 47 contaminants, e.g. chlorinated ethenes (Fu et al., 2014; Yan et al., 2013, Dong et al., 2018). 48 Especially nanoscale zero-valent iron (nZVI) with its large specific surface area and the 49 associated high reactivity towards organic pollutants received considerable attention in the 50 last decades. One development trend for ZVI-based in-situ reagents led to composite 51 materials, consisting of nZVI combined with sorption-active carbonaceous carriers, such as 52 activated carbon (AC), which allow the collection of organic pollutants in the vicinity of 53 54 reactive iron centers (Chen et al., 2014; Han et al., 2015; Liu et al., 2016; Mackenzie et al., 2012; Peng et al., 2017). The application of such materials in permeable reaction zones 55 56 within a contaminated aquifer means an increased retention of the pollutants in this zone and more efficient iron utilization for contaminant reduction, which is pronounced especially 57 58 for low-concentrated pollutants. Although the supported iron systems show in comparison to pure ZVI a similar ability to degrade organic contaminants, the distinct reaction 59 mechanisms might differ due to the different sorption properties of the systems (Kopinke et 60 al., 2016; Mackenzie et al., 2012; Tang et al., 2011). In case of pure ZVI, both adsorption and 61 reaction of the pollutants take place at the iron surface, while in the case of ZVI/AC 62 composite materials the contaminants are predominantly adsorbed at the inner AC surface 63 and are therefore spatially separated from ZVI as the production site of reactive species 64 (Kopinke et al., 2016; Tang et al., 2011). 65

66 A general obstacle against a wider utilization of nZVI and iron-based composite materials in the field is their limited longevity. With the high reactivity of such materials also a high 67 susceptibility to undesired electron-consuming reactions such as anaerobic corrosion 68 according to  $Fe^0 + 2 H_2O \rightarrow Fe^{2+} + H_2 + 2 OH^-$  are associated (Tratnyek and Johnson, 2006). 69 70 The extent of this "parasitic" reaction depends on the particle properties and the chemical composition of the water, but is never a negligible side reaction. Recent studies showed that 71 72 over 95 % of the reduction equivalents of ZVI can be consumed due to the reaction with 73 water (Fan et al., 2016; Schöftner et al., 2015). Omnipresent groundwater constituents, such as bicarbonate or natural organic matter, but also a low pH value can accelerate the iron 74 consumption (Klausen et al., 2003; Liu and Lowry, 2006; Nurmi and Tratnyek, 2008; Reardon, 75 76 1995), leading to particle lifetimes of only a few hours to several weeks (Agrawal et al., 2002; Eglal and Ramamurthy, 2014; Liu et al., 2005a; Liu et al., 2005b; Schöftner et al., 2015;
Velimirovic et al., 2014).

A promising method to improve the performance of ZVI is the addition of reduced sulfur 79 compounds, e.g. sulfide or dithionite during or after the synthesis of the particles (Fan et al., 80 2017; Li et al., 2017b, Dong et al. 2018). An acceleration of the contaminant removal and a 81 simultaneous decrease of the anaerobic corrosion rate could be achieved, which brings a 82 83 double positive effect for the utilization of the metal (Hassan, 2000; Butler and Hayes, 2001; Kim et al., 2011; Rajajayavel and Ghoshal, 2015; Han and Yan, 2016; Fan et al., 2016; Tang et 84 85 al., 2016; Fan et al., 2017; Gu et al., 2017). Unfortunately, long-term studies of the reaction behavior of sulfidated nZVI are missing. 86

87 Besides the reports on selectivity enhancement in the desired direction (dechlorination versus corrosion), there are also some studies where the presence of sulfide leads to an 88 increased corrosion rate of ZVI (Turcio-Ortega et al., 2012; Hansson et al., 2008). Also other 89 iron-based structures, such as pipelines and storage tanks can undergo accelerated 90 anaerobic corrosion due to biogenically formed sulfide ("chemical microbially influenced 91 92 corrosion") (Enning and Garrelfs, 2014). These studies show how complex the consequences 93 of a sulfidation on iron are and that the sulfur treatment can lead to a highly protective, but 94 in some cases also to a corrosion-promoting effect.

95 Some of the most recent reviews on sulfidation of iron-based materials (Fan et al., 2017; Li 96 et al., 2017b, Dong et al., 2018) reveal another limitation of the present state of knowledge: 97 most experimental studies with nZVI have been conducted with borohydride-reduced 98 materials. Such materials are less suitable to represent full-scale applications, due to their 99 high cost of preparation.

100 For us the question arose which influence a sulfidation treatment would have on the 101 reactivity behavior of the ZVI/AC composite particles, which might differ from that of bare 102 nZVI. The present study focused on the composite material Carbo-Iron, which consists of AC 103 and embedded nanoscale ZVI structures and has been successfully applied at laboratory and 104 field scale (Bleyl et al., 2012; Bleyl et al., 2013; Mackenzie et al., 2012; Mackenzie et al., 105 2016). With its carbon carrier and the embedded crystalline iron the composite has possibly 106 other ways to interact with the sulfidation reagent compared to the previously studied nZVI, which was synthesized by reduction of iron salts with NaBH<sub>4</sub> (Fan et al., 2017; He et al., 107 108 2018). In batch experiments the influence of different post-synthesis sulfidation methods on 109 the dechlorination of tetrachloroethene (PCE) and the anaerobic iron corrosion of Carbo-110 Iron's ZVI were investigated, considering the dependence of the applied sulfur amount and 111 its interaction with the omnipresent groundwater constituent bicarbonate. In contrast to 112 previous reports, we also performed a long-term study over 160 days and tested the residual 113 dehalogenation activity of the sulfur-treated particles. In order to gain information about the 114 alteration of mineral phases of the iron, X-ray diffraction (XRD) analysis of sulfidated Carbo-115 Iron particles was performed.

- 116
- 117 **2. Experimental section**
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#### 119 2.1. Chemicals and reagents

PCE (99 %) and 1,2-dibromoethane (DBA) (98 %) were purchased from Sigma Aldrich and ABCR, respectively, and used without further purification. Na<sub>2</sub>S · 9 H<sub>2</sub>O, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and NaHCO<sub>3</sub> (all p.a.), H<sub>2</sub>S (> 99.5 %), L-cysteine (97 %) were obtained from Sigma Aldrich. Methanol (99.7 %) was provided by Chemsolute. Deionized water (Millipore Simplicity 185, 18.2 MΩ cm) was used for the preparation of the reaction media of all batch experiments.

The synthesis of Carbo-Iron was carried out by the carbothermal method which is described 126 in detail in a former study (Bleyl et al., 2012). Briefly, AC particles were loaded with Fe(NO<sub>3</sub>)<sub>3</sub> 127 from aqueous solution, dried and thermally converted at 700 to 850°C (Fe<sub>2</sub>O<sub>3</sub> + C  $\rightarrow$  Fe<sup>0</sup> + 128 CO/CO<sub>2</sub>). The prepared particles consisted of approximately 20 wt-% nanoscale ZVI and 129 55 wt-% AC and (even though stable at dry air) were stored under argon atmosphere in 130 order to avoid moisture contact. A specific surface area (SSA) of nanostructured ZVI particles 131 in Carbo-Iron of about 15.5 m<sup>2</sup> g<sup>-1</sup> was estimated based on the mean ZVI cluster size which 132 133 was derived from transmission electron microscopy (TEM) and X-ray diffraction analysis 134 (XRD) (Mackenzie et al., 2012). The SSA of Carbo-Iron, determined by nitrogen adsorption, is about 600 m<sup>2</sup> g<sup>-1</sup> (Mackenzie et al., 2012). 135

Commercially available Nanofer Star was supplied by NANO IRON, s.r.o. Czech Republic, stored under aerobic conditions at 4°C and utilized within five months after arrival. At the time of utilization, the sample contained 75 wt-% Fe<sup>0</sup>. According to the technical data sheets from NANO IRON s.r.o. the SSA amounts to  $20 - 25 \text{ m}^2 \text{ g}^{-1}$  and the primary particle size is about 50 nm.

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#### 142 2.2. Analytical methods

The X-ray diffraction (XRD) pattern of sulfidated Carbo-Iron was studied at room
temperature using a Bruker D8-Advance diffractometer (LynxEye), equipped with a onedimensional silicon strip detector and operated with Cu-Kα radiation (step size of 0.02°).
Energy dispersive X-ray analysis (EDX) was conducted by using a scanning electron
microscope (Zeiss Merlin VP Compact) equipped with a Bruker Quantax X-ray detector
(XFlash 5060F). Transmission electron microscopy (TEM) was used to depict Carbo-Iron.
Particles were embedded into glue (M-Bond 610) and cut by Ar+ ion thinning.

- 150 The TEM examinations were carried out in a Philips CM 200 STEM equipped with a super 151 twin objective lens (point resolution 0.23 nm).
- 152 In XPS studies Fe and S pattern were measured using an ESCALAB 220i-XL with 153 monochromatic Al  $K\alpha$  radiation.
- Headspace gas chromatography was chosen for analysis of the fully dechlorinated products
  ethane, ethene and acetylene using a GC-FID device (GC-2010 plus, Shimadzu Corp.,
  equipped with a GS-Q PLOT-column).
- 157 The reaction products chloride and bromide were analyzed by ion chromatography (IC25, 158 Dionex, equipped with an IonPacAS15/AG15 column).
- Anaerobic corrosion was monitored by measuring the formation of molecular hydrogen byGC-TCD (HP6850, HP PLOT 30 m x 0.32 mm).
- For analysis of the Fe<sup>0</sup> content of the particles, the reaction of ZVI in acidic suspension forming molecular hydrogen according to Fe<sup>0</sup> + 2 H<sup>+</sup>  $\rightarrow$  Fe<sup>2+</sup> + H<sub>2</sub> was utilized. The H<sub>2</sub> evolved was measured by means of GC-TCD as described above.
- 164

#### 165 2.3. Sulfidation procedure

The sulfidation of Carbo-Iron was performed after the synthesis of the particles by applying three different methods: i) a dry pre-treatment of the particles with gaseous H<sub>2</sub>S in a nitrogen stream, ii) the addition of an anoxic solution of the sulfur substance to the reaction medium, which contained suspended Carbo-Iron, and iii) a separate wet pre-treatment of the composite material with sulfur species prior to dechlorination tests. This was performed as follows: the particles were conditioned for 24 h in a 50 mM bicarbonate solution, which contained the sulfur species. Subsequently, sulfidated Carbo-Iron was separated from the supernatant by centrifugation under anoxic conditions, re-suspended in a fresh sulfur-free bicarbonate solution and shaken for two hours on a horizontal shaker. After this washing step was repeated three times in order to remove soluble sulfur species, the particles were re-suspended in the fresh reaction medium.

The sulfidation of Carbo-Iron was performed after the synthesis of the particles by applying 177 178 gas-solid and aqueous-solid phase sulfidation processes. Gas-solid sulfidation was performed by a dry treatment of the particles with gaseous H<sub>2</sub>S (diluted with N<sub>2</sub>) at room temperature 179 180 (g/s sulfidation). Aqueous-solid phase sulfidation (aq/s sulfidation) involved the addition of 181 an anoxic solution of the sulfur substance to the anoxic bicarbonate solution, which 182 contained suspended Carbo-Iron particles. In the latter process the duration of sulfidation 183 was varied. The sulfur species were allowed to remain in solution during the entire 184 dechlorination reaction. In a third sulfidation variant, the particles were conditioned with sulfur species for 24 h in 50 mM bicarbonate solution (aq/s pre-treatment). The sulfidated 185 186 Carbo-Iron was separated in that case from the supernatant by centrifugation under anoxic conditions, re-suspended in a fresh sulfur-free bicarbonate solution and shaken for two 187 188 hours on a horizontal shaker. After the washing step was repeated three times in order to 189 remove soluble sulfur species, the particles were re-suspended in fresh reaction medium and used as reactant. 190

Unless otherwise noted, the sulfidation was performed as aq/s sulfidation process where thesulfur species remained in the reaction medium.

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## 194 2.4. Reactivity tests

Batch experiments were performed to study the influence of sulfidation treatments on the reaction behavior of Carbo-Iron, considering PCE dechlorination and anaerobic corrosion of the composite's ZVI. The reactivity of the composite material was tested after the sulfidation procedures (see 2.3), with variation of the kind of sulfur species (Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or cysteine were used), their concentration and the concentration of bicarbonate in the reaction medium. 201 The batch experiments were commonly performed as follows: 60 mL of a bicarbonate 202 solution was added to a 120 mL crimped serum bottle and purged with argon. After the addition of a defined mass of (sulfidated) Carbo-Iron or nZVI, the suspension was further 203 204 purged with argon. If specified, an anoxic solution containing sulfur compounds was added. 205 The bottle was crimped and particles were dispersed for 20 min in an ultrasonic bath. Then a defined volume of methane was added as internal standard for the headspace analysis and 206 207 the reaction was started by injecting an aliquot of a methanolic stock solution of PCE  $(t_{\text{reaction}} = 0)$ . The bottles were continuously shaken on a horizontal shaker (90 rpm) at room 208 209 temperature.

In long-term experiments over 160 days the effect of a sulfidation on the anaerobic 210 corrosion of Carbo-Iron and the residual reduction capacity of the remaining ZVI after the 211 monitoring period were examined. The sulfidation treatment of the composite material was 212 performed as described in section 2.3. by direct addition of an anoxic Na<sub>2</sub>S solution to the 213 Carbo-Iron suspension (S/Fe = 0.003 moles mol<sup>-1</sup>, aq/s sulfidation), by aq/s pre-treatment in 214 bicarbonate solution with washing steps prior use (S/Fe = 0.003 and 0.33) and of dry 215 216 composite particles with H<sub>2</sub>S (g/s sulfidation S/Fe  $\approx$  0.33). The sulfide-treated samples were 217 compared to a sulfur-free batch. At the end of the monitoring period after 160 days, the 218 residual reduction capacity of Carbo-Iron was measured by adding DBA in excess (35 g  $L^{-1}$ ) as dehalogenation probe. This substance was previously identified for its fast reaction with ZVI, 219 220 forming almost completely ethene and only traces of ethane (observed first-order rate constant  $k_{obs,DBA} = 0.03 \text{ h}^{-1}$  at  $c_{Carbo-Iron} = 5 \text{ g L}^{-1}$  with a reaction selectivity close to 100 % 221 222 towards the bromine-free C<sub>2</sub> hydrocarbons. This method offers a fast quantification of the 223 remaining ZVI content without separation of the solid fraction.

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#### 225 **2.5.** Calculation of dechlorination efficiency

In the literature there exist several approaches to describe the relation between dechlorination and anaerobic corrosion of ZVI. Terms such as "particle efficiency" or "electron efficiency" are often used in a similar meaning, but the definitions vary widely between the various studies (Fan et al., 2016; Gu et al., 2017; Liu et al., 2005b; Liu et al., 2013; Schöftner et al., 2015; Tang et al., 2017, Dong et al., 2018). In the present work, we define two types of dechlorination efficiencies to describe the relation between the two parallel occurring reactions. Firstly, the dechlorination efficiency  $\varepsilon_1$  is defined in accordance

to Gu et al. (2017) as the ratio of iron amount used for dechlorination ( $n_{ZVI,dechlor}$ ) and the overall consumed amount of iron, considering dechlorination and the anaerobic corrosion ( $n_{ZVI,corr}$ ) within a certain time interval. It was calculated according to eq. (1), where  $n_i$  is the molar quantity of the dechlorination product *i* (e.g. ethene),  $n_{H2}$  is the molar quantity of H<sub>2</sub> formed and  $v_i$  are stoichiometric factors of the respective half reactions.

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239 
$$\varepsilon_1 = \frac{n_{ZVI,dechl}}{n_{ZVI,dechl} + n_{ZVI,corr}} \cdot 100 \% = \frac{\sum_i \nu_i n_i}{\sum_i \nu_i n_i + \nu_{H2} n_{H2}} \cdot 100 \%$$
 (1)

240

The stoichiometric factor per converted molecule PCE varied depending on the spectrum of 241 products formed. For the formation of acetylene, ethene and ethane stoichiometric factors 242 243 of  $v_i = 3$ , 4 and 5 were applied, respectively (according to the PCE reduction equation  $C_2Cl_4 + (4 + n) e^- + (4 + n) H_2O \rightarrow C_2H_n + (4 + n) OH^- + 4 Cl^-$ , with n = 2, 4 or 6), while for the 244 245 residual fraction of higher molecular weight hydrocarbons a mean stoichiometric factor of  $v_i$ = 4 was assumed. For the hydrogen formation (2 H<sup>+</sup> + 2 e<sup>-</sup>  $\rightarrow$  H<sub>2</sub>) a stoichiometric factor  $v_i$  = 1 246 was applied (Fe  $\rightarrow$  H<sub>2</sub> + 2 e<sup>-</sup>). In the batch system the value for  $\varepsilon_1$  depends on the initial 247 concentration and the conversion degree of the chlorocompound. The calculated value has 248 249 therefore only a limited significance for general comparisons and conclusions, although it is a 250 plausible percentage value.

251 Alternatively, we propose the calculation of the dechlorination efficiency  $\varepsilon_2$  by comparing 252 second-order rate constants (in L mol<sup>-1</sup> h<sup>-1</sup>) of the dechlorination  $(k''_{dechl})$  and the anaerobic corrosion ( $k''_{corr}$ ), which should be independent of the applied reactant concentrations. The 253 overall iron consumption can be described by eq. (2) with  $n_{ZVI}$  as the molar amount of ZVI in 254 the reaction batch, c<sub>PCE,pore</sub> in mol L<sup>-1</sup> as the pore volume ("local") concentration of PCE in the 255 pore volume of Carbo-Iron. The idea of eq. (2) is that the reaction rates are controlled by the 256 257 local reactant concentrations rather than those in the suspension bulk phase (Mackenzie et 258 al., 2012). The concentration of the reactant water  $c_{H2O}$  is independent of the place of 259 reaction, i.e.  $c_{H2O,bulk} = c_{H2O,pore} = c_{H2O} = 55.6 \text{ mol } L^{-1}$ .

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261 
$$-\frac{\mathrm{d}n_{\mathrm{ZVI}}}{\mathrm{d}t} = k_{\mathrm{corr}}^{\prime\prime} \cdot c_{\mathrm{H2O}} \cdot n_{\mathrm{ZVI}} + k_{\mathrm{dechl}}^{\prime\prime} \cdot c_{\mathrm{PCE,pore}} \cdot n_{\mathrm{ZVI}}$$
(2)

The local PCE concentration at the reactive iron centers can be calculated from the total PCE concentration  $c_{PCE,bulk}$  (moles of PCE per volume of reaction suspension) by eq. (3), under conditions where PCE adsorption is quite dominant ( $n_{PCE,adsorbed} >> n_{PCE,freely dissolved}$ ) with  $c_{Carbo-Iron}$  as the Carbo-Iron concentration in the bulk phase (suspension) in g L<sup>-1</sup> and p as the Carbo-Iron intraparticle porosity in L g<sup>-1</sup> (0.8 mL g<sup>-1</sup>, Bleyl et al. 2012).

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269 
$$C_{\text{PCE,pore}} = \frac{c_{\text{PCE,bulk}}}{c_{\text{Carbo-Iron}} \cdot p}$$
 (3)

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We are aware of the fact that  $c_{PCE,pore}$  considers PCE as dissolved in the pore water, whereas actually it is adsorbed on the AC surface. The calculation of the second-order rate constants  $k_i''$  was performed on the basis of eqs. (4) and (5) using initial reaction rates (t  $\rightarrow$  0) and with  $n_i$  and  $v_i$  as molar amounts and stoichiometric factors of the dechlorination products.

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276 
$$k_{\rm corr}'' = \frac{\nu_{\rm i}}{n_{\rm ZVI} \cdot c_{\rm H2O}} \cdot \left(\frac{\mathrm{d}n_{\rm H2}}{\mathrm{d}t}\right)_{t\to 0}$$
 [L mol<sup>-1</sup> h<sup>-1</sup>] (4)

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278 
$$k_{\text{dechl}}^{\prime\prime} = \frac{\sum_{i} v_{i}}{n_{\text{ZVI}} \cdot c_{\text{PCE,pore,0}}} \cdot \left(\frac{\mathrm{d}n_{i}}{\mathrm{d}t}\right)_{t \to 0} \qquad [\text{L mol}^{-1} \text{ h}^{-1}]$$
(5)

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The dechlorination efficiency  $\varepsilon_2$ , as ratio of the second-order rate constants for dechlorination and corrosion (eq. (6)) is a dimensionless number with some general significance and can be used for comparing properties of unsulfidated and sulfidated materials.

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285 
$$\varepsilon_2 = \frac{k_{\text{dechl}}^{\prime\prime}}{k_{\text{corr}}^{\prime\prime}}$$
 [-] (6)

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288 3. Results and discussion

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## 290 **3.1.** XRD analysis of sulfidated Carbo-Iron

291 Previous studies on nZVI showed that different sulfidation treatments of iron particles lead 292 to the formation of FeS at the metal surface, which is considered as reason for the improved 293 reaction behavior of nZVI (Fan et al., 2017, Dong et al., 2018). Beside the formation of FeS, also the generation of other iron-sulfur minerals (e.g., greigite Fe<sub>3</sub>S<sub>4</sub> or pyrite FeS<sub>2</sub>) or iron 294 295 polysulfides was observed (Fan et al., 2017, Heift et al, 2018). The sulfidation methods used in this study had similar impacts on the Carbo-Iron samples. No substantial differences in 296 reaction behavior as aqueous suspensions were found. Dechlorination and corrosion studies 297 were carried out using all three sulfidation methods (see section 3.2.). In order to avoid a 298 drying step, which could alter the sample surfaces, we decided to use samples generated by 299 300 g/s sulfidation for surface analysis.

In order to gain information about the modification of the particle surface and the mineral phases of Carbo-Iron's ZVI during a sulfidation treatment, H<sub>2</sub>S-treated Carbo-Iron (g/s sulfidation) was analyzed by XPS, EDX and XRD analysis.



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Fig. 1. Stacked depiction of EDX analysis data of A) untreated Carbo-Iron (focus on region rich in
 carbon); B) untreated Carbo-Iron (focus on region rich in iron); C) Carbo-Iron, treated with gaseous
 H<sub>2</sub>S (focus on region rich in carbon); D) Carbo-Iron, treated with gaseous H<sub>2</sub>S (focus on region rich
 in iron); E) TEM bright-field image of a thin cut of resin-embedded Carbo-Iron particles

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Unfortunately, the analysis of the porous composite by XPS did not reveal any information about the oxidation state of the sulfur, which could be possibly explained by the low amount of sulfur species at the surface. However we gain the qualitative information by EDX analysis that sulfide distributes between the iron and the activated carbon surfaces. Figure 1 shows EDX data which were taken in iron-rich and carbon-rich regions of the composite particle surface before (Fig. 1A and B) and after sulfidation (g/s sulfidation; Fig. 1C and D). A typical TEM image of Carbo-Iron generated by carbothermal synthesis is added in Fig. 1E.

The XRD pattern of sulfidated Carbo-Iron is shown in Fig. 2 (g/s sulfidation) and reveals dominant signals which are characteristic of  $\alpha$ -Fe. This verifies the high crystallinity of the incorporated ZVI. A rather high degree of iron crystallinity has to be expected for Carbo-Iron due to the thermal synthesis of the particles at temperatures  $\geq$  700°C.







323 Fig. 2. XRD pattern of Carbo-Iron particles pre-treated with gaseous H<sub>2</sub>S in a nitrogen stream

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325 Next to those of  $\alpha$ -Fe, reflections of mackinawite (crystalline FeS) at 18°, 31° and 39° (2 $\theta$ ) 326 were observed. Despite the high noise in the spectrum, FeS signals are assignable. For sulfidated nZVI which was synthesized by reduction with sodium borohydride (nZVI<sub>NaBH4</sub>) also 327 the formation of FeS at the iron surface is described in literature (Kim et al., 2011; 328 Rajajayavel and Ghoshal, 2015). In contrast to Carbo-Iron, which has at least partially a 329 crystalline FeS shell, the formed FeS phase at the surface of nZVI<sub>NaBH4</sub> is characterized by a 330 low degree of crystallinity, which could potentially lead to a somewhat different reaction 331 332 behavior of the particles.

#### **334 3.2.** Influence of sulfide and bicarbonate on the reactivity of Carbo-Iron

Former studies demonstrated that the effect of sulfur on the nZVI reactivity is concentration 335 336 dependent (Fan et al., 2017; Li et al., 2017b). Therefore, also a variation in properties has to 337 be expected for the ZVI/AC-composite Carbo-Iron when treated with different amounts of 338 reduced sulfur. In a first set of experiments, the sulfidation was performed after the synthesis of the particles in the reaction medium by adding an anoxic sodium sulfide solution 339 340 (aq/s sulfidation). Although being aware that bisulfide (HS<sup>-</sup>) is the dominant species under the applied conditions (pH = 8.5,  $pK_{a,HS}$  = 12), we use the term sulfide when describing the 341 interaction with Carbo-Iron for reasons of convenience. For an accurate comparison of 342 literature data with various iron samples, the ratio of sulfur atoms applied to the iron surface 343 344 atoms would be the most appropriate parameter. However, as the surface area of the 345 investigated particles is not always given in the various data sets, the introduced molar S/Fe 346 ratio remains as reasonable compromise as a comparative measure of sulfur doses.

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#### 348 3.2.1. Anaerobic corrosion of Carbo-Iron's ZVI

The anaerobic corrosion of Carbo-Iron's ZVI was studied by analyzing the formation of 349 molecular hydrogen over a time period of 5 to 20 days varying the S/Fe ratio (aq/s 350 sulfidation) and the bicarbonate concentration of the reaction medium. Bicarbonate 351 concentrations of 0.2 mM represent very soft water, 5 mM are in the range of very hard 352 353 water and 50 mM can be seen as worst case scenario. For sulfide, we chose a S/Fe ratio up 354 to 0.33 which is in a range where the effect of sulfidated nZVI can already reach a 355 plateau (Fan et al., 2017). With S/Fe = 0.004 we chose a sulfidation degree which is an order 356 of magnitude lower than that used as the lower limit in other studies. In order to compare the corrosion activity of different samples, the hydrogen evolution rate at the beginning of 357 the reaction was used and a ZVI-mass-normalized rate constant  $k_{m,corr}$  [µmol h<sup>-1</sup> g<sup>-1</sup>] was 358 359 determined as a parameter which is frequently reported in literature. In Fig. 3A the results for the anaerobic corrosion of Carbo-Iron's ZVI in the presence of various S/Fe ratios and 360 bicarbonate concentrations are depicted. Note that  $k_{m,corr}$  is related to  $k''_{corr}$  in eq. (7) by 361

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$$k_{\rm m,corr} = k_{\rm corr}^{\prime\prime} \cdot \frac{c_{\rm H2O}}{M_{\rm Fe}}$$
 (7)

with  $M_{\text{Fe}}$  as molecular weight of Fe. PCE dechlorination follows pseudo-first order kinetics and the respective rate constants ( $k_{\text{obs,dechl}}$ ) are shown in Fig. 3B. They can be converted into second-order rate constants  $k''_{\text{dechl}}$  as used in eq. (5) by eq. (8):

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$$k''_{\text{dechl}} = \frac{c_{\text{Carbo-Iron}} \cdot p}{c_{\text{ZVI}}} \cdot k_{\text{obs,dechl}}$$
 (8)

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Generally, a strong corrosion-inhibiting effect of sulfide on the embedded ZVI was observed
(note the divided Y axis). Although bicarbonate accelerates the iron corrosion, the protecting
sulfur effect was significant even for the lowest sulfide concentration (factor of 30 to 65).



Fig. 3. A) Mass-normalized rate constants for anaerobic corrosion of Carbo-Iron's ZVI  $k_{m,corr}$  and B)

377 observed first-order rate constants for PCE dechlorination  $k_{obs,dechl}$  by Carbo-Iron in the presence of

378 different bicarbonate and sulfide concentrations ( $c_{0,PCE} = 33 \text{ mg L}^{-1}$ ,  $c_{Carbo-Iron} = 4 \text{ g L}^{-1}$ )

Under the applied conditions a maximum coverage of 20 % of the iron surface with a FeS monolayer would be achieved when we assume that the sulfide is exclusively attached to the Fe surface and the Fe surface is provided by 50 nm spherical clusters (Mackenzie et al., 2012). We assumed body-centered cubic structure for the iron species and a 1:1 Fe:S stoichiometry. In practice the sulfide coverage will be much lower due to partial distribution of sulfide to the AC surface (see Fig. 1).

However, the low sulfide coverage seems to be sufficient for deactivation of the corrosionsensitive sites. The presence of higher sulfide concentrations led to a further slight decrease of hydrogen evolution reaching a minimum when 0.2 mM NaHCO<sub>3</sub> and S/Fe of 0.33 were applied (pH = 7.6, while at higher NaHCO<sub>3</sub> concentrations the system shows a slight buffer effect reaching a pH value of 8.5).

391 Under these conditions essentially no hydrogen evolution was detected within 18 days (detection limit  $\approx 1 \ \mu$ mol H<sub>2</sub>). This finding corresponds to an upper limit of the corrosion rate 392 coefficient  $k_{ZVI,corr} < 3 \times 10^{-6} h^{-1}$  or an estimated half-life of the ZVI of more than 25 years. 393 394 Under these conditions, the applied sulfide concentration would be theoretically sufficient 395 to 6-fold cover the iron surface with a monolayer of FeS. Consequently, it can be assumed that under sulfide excess conditions beside FeS, also FeS<sub>2</sub> and polysulfides are generated at 396 397 the iron surface (Heift et al., 2018), which can have passivating effects. However, this 398 complete corrosion inhibition is reached at the expense of the dechlorination activity. Therefore, such a high sulfidation degree is not our preferred layout. 399

Generally, the sulfide-induced suppression of the anaerobic corrosion of nZVI is a known 400 401 effect, which is described in literature and is explained by an inhibition of the recombination 402 reaction of surface-attached hydrogen atoms (lyer et al., 1990; Oudar, 1980). However, the corrosion-inhibiting effect found in the present study for Carbo-Iron is much higher than 403 404 observed for non-supported nZVI with comparable S/Fe ratios. Rajajayavel and Ghoshal 405 (2015) observed a decrease in the hydrogen generation rate by a factor of 2 to 3 at S/Fe ratios between 0.02 to 0.07 compared to the untreated particles. Han and Yan (2016) 406 achieved a suppression of the corrosion rate constant by a factor of four from  $k_{m,corr} = 50$  to 407 408 13 µmol g<sup>-1</sup> h<sup>-1</sup> at S/Fe ratios of 0.05 and 0.25, while at a S/Fe ratio of 0.01 nearly no 409 inhibition effect was observed. Fan et al. (2016) demonstrated that the presence of higher amounts of reduced sulfur species (S/Fe ratio  $\geq$  0.33) leads to a stronger inhibition of the 410

411 hydrogen evolution. However, the presented data do not allow derivation of quantitative412 parameters for the remaining corrosion rates.

This leads to the question why Carbo-Iron's ZVI showed such a high corrosion inhibition 413 (about one to two orders of magnitude) at even low S/Fe ratios and how the differences 414 compared to the previously studied nZVI particles can be explained. Firstly, the morphology 415 of the iron particles is different. In previous studies, mostly nZVI synthesized by reduction 416 with NaBH<sub>4</sub> was applied, which has an amorphous structure with more surface defects in 417 contrast to ZVI in Carbo-Iron, which has a crystalline structure due to high temperature 418 419 reduction (Liu et al. 2005b). It is known that nZVI<sub>NaBH4</sub> particles undergo dissolution during aging (Liu et al., 2005a), so that corrosion-sensitive fresh subjacent ZVI is consistently 420 exposed to the water phase. Crystalline nZVI, as it is present in Carbo-Iron, rather forms 421 422 more stable core-shell-structures, protecting the iron core from corrosion much better (Liu et al., 2005a). In order to evaluate the influence of the crystallinity of ZVI particles on the 423 response behavior towards a sulfidation treatment, the thermally reduced and commercially 424 425 available nZVI Nanofer Star was examined regarding its corrosion activity in absence and 426 presence of sodium sulfide. While untreated Nanofer Star showed a comparably high corrosion rate of 238 ± 15  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> in a 50 mM bicarbonate solution (pH = 8.5), the 427 428 presence of sodium sulfide (S/Fe = 0.06) decreased the anaerobic corrosion by a factor of about 7 ( $k_{m,corr}$  = 33.3 ± 1.3 µmol L h<sup>-1</sup> g<sup>-1</sup>). This inhibition effect is substantially lower 429 compared to Carbo-Iron's ZVI thus indicating that crystallinity of ZVI is not the only relevant 430 431 property. Rather, carbon enrichment in the ZVI crystallites and the AC backbone itself could 432 play a role in the different reaction behavior. Another possible benefit of the ZVI/AC-system 433 could be the protection of FeS layers against mechanical stress due to their intrapore position. As a consequence a more uniform FeS shell could be formed, protecting the 434 435 underlying ZVI better.

436

#### 437 **3.2.2. PCE dechlorination**

The effect of a sulfidation on TCE dechlorination by nZVI has been described in several publications (He at al., 2018; Fan et al., 2016; Han and Yan, 2016; Kim et al., 2011; Rajajayavel and Ghoshal, 2015), while the impact on PCE dechlorination has not been examined so far. It is reasonable to expect similar effects. In the present study, the 442 degradation of PCE in absence and presence of sulfide was studied by analyzing the chlorinefree C<sub>2</sub>-hydrocarbons and chloride over a time period of 5 to 20 days. Both products offer 443 the advantage of only marginal sorption to the AC surface in contrast to the educt PCE, 444 445 which facilitates the kinetic evaluation of the measured data. The obtained first-order rate constants  $k_{obs,dechl}$  are not converted into the metal surface-normalized second-order rate 446 447 constant  $k_{SA}$  as commonly applied for pure ZVI systems. The normalization is inappropriate for ZVI/AC composites like Carbo-Iron, since  $k_{obs}$  for pollutant reduction is more or less 448 independent of the applied total ZVI concentration (Mackenzie et al., 2012). The more 449 450 suitable parameter for comparing material reactivities is  $k_{obs,dechl}$ .

451 The  $k_{obs,dechl}$  values obtained for Carbo-Iron in the presence of various sulfide and bicarbonate concentrations are shown in Fig. 3B. Sulfidation of Carbo-Iron leads in most 452 453 cases to an enhancement of the PCE dechlorination rate by a factor of about three over a wide range of S/Fe ratios between 0.004 and 0.11 at all applied bicarbonate concentrations. 454 455 Only for the highest S/Fe ratio tested (S/Fe = 0.33) the dechlorination rate decreased again. 456 Such an 'over-sulfidation' effect was not observed for TCE (Fan et al., 2016; Han and Yan, 457 2016; Kim et al., 2011; Rajajayavel and Ghoshal, 2015). Along with the sulfide-induced altered PCE dechlorination rates we observed a significant change of the product pattern 458 459 towards less hydrogenated products. In Fig. 4 exemplary the product distribution for C2hydrocarbons and chloride over time is shown in absence and presence of sodium sulfide 460 (S/Fe = 0.06). Ethene and ethane are the main products in nearly equal ratios for 461 dechlorination with untreated Carbo-Iron. The addition of sulfide led to a dominant 462 463 formation of acetylene, which was then subsequently hydrogenated. In the presence of high 464 sulfide concentrations (S/Fe = 0.33) in a 0.2 mM bicarbonate solution, acetylene was the sole C2-hydrocarbon, while hydrogenation to ethene and ethane was largely suppressed (data 465 466 not depicted in Fig. 4).





Fig. 4. Kinetic evaluation of the PCE dechlorination with Carbo-Iron A) without Na<sub>2</sub>S and B) in the presence of Na<sub>2</sub>S with S/Fe = 0.06 ( $c_{0,PCE}$  = 33 mg L<sup>-1</sup>,  $c_{Carbo-Iron}$  = 4 g L<sup>-1</sup>,  $c_{NaHCO3}$  = 50 mM, pH<sub>start</sub> = 8.5).

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473 Fig. 5. Scheme of sulfidation states and their effects on ZVI reactions in Carbo-Iron pores (AC

backbone in light gray with embedded ZVI in core-shell-structure); A) untreated Carbo-Iron, B) low

475 S/Fe ratios and C) high S/Fe ratios.

476

477 The changed reaction behavior of sulfidated Carbo-Iron in the PCE dechlorination could be explained by the modified surface properties of the embedded ZVI, as shown schematically 478 in Fig. 5. While untreated ZVI is characterized by an oxide shell (Fig. 5A), a low degree of 479 480 sulfidation leads to the formation of a thin and uncomplete FeS shell (Fig. 5B) (Fan et al., 2017; Li et al., 2017a; Li et al., 2017b). In the literature, it is generally assumed that the FeS 481 482 layer at the iron surface can accelerate the degradation of the TCE as it i) improves the adsorption of the pollutant at the cluster surface and ii) has advantageous electron-483 484 conducting properties compared to iron oxides (Fan et al., 2017; Li et al., 2017b). iii) The contribution of an increased availability of reactive hydrogen for pollutant degradation, due 485 to suppression of hydrogen recombination by sulfide was suggested but is controversially 486 487 discussed (Fan et al., 2017). For the ZVI/AC composite Carbo-Iron an improved sorption of 488 the chlorinated compound at a sulfidated ZVI surface should not play a dominant role, as the 489 contaminant is adsorbed at the much larger AC surface, where the dechlorination reaction is 490 supposed to take place. This assumption is based on dechlorination experiments where the 491 two reactants, TCE adsorbed on AC particles and suspended nZVI particles, were spatially 492 separated (Kopinke et al., 2016; Tang et al., 2011). This however poses the question, how the 493 sulfidation of ZVI does affect the dechlorination reaction at the carbon surface. Generally, carbonaceous materials are known to take an active part in chemical reactions by allowing 494 495 electron transfer and most likely also hydrogen spill-over (Kopinke et al., 2016; Oh et al., 496 2002; Tang et al., 2011). The product pattern of the PCE dechlorination, which is shifted from 497 ethene plus ethane to acetylene upon sulfidation, indicates that the ratio of electrons and 498 reactive hydrogen available at the reaction site (i.e. the carbon surface) is increased if sulfide 499 is present. This could be explained by the improved electron conductivity of FeS (Li et al., 500 2017b) which facilitates the electron transfer from ZVI to carbon and therefore accelerates 501 the PCE dechlorination. Beside the modified iron surface, also the alteration of the carbon 502 surface by sulfide could be a possible reason for the observed dechlorination acceleration. 503 Previous studies on the reduction of nitroaromatic compounds showed that carbonaceous 504 materials can mediate the reaction in the presence of sulfide as reductant. As reduction 505 mechanisms (i) the electron transfer from sulfides through the carbon phase to the target compound and (ii) mediation by sulfur-based intermediates at the carbon surface were 506 507 discussed (Amezquita-Garcia et al., 2013; Fu and Zhu, 2013; Xu et al., 2010; Xu et al., 2015).

508 A higher sulfidation degree (Fig. 5C) will proceed to modify the iron surface in such a way 509 that electrons but not atomic hydrogen are available. Inhibition of PCE degradation at high sulfidation degree (S/Fe = 0.33) might be due to a passivation process of the ZVI surface, e.g. 510 by FeS<sub>2</sub> or polysulfides, which are less conductive compared to FeS, leading to an insulation 511 512 of the iron core. In this context, the tendency of crystalline nZVI to form stable sulfidation shells can be disadvantageous. In particular, the inhibited formation of reactive hydrogen 513 514 may slow down the PCE dechlorination (Jayalakshmi and Muralidharan, 1992). Nevertheless, long-living particles with a sufficient dechlorination activity are created. What does this 515 516 scenario mean for ZVI embedded in an AC matrix for its field relevance? The chlorinated pollutants are "trapped" within the AC pores, providing a long residence time within a 517 treatment zone. Hence, even a reduced chemical reactivity of sulfidated (long-lived) ZVI may 518 519 be sufficient for the contaminant degradation in Carbo-Iron. The advantage of markedly 520 improved longevity might outcompete the disadvantage of lower reactivity by means of the 521 outstanding sorption affinity of the AC support toward chlorohydrocarbons.

522

#### 523 3.2.3. Dechlorination efficiency

524 The efficient utilization of the reduction equivalents of ZVI is decisive for the particle longevity and their impact on the intended treatment goal. With the iron 'dechlorination 525 526 efficiency' we evaluate the two main iron consumption pathways occurring in parallel, the 527 dechlorination of PCE and the anaerobic corrosion of the ZVI in Carbo-Iron (see eq. (1)). In former studies the focus was often placed on chemical reactivity for contaminant 528 529 degradation alone. However, it is plausible that for field applications the ratio between 530 dechlorination and corrosion rates is a more conclusive parameter. The calculated 531 dechlorination efficiencies  $\varepsilon_1$  for the reduction of PCE by various concentrations of untreated 532 and sulfidated Carbo-Iron are shown in Fig. 6. Note that the efficiency parameter  $\varepsilon_1$  as 533 defined in eq. (1) is not a unique material property but depends on the experimental conditions, in particular on reactant concentrations, e.g. CPCE. For untreated Carbo-Iron, the 534 535 dechlorination efficiency is the highest for its lowest concentration. This can be explained by means of the local concentrations of the reactants PCE and water (eq. (2) and Mackenzie et 536 537 al., 2012). PCE is almost completely adsorbed to Carbo-Iron (at the applied concentration of 538  $c_{Carbo-Iron} \ge 1.25$  g L<sup>-1</sup>). This means, the loading of Carbo-Iron with PCE, expressed by  $c_{pore,PCE}$  in 539 eq. (2), is the highest for the lowest Carbo-Iron concentration. In contrast,  $c_{H2O}$  is

540 independent of the Carbo-Iron concentration (as long as its loading with PCE is low, i.e. the 541 AC pores are filled with water). Hence, the dechlorination reaction (represented by the 542 second summand in eq. (2)) can better compete for electrons from ZVI. For the case of 543 sulfide absence, the dechlorination efficiency was calculated to be about 27 to 60 %. This 544 means that a significant part of the ZVI is 'wasted' by the corrosion pathway.





Fig. 6. Dechlorination efficiencies  $\varepsilon_1$  of original and sulfide-treated particles at three Carbo-Iron concentrations ( $c_{Carbo-Iron} = 1.25 - 5 \text{ g L}^{-1}$ ,  $c_{0,PCE} = 33 \text{ mg L}^{-1}$ ,  $c_{NaHCO3} = 0.2 \text{ mM}$ , pH<sub>start</sub> = 8.5, S/Fe = 0 and 0.004 mol mol<sup>-1</sup>)

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The tendency that a majority of the reduction equivalents are consumed by anaerobic 551 corrosion is already described for nZVI (Fan et al., 2016; Gu et al., 2017; Liu et al., 2013; 552 Schöftner et al., 2015). This is highly undesired from the economic point of view, especially 553 against the background of the high costs and effort for nanoparticle synthesis. The 554 555 sulfidation of Carbo-Iron particles led already for the lowest sulfidation degree (S/Fe = 0.004) to a vast increase of the dechlorination efficiency up to 97 to 99%. This means that 556 sulfidation of Carbo-Iron can dramatically improve the performance of the particles, as the 557 majority of the electrons are used for dechlorination. In literature the enhanced 558 559 dechlorination efficiency of sulfidated ZVI is described by several working groups, but a direct comparison between the different studies is difficult. Fan et al. (2016) only showed a 560 561 scheme to illustrate the change in usage of reducing equivalents, but specific calculations are missing. Gu et al. (2017) determined in their study the dechlorination efficiency to 0.2 % for 562

563 mZVI (at 90 % TCE conversion) and to 10 % for S-mZVI (at 40 % TCE conversion) when ZVI 564 was applied in excess ( $c_{0,TCE} = 76 \mu$ M,  $c_{0,mZVI} = 10 \text{ g L}^{-1}$ ). At these specific contaminant 565 conversion degrees for Carbo-Iron a dechlorination efficiency  $\varepsilon_1 = 16$  % for the untreated 566 and  $\varepsilon_1 = 98$  % for the sulfidated particles are calculated ( $c_{0,PCE} = 200 \mu$ M,  $c_{Carbo-Iron} = 4 \text{ g L}^{-1}$ ).

The dechlorination efficiency  $\varepsilon_2$ , defined by eq. (6), was calculated to about 420 for the untreated particles and 53,600 for sulfidated Carbo-Iron. The shift in the ratio by two orders of magnitude demonstrates the improved utilization of iron for the target reaction.

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- 571

# **3.3.** Influence of various sulfur species

In the literature, treatment of iron with sodium sulfide (S<sup>2-</sup>, HS<sup>-</sup>) but also with dithionite 572  $(S_2O_4^{2-})$  or thiosulfate  $(S_2O_3^{2-})$  showed beneficial effects on the iron dechlorination activity 573 574 (Fan et al., 2017; Han and Yan, 2016; Kim et al., 2011; Li et al., 2017b; Rajajayavel and 575 Ghoshal, 2015). Within the present study also other sulfur species were studied for their abilities to optimize the reactivity of Carbo-Iron. We tested Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 576 and cysteine bearing S in the oxidation states -2, +4, +3, +5 and -1, and -2, respectively. As 577 578 sulfur substances in the oxidation state +6 Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were also selected. The 579 applied S/Fe molar ratios were 0.04 for sulfate, sulfite, sulfide and cysteine and 0.08 for peroxodisulfate, dithionite and thiosulfate. The resulting  $k_{obs,dechl}$  for PCE dechlorination and 580  $k_{m,corr}$  for anaerobic corrosion of Carbo-Iron's ZVI in the presence and absence of sulfur 581 species are shown in Fig. 7 The addition of 'reduced' sulfur species (i.e., with S in oxidation 582 states <6) to Carbo-Iron causes a significant decrease in the corrosion rate by a mean factor 583 of more than 50 compared to untreated Carbo-Iron, while the dechlorination rates increased 584 585 by a factor of about three.

The presence of sulfate and peroxodisulfate had no impact on the performance of the ZVI in Carbo-Iron. It is remarkable that a broad pattern of different sulfur compounds produces quite similar effects. It was shown before for nZVI<sub>NaBH4</sub> particles that several reduced sulfur species are able to influence the iron reactivity in a similar way (Fan et al., 2016; Han and Yan, 2016; Kim et al., 2011). As mechanisms it has been assumed that the applied sulfur compounds are able to *in-situ* generate sulfide species with ZVI via several pathways, which finally precipitates as FeS at the iron surface. Kim et al. (2011) and Han and Yan (2016) assumed that dithionite and thiosulfate are converted to sulfide by hydrolysis anddisproportionation, whereby the participation of nZVI was neglected.





Fig. 7. Influence of sulfur species in various oxidation states on the observed rate constants for PCE dechlorination ( $k_{obs,dechl}$ ) and the mass-related rate constants for anaerobic corrosion of ZVI in Carbo-Iron ( $k_{m,corr}$  in µmol H<sub>2</sub> per g ZVI per hour). The rate constants in the presence of reduced species (Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and cysteine) and oxidized species (Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) are presented as mean values. The error bars represent the average deviation of the single values from the mean value. ( $c_{0,PCE}$  = 33 mg L<sup>-1</sup>,  $c_{Carbo-Iron}$  = 4 g L<sup>-1</sup>,  $c_{NaHCO3}$  = 50 mM, pH<sub>start</sub> = 8.5; S/Fe = 0.04 mol mol<sup>-1</sup> for Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, cysteine and S/Fe = 0.08 for Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>).

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However, sulfide formation by reduction of the various sulfur compounds consumes reduction equivalents of ZVI. This assumption is supported by data of Fan et al. (2016), which revealed that at a S/Fe molar ratio of 0.33 more than 70 % of nZVI was consumed when dithionite was applied, while sulfide did not consume a significant part of nZVI. Consequently, the direct application of sulfide is more favorable. In our study we found that the treatment of Carbo-Iron with sodium sulfide (S/Fe = 0.04) in aqueous solution led to a negligible loss of ZVI of less than 5 %.

611

## 612 3.3.1. Influence of medium exchange on the activity of sulfidated Carbo-Iron

613 In order to evaluate the stability of sulfur modification, the Carbo-Iron particles were 614 thoroughly washed several times with bicarbonate solution and suspended in fresh, anoxic

615 media. The obtained reaction rate constants before and after exchange of the reaction medium are shown in Fig. 8. 616





619 Fig. 8. Observed rate constants for the dechlorination of PCE ( $k_{obs,dechl}$ ) and mass-related rate constant for the anaerobic corrosion of ZVI in Carbo-Iron  $(k_{m,corr})$  in the presence of reduced sulfur 620 621 species and after exchange of the reaction medium ( $c_{0,PCE} = 33 \text{ mg } \text{L}^{-1}$ ,  $c_{Carbo-Iron} = 4 \text{ g } \text{L}^{-1}$ ,  $c_{NaHCO3} = 50$ 622 mM, pH<sub>start</sub> = 8.5). The mean values are derived from the obtained reaction rate constants in the 623 presence of the sulfur species Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, cysteine (S/Fe = 0.04) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (S/Fe = 624 0.08). The error bars represent the average deviations of the single values from the mean values.

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No significant changes in the reaction behavior were observed after the reaction media were 626 exchanged. This confirms that the sulfur-induced surface modification is not only chemically 627 resistant but also resistant against mechanical stress. Due to the low solubility of FeS 628 (solubility product  $K_{L,FeS} = 8 \cdot 10^{-19} \text{ mol}^2 \text{ L}^{-2}$ ), the proportion of FeS which undergoes 629 dissolution in neutral aqueous media is negligible (Hummel et al., 2002). This is of relevance 630 especially for placement of sulfidated particles in a flow-through aquifer system. In case of 631 sulfidated nZVI<sub>NaBH4</sub>, the surface modification by Na<sub>2</sub>S was found to be less stable due to a 632 rather brittle structure of FeS, which led to a decrease in protection after a washing step 633 634 (Rajajayavel and Ghoshal, 2015). There are two plausible reasons for the higher stability of the FeS surface coating in Carbo-Iron: (i) the crystallinity of the ZVI clusters in Carbo-Iron and 635 (ii) their placement inside the rigid pore structure of the AC particles. Furthermore, it is 636

hypothesized that AC can provide sulfide in low concentrations over a longer time interval
and can thus act as a sulfur reservoir which provides steadily low amounts of the passivating
species to the neighboring iron.

640

#### 641 **3.4.** Long-term effects of sulfidation treatments

642 Any application-relevant sulfide effect of corrosion suppression is desired to last as long as iron is still present as zero-valent metal. Therefore, the long-term effect of different 643 644 sulfidation treatment methods on the anaerobic corrosion of Carbo-Iron was examined over 160 days. Then the ability of the residual metal to act as dehalogenation reagent was 645 646 measured by adding the fast-reacting 1,2-dibromoethane as probe. Carbo-Iron samples were 647 differently treated with sodium sulfide: (i) by direct addition of an O<sub>2</sub>-free Na<sub>2</sub>S solution to 648 the Carbo-Iron suspension (S/Fe = 0.003 mol mol<sup>-1</sup>), (ii) by an aqueous pre-treatment in bicarbonate solution, containing sulfide (S/Fe = 0.003 and 0.33 mol mol<sup>-1</sup>) with subsequent 649 exchange of the aqueous phase by a S-free bicarbonate solution, and (iii) via the gas phase 650 651 as H<sub>2</sub>S pre-treatment of dry Carbo-Iron particles. As a "worst case" scenario in terms of 652 corrosion, a 50 mM bicarbonate solution was chosen for the long-term tests as reaction 653 medium. The kinetics of the anaerobic corrosion of sulfide-treated and unmodified Carbo-654 Iron over 160 days alteration time are shown in Fig. 9A.

655 For all sulfidated samples a similar extent of corrosion suppression was observed. Based on 656 the measured H<sub>2</sub> formation, only 20 – 25 % of the ZVI underwent anaerobic corrosion within 160 days, while the untreated sample had lost already 70 % of its reduction capacity within 657 658 the first 15 days due to corrosion. The observation that all sulfide-treated samples showed 659 similar stabilities can be explained by the fact that the degree of corrosion suppression does 660 not strongly depend on the applied sulfide amount (see section 3.2.1 and Fig. 3). Qin et al. (2018) reported biphasic kinetics for corrosion of sulfidated and non-sulfidated ZVI samples 661 with a higher initial rate (first 8-10 h) and a slower second stage (10-120 h). However, Fig. 9A 662 shows that corrosion of the sulfidated Carbo-Iron samples runs with a constant rate over the 663 664 whole observation period of 160 d. Also for corrosion of non-sulfidated Carbo-Iron no 665 indication on a deviation from pseudo-first-order kinetics was observed even in experiments with higher initial time resolution of sampling (data not shown). 666

667 After 160 days reaction time the residual dehalogenation activity of sulfidated Carbo-Iron 668 was examined. We developed an easy to use and reliable method to analyze low-

669 concentrations of Fe(0) in suspension. 1,2-Dibromoethane (DBA) reacts fast and completely to ethene/ethane with 100% selectivity towards the fully debrominated C<sub>2</sub> hydrocarbons. 670 Fe(0) can be quantified from their yield. We recommend this method as excellent means for 671 Fe(0) determination in highly diluted suspensions. In order to examine the residual Fe(0) 672 content in the sulfidated Carbo-Iron sample after 160 days, a large excess of DBA was added 673 to the batches. It is an alternative to the colorimetric redox probe indigo-5,5'-disulfonate 674 (I2S) used by Fan et al. (2016) for quantification of the reducing agent concentration; in the 675 676 case of Fe/C composites, adsorption processes of I2S and its reduction products would interfere. The conversion of DBA was monitored by analysis of bromide and C<sub>2</sub> hydrocarbons 677 over a period of eight days and used to calculate the residual fraction of reactive ZVI. The 678 679 results for the sulfidated Carbo-Iron particles are presented in Fig. 9B.



680 681

Fig. 9. Long-term monitoring of the anaerobic ZVI corrosion in Carbo-Iron, which was modified by different sulfidation methods. A) Fraction of corroded iron based on H<sub>2</sub> formation within 160 d and B) fraction of residual metallic ZVI after 160 d determined by conversion of 1,2-dibromoethane. The following reaction conditions were used:  $c_{Carbo-Iron} = 4 \text{ g L}^{-1}$ ,  $c_{NaHCO3} = 50 \text{ mM}$ ,  $pH_{start} = 8.5$ ,  $c_{DBA,0} =$ 35 g L<sup>-1</sup>.

688

689 For the sulfidation treatments in the aqueous phase similar residual iron fractions of about 690 50 % were observed, while the lowest was found for particles, which where pre-treated by 691 gaseous H<sub>2</sub>S (37 %). It can be assumed that the very low amount of sulfide during the aqueous sulfidation is sufficient to induce the desired effect on a minimal expense of iron 692 content, while the dry sulfidation using gaseous H<sub>2</sub>S consumed more reduction equivalents 693 of the embedded ZVI. A closed balance of ZVI reduction equivalents (for H<sub>2</sub> formation and 694 695 DBA reduction) was not reached which could possibly be explained by side reactions, e.g. with residual oxygen penetrating slowly into the system. Nevertheless, such a remaining 696 high availability of nZVI (as directly confirmed by DBA conversion) after 160 days under 697 corrosion-promoting conditions (50 mM NaHCO<sub>3</sub>) is promising for the *in-situ* application of 698 699 the particles in the field. In the presence of soft water (0.2 mM NaHCO<sub>3</sub>) an about 16-fold 700 and in the presence of very hard water (5 mM NaHCO<sub>3</sub>) an even 3-fold lower corrosion rate can be expected (see section 3.2.1 and Fig. 3), which would be associated with an even more 701 extended life-time of the particles ( $t_{1/2} \ge 2-8$  years in absence of halogenated pollutants). To 702 the best of our knowledge, such a long life-time has never been demonstrated for 703 704 conventional nZVI<sub>NaBH4</sub>.

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706

### 707 **4. Conclusions**

708 In the present study we were able to show that sulfidation has a very positive effect on the reaction behavior of the ZVI/AC composite material Carbo-Iron. In contrast to previously 709 710 studied nZVI<sub>NaBH4</sub> the composite particles showed already at low molar S/Fe ratios of 0.004 a 711 30 to 65-fold decrease of the anaerobic corrosion rate, which ensured a prolonged metal 712 life-time. Under the same conditions, the PCE dechlorination could be accelerated by a 713 factor of about three leading to an overall dechlorination efficiency of the Carbo-Iron particles of > 98 % (at  $c_{PCE,0}$  = 200  $\mu$ M and pH = 8.5). As reasons for the strong sulfidation 714 effects, the high degree of crystallinity of the embedded ZVI and the participation of the AC 715 as "sulfide buffer" are discussed. The combination of ZVI, AC and sulfide leads to efficient 716 717 and long-living particles, which are perfectly suitable for aquifer *in-situ* applications.

719

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