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Characterizing the Suitability of Granular Fe^0 for the Water Treatment Industry

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Received: 23 August 2019; Accepted: 20 September 2019; Published: 24 September 2019

Abstract: There is a burgeoning interest in reliably characterizing the intrinsic reactivity of metallic iron materials (Fe^0) or zero-valent iron materials (ZVI) used in the water treatment industry. The present work is a contribution to a science-based selection of Fe^0 for water treatment. A total of eight (8) granular ZVI materials (ZVI1 to ZVI8) were tested. Fe^0 dissolution in ethylenediaminetetraacetic acid (EDTA test) and 1,10-Phenanthroline (Phen test) is characterized in parallel experiments for up to 250 h (10 days). 50 mL of each solution and 0.1 g of each Fe^0 material are equilibrated in quiescent batch experiments using 2 mM EDTA or Phen. Results indicated a far higher extent of iron dissolution in EDTA than in Phen under the experimental conditions. The tested materials could be grouped into three reactivity classes: (i) low (ZVI4, ZVI6, ZVI7, and ZVI8), (ii) moderate (ZVI1 and ZVI5) and (iii) high (ZVI2 and ZVI3). The order of reactivity was the same for both tests: ZVI2 ≅ ZVI3 > ZVI1 ≅ ZVI5 > ZVI4 ≅ ZVI6 ≅ ZVI7 ≅ ZVI8. Phen results revealed for the first time the time-dependent variation of the kinetics of iron corrosion (corrosion rate) in short-term batch experiments. Overall, the results demonstrated the superiority of the Phen test for evaluating the initial stage of Fe^0 dissolution. Long-term column experiments are recommended to deepen the acquired knowledge.

Keywords: 1,10-phenanthroline; ethylenediaminetetraacetic acid; intrinsic reactivity; material selection; quality control; zero-valent iron

1. Introduction

Metallic or zero-valent iron materials (Fe^0 or ZVI) are widely used in the water remediation industry [1–7]. Employing Fe^0 for water remediation involves the selection of appropriate materials that chemically interact with water to produce iron corrosion products (FeCPs), which in turn act as contaminant scavengers [3,5,8–13]. Establishing the rationale for the selection of Fe^0 materials for field applications would enable water professionals (e.g. engineers) to choose suitable materials for specific purposes [6,14,15]. Yet data on the reactivity of Fe^0 materials is still lacking.

Information regarding the selection of Fe^0 materials for water remediation is confusing and even conflicting [6,16,17]. According to Miyajima and Noubactep [18], the main cause of this situation has been a semantic issue. Specifically, the expressions "Fe^0 efficiency" and "Fe^0 reactivity" are often randomly interchanged in the scientific literature [2,4,6,19,20]. In fact, Fe^0 has been introduced in the 1990s as a reducing agent for chlorinated hydrocarbons and other contaminants, mainly in groundwater [21,22]. Viewing Fe^0 as a reducing agent is a frontal contradiction with the knowledge that Fe^0 is particularly efficient for water decontamination because it generates in-situ nascent contaminant scavengers [8,12,13,23–30].

The prevailing perception of a reducing Fe^0/H_2O system, in which contaminant reductive transformation is (mostly) considered the cathodic reaction occurring simultaneously with iron oxidative dissolution (iron corrosion), has also guided the majority of past efforts to rationalize Fe^0 selection [6,17,19,20]. For example, Li et al. [20] purposefully stated that "Fe^0 reactions are mostly surface-mediated redox processes" but the intended redox processes were the ones implying contaminant reduction by an electro-chemical mechanism (electrons from Fe^0). Following this line, Li et al. [20] proposed a potential standard test for characterizing the suitability of Fe^0 materials used for water remediation (Table 1). The method is based on the oxidative dissolution of Fe^0 ($E^0 = -0.44$ V for the redox couple Fe^{II}/Fe^0) by Fe^{III} solutions ($E^0 = 0.77$ V for the redox couple Fe^{III}/Fe^{II}). The stoichiometry of the Fe^{III}/Fe^0 oxidation is simple and the reaction is fast. A second example is the one introduced by Kim et al. [19] to "evaluate the reductive power" of Fe^0 materials. This is achieved by using tri-iodide (I_3^-) as the "representative oxidizing agent" for Fe^0. In both cases, the tests are validated by comparing the results to those of the removal of various kinds of pollutants used as probing agents. Currently, using relevant contaminants as probing agents to assess the reactivity of Fe^0 materials is the most common approach [6,31,32]. However, rationally selecting a probing agent is controversial due to the following reasons: (i) hundreds of compounds are relevant contaminants [29], (ii) metabolites may form in-situ [13], and (iii) at many sites, water is polluted by several species [33]. Thus, other approaches for characterizing Fe^0 intrinsic reactivity have been explored [6,34–36].

Table 1. Overview of the available contaminant-independent approaches to characterize the intrinsic reactivity of Fe^0 materials. In this study, intrinsic reactivity is characterized by the initial dissolution kinetics of tested Fe^0 in EDTA and Phen.

Test	Anno	Fe^0	Rationale	Comments
	(-)	(g)		
H_2 evolution	1995	> 500	Fe^0 corrosion by H_2O	too large Fe^0 amounts
EDTA test	2005	0.1	Fe^0 corrosion by H_2O	disturbed by dissolved O_2
Tri-iodide (I_3^-)	2014	0.2	Fe^0 corrosion by iodine	past efforts ignored
Fe^{III}	2016		Fe^0 corrosion by Fe^{III}	I_3^- test considered
Phen test	2019	0.1	Fe^0 corrosion by H_2O	very simple to operate

The intrinsic reactivity results form a complex cause-and-effect relationship with a number of chemical and physical properties of a Fe^0 material. Relevant influencing parameters include; crystallinity, elemental composition, particle size, surface area, and surface morphology. As a matter of fact, the Fe^0 intrinsic reactivity cannot be inferred directly from these parameters [6]. In fact, the intrinsic reactivity cannot be directly measured, but can just be accessed by appropriate tools [34,37]. Tools based on oxidizing probing agents [19,20] are problematic because they consider Fe^0 as a reducing agent and parent of electrons for reductive transformation of contaminants [12,13,22,38]. On the other hand, they overlook two key issues: (i) the solvent, H_2O ($E^0 = 0.00$ V) is also an oxidizing agent for Fe^0, and (ii) the omnipresent dissolved oxygen ($E^0 = 0.83$ V) is a further relevant oxidizing agent for Fe^0. This observation implies that tools based on Fe^0 oxidation by selected probing agents should properly consider the confounding effects of H_2O and O_2 [39]. Such an approach was independently introduced by Noubactep et al. [40] and Pierce et al. [41]. Both research groups used ethylenediaminetetraacetic acid (EDTA) to sustain iron oxidative dissolution by complexing generated Fe^{II} and Fe^{III}. During the past 15 years, the EDTA test was further developed by Noubactep and colleagues to address several aspects of the design of efficient Fe^0/H_2O systems for water remediation [14,16,42,43]. The rationale for the EDTA test is that the initial iron dissolution in a 2 mM EDTA solution is a linear function of the time [38]. The slope of the corresponding line is a unique characteristic property (i.e., intrinsic reactivity) for the used Fe^0 (Section 3.5).

The suitability of the EDTA test for mimicking real-world situations suffers from the inherent evidence that aqueous Fe^{III}-EDTA complexes are very stable and induce: (i) accelerated Fe^0 dissolution, and (ii) dissolution of FeCPs [44–47]. Thus, the EDTA test does not only characterize the extent of iron corrosion as this is accelerated by the consumption of Fe^{II} species after Le Chatelier's Principle. In particular, it was very challenging to characterize steel wool specimens and granular materials covered with fine FeCPs using the EDTA test [14,16]. Recently, Lufingo [36] has solved this problem by introducing 1,10-Phenanthroline as complexing agent (Phen test). The Phen test only addresses Fe^{II} species and thus characterizes the forward dissolution of Fe^0 despite the presence of dissolved oxygen (and FeCPs). The question then arises, which test (EDTA or Phen) is better for characterizing the reactivity of Fe^0 materials? The present work is the first attempt to apply the Phen test to Fe^0 granular materials. Eight (8) commercial materials are tested in parallel experiments using both EDTA and Phen (2 mM) to enable comparison of the results.

2. Materials and Methods

2.1. Solutions

Working solutions were prepared from a monohydrated 1,10-Phenanthroline (Phen) (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and a disodium salt of ethylenediaminetetraacetic (EDTA) (Sinopsin group chemical reagent co. LTD, Shanghai China). An iron standard solution (1000 mgL^{-1}), (National Centre for Analysis and Testing of Non-ferrous and Electronic Materials) from General Research Institute for Nonferrous Metals was used to calibrate the used UV/VIS spectrophotometer. Other used chemicals included ascorbic acid. All used chemicals were of analytical grade.

2.2. Fe^0 Materials

A total of seven (7) locally available granular iron specimens (Fe^0) were used. The Fe^0 were purchased from three different factories in China. One Fe^0 specimen was obtained twice to characterize the possible variability of the intrinsic reactivity of the same material in two different manufacturing batches (ZVI4 and ZVI8). Thus, a total of eight (8) Fe^0 samples (Figure 1) were tested in the current study. Table 2 summarizes their main characteristics together with their iron content, as specified by the supplier.

Table 2. Iron content, origin, name and main characteristics of tested Fe^0 materials as specified by the supplier. SSA stands for specific surface area. 'n.s.' stands for not specified.

Code	Shape	Size	Color	SSA	Fe	Supplier
		(mm)		(m^2/g)	(%)	
ZVI1	nail	1.5 / 22	black	n.s.	n.s.	Pinnacle hardware store
ZVI2	scrap	0.05–5.0	black	n.s.	n.s.	Shanghai Institute of Fine Technology
ZVI3	irregular	0.50–1.5	grey	n.s.	n.s.	Tongda alloy material factory
ZVI4	spherical	2.0	grey	0.39	99.99	Tongda alloy material factory
ZVI5	spherical	0.6	grey	1.26	99.99	Tongda alloy material factory
ZVI6	spherical	1.0	grey	0.74	99.99	Tongda alloy material factory
ZVI7	spherical	1.5	grey	0.50	99.99	Tongda alloy material factory
ZVI8	spherical	2.0	grey	0.39	99.99	Tongda alloy material factory

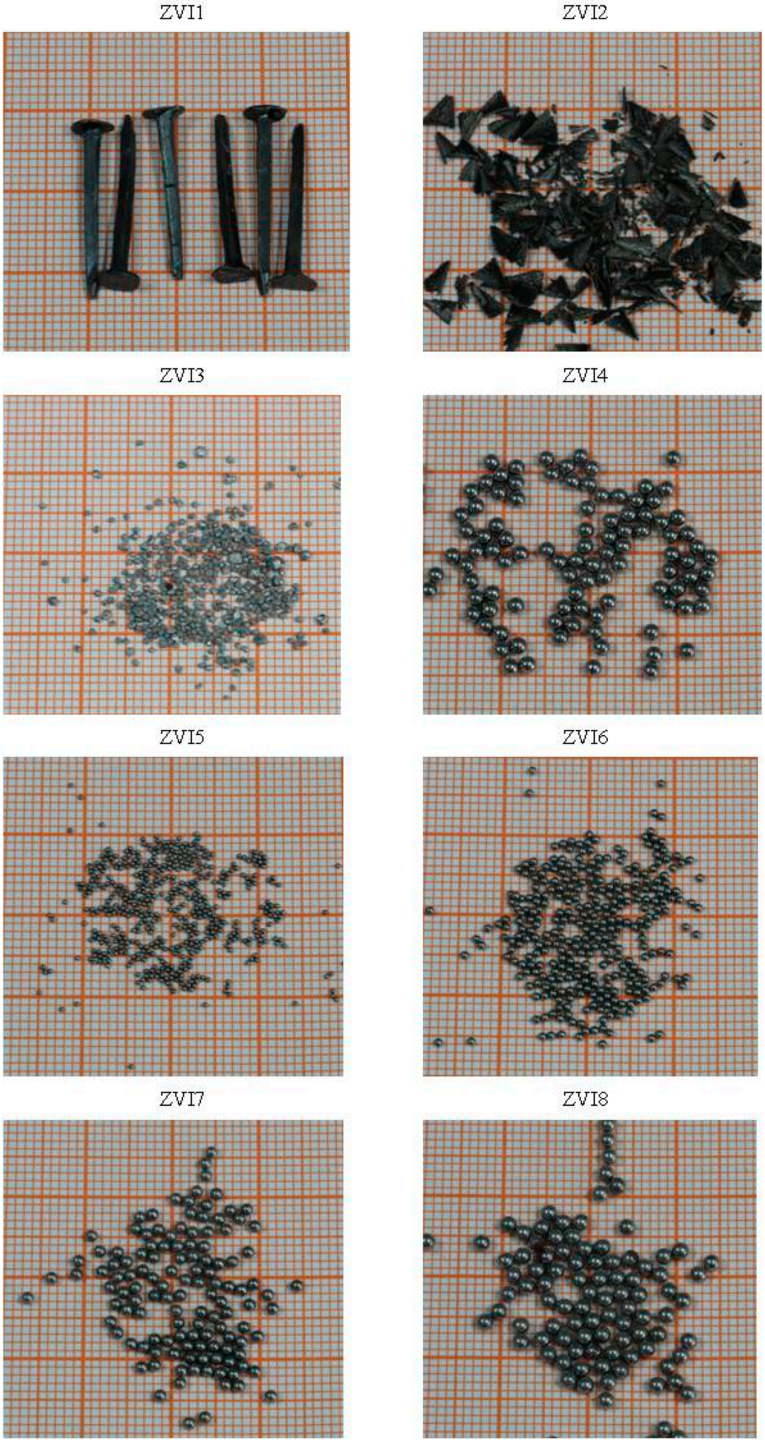


Figure 1. Photographs of the eight tested metallic iron materials. Apart from iron nails (ZVI1), 500 mg of each material was put on a graph paper. Distances of lines in the background are 1 mm in vertical and horizontal directions.

2.3. Experimental Procedure

Iron dissolution experiments were conducted in triplicate using 0.10 g of each Fe^0 in 50 mL of the complexing agent (2 mM Phen or 2 mM EDTA) for up to 10 days. Experiments were performed with the conventional quiescent experimental protocol for the both the EDTA and Phen tests [40]. The experimental vessels were protected from direct sunlight and atmospheric dust. For the EDTA test with ZVI5 through ZVI8 (4 specimens), parallel experiments with as received and H_2O washed materials were performed. Washing with H_2O entailed immersing weighed materials overnight in tap water [14]. After washing, the Fe^0 material was separated from any visible particles and the EDTA or Phen solution immediately added ($t_0 = 0$). Each experiment was performed in triplicate and average results are presented.

2.4. Analytical Method

The aqueous iron concentration was determined with a 752 UV/VIS Spectrophotometer (automatic) (Shanghai Jing Hua Technology Instrument Co., LTD), at a wavelength of 510 nm using a 1 cm cuvette. The instrument was calibrated for iron concentration ≤ 10 mgL^{-1}. All samples were reduced to Fe^{II} before complexation using ascorbic acid as discussed elsewhere [14].

2.5. Expression of Results

Given that iron dissolution (from Fe^0 and FeCPs) is initially a linear function of the time [38], for a certain time ($t_1 > t_0$) after the initiation of the experiment (t_0), the total iron concentration ($[Fe]_t$) as defined in Equation (1) is a linear function (of time).

$$[Fe]_t = a \times t + b \tag{1}$$

Therefore, the goal of this study is to identify the timeframe for the linearity of Equation (1). The regression coefficients (a and b) are characteristic for each individual Fe^0 specimen. In fact, "a" is the rate of Fe dissolution from Fe^0 while "b" gives an estimation of the amount of FeCPs on the material or the fraction thereof that is dissolved by the used complexing agent (here EDTA and Phen). It is recalled that Phen dissolves only Fe^{II} species. Accordingly, lower 'b' values are expected in Phen tests. The 'a' (mg L^{-1} h^{-1}) and 'b' (mg L^{-1}) values derived from Eq. 1 are related to the used 50 mL (factor 1/20) of working solution and converted to μg h^{-1} and μg respectively. The dissolution rates ('a' values, k_{EDTA} and k_{Phen}) were calculated using the Origin Package (Version 8.0).

3. Results and Discussion

3.1. Suitability of the Experimental Protocol

Figure 2 compares dissolved iron concentration from ZVI3 in EDTA and Phen as a function of the time. It is evident that in both cases, iron dissolution is initially a linear function of time. This linearity is observed for the first 80 h in EDTA and the first 100 h for Phen. After this initial step, the [Fe] value still continually increases but at a much lower rate. The increase of [Fe] values from hour 5 to hour 96 was 6.0 to 54.0 and 1.0 to 29.0 in EDTA and Phen systems, respectively. [Fe] values at the end of the experiment (hour 250) were 73.0 and 41.0 for the EDTA and Phen systems, respectively. This means that, under the same experimental conditions, almost twice more iron is dissolved in EDTA than in Phen. The idea behind both methods is that the slope of the initial line is a characteristic of each material [40]. The suitability of both tests is comparatively discussed.

Using a 2 mM EDTA solution and assuming a 1:1 complexation with Fe suppose that the solution is saturated when the [Fe] value is 112 mg L^{-1} (2 mM). This value was not achieved, indicating a rather slow kinetics of iron dissolution from ZVI3 in both solutions. The experimental vessels were not homogenized (e.g. agitated or stirred) to let mass transfer in the bulk solution be rate-limiting [42]. Hence, the data in Figure 2 indicate the differential occurrence of oxidative iron dissolution as impacted by EDTA and Phen. With respect to stoichiometry, the Phen solution contains only 1/3 of the required amounts, but the extent of iron dissolution was lesser than in EDTA [36], confirming that intrinsic properties could be addressed using 2 mM of both complexing agents [36,39].

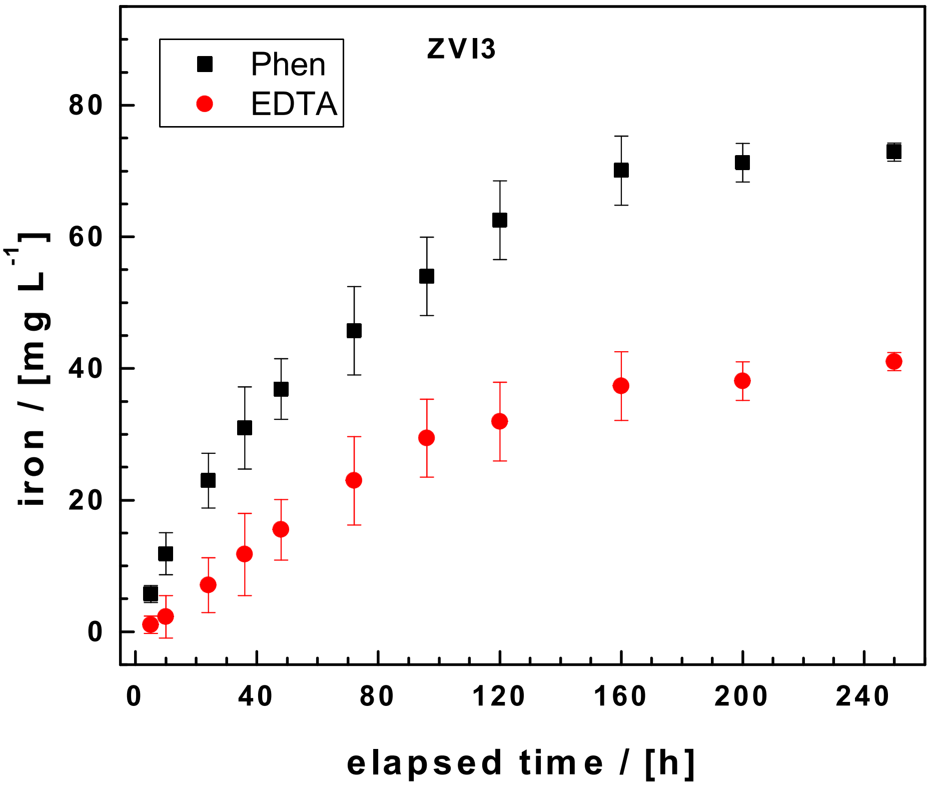


Figure 2. Iron dissolution from ZVI3 by 2 mM EDTA and 2 mM Phen under quiescent conditions for 10 days (250 h). Error bars denote the standard error for triplicate experimental results. Experimental conditions: V = 50 mL, m_{ZVI} = 0.1 g.

Iron corrosion by water (Equation (2)) is the continuous source of dissolved iron under the experimental conditions. At the end of the experiment, Fe^0 is not exhausted and the solution is not saturated. This is an ideal situation to assess the intrinsic reactivity of several materials as some could be more reactive than ZVI3 (and others less). The fundamental reasons for the differential behavior of a Fe^0 in EDTA and Phen are addressed herein.

$$Fe^0 + 2\,H^+ \Rightarrow Fe^{2+} + H_2 \tag{2}$$

$$4\,Fe^{2+} + O_2 + 4\,H^+ \Rightarrow 4\,Fe^{3+} + 2\,H_2O \tag{3}$$

In EDTA solutions, Fe^{II} species from Equation (2) is rapidly oxidized by dissolved oxygen (O_2) (Equation (3)) to Fe^{III} as Fe^{III}-EDTA complexes are far more stable than Fe^{II}-EDTA [39,44,47]. The same extreme stability of Fe^{III}-EDTA also explains the dissolution of Fe^{III}-oxides. Thus, in the EDTA system, increased [Fe] values result from intensified iron corrosion and (partial) dissolution of FeCPs.

On the contrary, in Phen solutions, Fe^{II} species from Equation (2) is strongly complexed by Phen and any further oxidation (Equation (3)) is blocked [45,47]. On the other hand, Fe^{III} species in atmospheric FeCPs are not dissolved by Phen. Atmospheric FeCPs are FeCPs formed at Fe^0/atmosphere interface before immersion. This evidence accounts for the observed huge difference of [Fe] values in both systems. Clearly, in the Phen system, forward oxidative Fe^0 dissolution is addressed and is not disturbed by dissolved O_2 (Equation (3)). This makes the Phen test more suitable than the EDTA test for characterizing the Fe^0 intrinsic reactivity under ambient (oxic) conditions.

3.2. The EDTA Test

Figure 3a summarizes the time-dependent changes of the dissolved iron concentration as a function of time for ZVI2, ZVI7, and ZVI8. It is seen that ZVI2 is the most reactive of the three materials.

The linearity of [Fe] as a function of time (t) is observed only for t < 80 h (n = 7). For the two other materials, the linearity is observed through the end of the experiment (n = 11). The k_{EDTA} values are displayed in Table 3 and vary in increasing order from 11.4 μg h^{-1} for ZVI4 to 27.8 μg h^{-1} for ZVI1. The overall increasing order of reactivity based on the k_{EDTA} values is: ZVI4 < ZVI8 < ZVI7 < ZVI6 < ZVI5 < ZVI3 < ZVI2 < ZVI1.

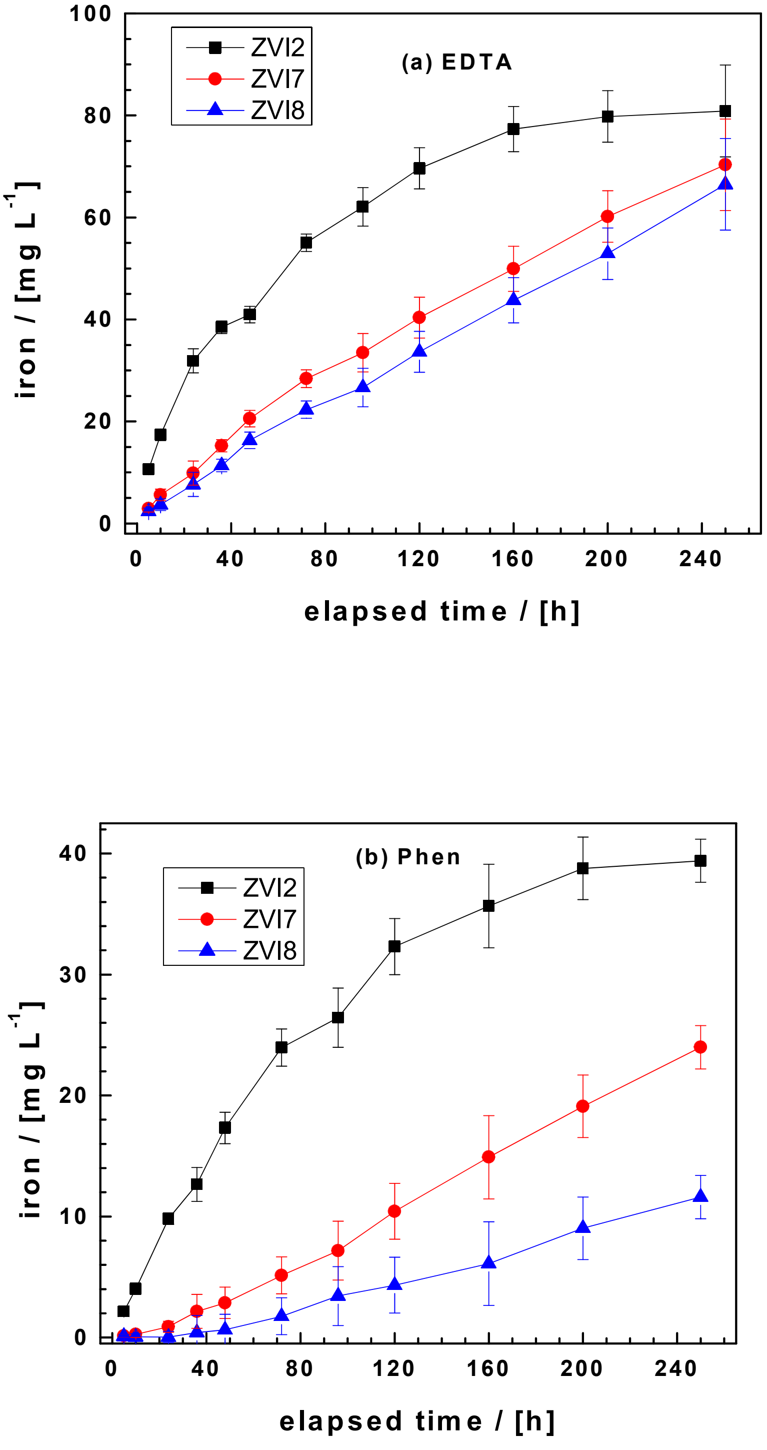
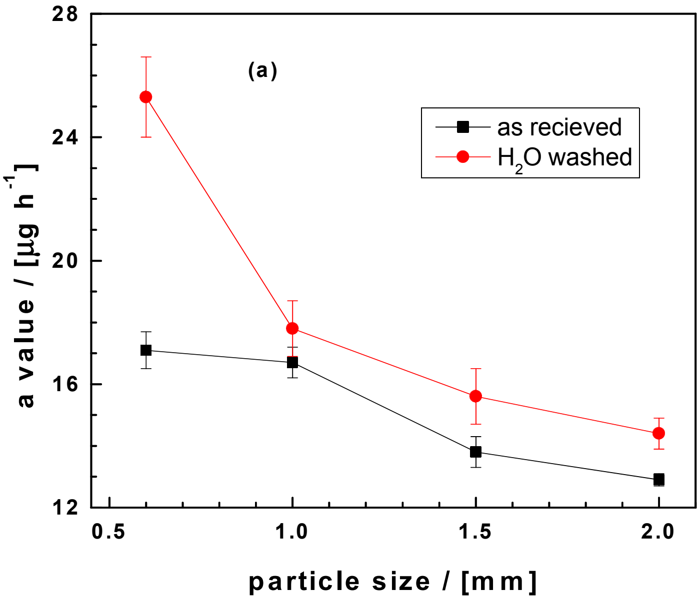


Figure 3. Iron dissolution from ZVI2, ZVI7, and ZVI8 by 2 mM EDTA and 2 mM Phen under quiescent conditions for 10 days (250 h). The three samples are representative of the tested materials. Error bars denote the standard error for triplicate experimental results. Experimental conditions: V = 50 mL, m_{ZVI} = 0.1 g.

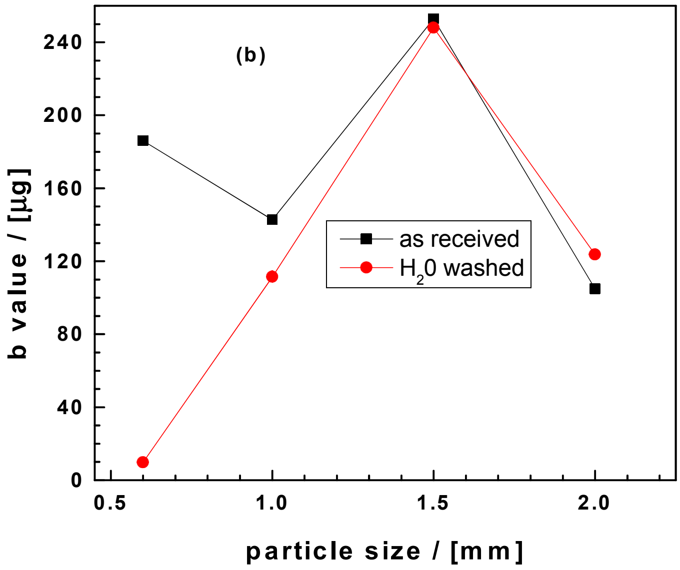
Table 3. Corresponding correlation parameters (a, b, R^2) for the 8 metallic iron materials. As a rule, the more reactive material is under given conditions the larger the 'a' value. Within the text, 'a' values are termed as k_{EDTA} and k_{Phen} for EDTA and Phen, respectively. General conditions: initial EDTA and Phen concentration 2 mM, room temperature 23 ± 2 C, and Fe^0 mass loading 2 g L^{-1}. 'a', 'b' and R^2 values were calculated using Origin 8.0. n is the number of experimental points used to obtain $R^2 > 0.9$.

Fe^0	**a**	**Δa**	**b**	**Δb**	**n**	**R^2**
	(µg/h)	**(µg/h)**	**(µg)**	**(µg)**	**(-)**	**(-)**
			EDTA			
ZVI1	27.8	1.2	88.2	60.1	7	0.990
ZVI2	27.3	2.9	697.1	149.5	7	0.936
ZVI3	25.8	2.5	413.7	127.6	7	0.947
ZVI4	11.4	0.2	136.8	29.9	11	0.994
ZVI5	17.1	0.6	186.0	60.4	7	0.989
ZVI6	16.7	0.5	142.7	44.1	9	0.992
ZVI7	13.8	0.5	252.9	61.0	11	0.987
ZVI8	12.9	0.2	104.9	24.2	11	0.990
			EDTA, H_2O washed			
ZVI5	25.3	1.3	9.8	67.4	7	0.984
ZVI6	17.8	0.9	111.4	70.2	9	0.981
ZVI7	15.6	0.9	248.0	114.6	11	0.965
ZVI8	14.4	0.5	123.6	61.1	11	0.990
			Phen			
ZVI1	7.1	0.1	−72.4	14.0	11	0.997
ZVI2	12.9	0.9	138.8	55.3	8	0.970
ZVI3	15.9	0.3	−17.5	19.5	7	0.997
ZVI4	3.5	0.2	−70.6	21.1	11	0.976
ZVI5	6.8	0.3	−37.6	30.6	11	0.986
ZVI6	5.8	0.2	−64.5	18.2	11	0.993
ZVI7	5.0	0.1	−70.8	15.2	11	0.994
ZVI8	2.4	0.1	−55.1	14.0	11	0.978

To the best of the authors' knowledge, none of the used Fe^0 samples has ever been characterized using the EDTA test. Btatkeu-K et al. [16] reported k_{EDTA} values for ten granular materials varying from 11.0 to 37.0 µg h^{-1}. In particular, the iPutec sample that has been largely used in Europe, depicted a k_{EDTA} value of 24.1 µg h^{-1}, suggesting that the Fe^0 specimens tested herein are potential candidate materials for the water treatment industry. As concerning the 'b' values (Table 3), those of the ten samples characterized by Btatkeu-K et al. [16] varied from 65 to 1780 µg. All the ten samples were visibly covered with atmospheric FeCPs. On the contrary, all samples tested herein were not visibly covered by FeCPs and were still depicting their metallic glaze even at the end of the experiment. Accordingly, lower 'b' values (105 µg for ZVI8 to 697 µg for ZVI3) were obtained. As expected, H_2O pre-washing Fe^0 increased k_{EDTA} values (Figure 4a), but decreased 'b' values (Figure 4b). The lack of a monotonous trend in changes of 'b' values by pre-washing is explained by disturbances induced by dissolved O_2 and/or fines from atmospheric corrosion. The Phen test was introduced to address these issues [39].



(**a**)



(**b**)

Figure 4. Changes of the regression parameters (**a**,**b**) for the EDTA test for four Fe^0 samples as influenced by pre-washing in tap water for 14 h. The selected samples (ZVI5 through ZVI8) are represented by their mean particle size (Table 1). Error bars denote the standard error for triplicate experimental results. Experimental conditions: V = 50 mL, m_{ZVI} = 0.1 g. The lines are not fitting functions, they simply connect points to facilitate visualization.

3.3. The Phen Test

Figure 3b summarizes the results of [Fe] as a function of time (t) for the same three materials as in Section 3.2 (ZVI2, ZVI7, and ZVI8). It is obvious that the maximal iron concentration is only about 40 mg L^{-1} for Phen test against 80 mg L^{-1} for the EDTA test. ZVI2 is the most reactive material of the three presented. The number of experimental points for linearity (n) is the same as for the EDTA test.

Table 3 summarizes the k_{Phen} values for the eight samples. They vary in increasing order from 2.4 µg h^{-1} for ZVI8 to 15.9 µg h^{-1} for ZVI3. The overall increasing order of reactivity after the k_{Phen} value is: ZVI8 < ZVI4 < ZVI7 < ZVI6 < ZVI5 < ZVI1 < ZVI2 < ZVI3. Apart from ZVI2, all other specimens depicted negative 'b' values, which actually have no physical meaning, except that atmospheric FeCPs are not disturbing the Phen test. On the other hand, the k_{Phen} values are constantly lower than the k_{EDTA} values. The ratio k_{EDTA}/k_{Phen} varies from 1.6 for ZVI3 to 5.3 for ZVI8. The overall results suggest that the test could be stopped after four days, Table 3 shows the number (n) of experimental points that were necessary to obtain linearity with $R^2 > 0.90$. n values ranged from 7 to 11. n = 11 corresponds to the least reactive materials, including ZVI4 and ZVI8 which are the same material in two different batches.

3.4. Method Validation

The H_2 evolution test [48,49] and the EDTA test [40] examine their reliability by comparing the extent of H_2 evolution and Fe dissolution to that of contaminant reductive transformation by the same materials. Btatkeu-K et al. [16] argued that, in the absence of a standard reference Fe^0 material, a real comparison of independent results is challenging. The other two tests (Fe^{III} and tri-iodide) examined their reliability by using various Fe^0 specimens and the respective probe solution [19,20] (Table 1). For example, to validate the Fe^{III}-test, Li et al. [20] used 15 Fe^0 from different sources with sizes ranging from nanometers to centimeters. As already discussed herein (Section 3.1), these two tests suffer from their inherent design considering Fe^0 as the reducing agent for the probe substance (Fe^{III} and/or tri-iodide). Surprisingly, both tests have not considered the EDTA test in their presentation despite being available for a decade [40]. Again, the EDTA test assesses the Fe^0 intrinsic reactivity by considering water (the solvent) as the oxidizing agent (Equation (2)). The EDTA test has been validated in a similar way like all other tests by comparing the observed order of the reactivity to the extent of U^{VI} removal [40] or methylene blue discoloration [16]. Moreover, the EDTA test was extended to the EDTA method and used to characterize the impact of various operating parameters on the efficiency of the Fe^0/H_2O system [14,42,43]. The Phen test is an extension of the EDTA test [39].

Applying the same experimental conditions ($[Fe^0] = 5$ g L^{-1}, V = 50 mL) to eight Fe^0 specimens, a comparative discussion of the intrinsic reactivity of individual materials has been achieved (Section 3.1 through Section 3.2). The Phen test was 'validated' by using key information from the supplier: (i) the particle size (mm), and (ii) the specific surface area (m^2 g^{-1}). Figure 4 compares 'a' values for both EDTA and Phen as a function of the Fe^0 particle size (Figure 4a) and the Fe^0 specific surface area (Figure 4b). Figure 5 further shows that for the same material $k_{EDTA} > k_{Phen}$ (Section 1). Figure 5a shows no monotonous decrease of a values with an increasing particle size as theoretically expected [50]. This corresponds to the observations of the past 30 years that the particle size alone is not enough to assess the reactivity of a Fe^0 specimen [6,17,31,51]. The results in Figure 5b conveys the same message as the particle size is directly related to the specific surface area [50]. In other words, just like the EDTA test, the Phen test is a powerful tool to characterize the reactivity of Fe^0 materials. The additional value of the Phen test is that it is not disturbed by the presence of dissolved oxygen.

Lastly, the following procedure for the proposed standardized Phen test is suggested: (i) equilibrate 0.1 g Fe^0 in 50 mL Phen (Fe^0 loading: 5.0 g L−1) at room temperature for four days (96 h), (ii) avoid fixing the pH value of the solution, (iii) during assaying, collect samples for iron determination approximately after 6, 12, 24, 26, 48, 72, and 96 h, (iv) plot [Fe] versus elapsed time and used the linear part to derive k_{Phen} values. As a matter of fact, this suggestion can be improved in a concerted effort and be developed to a standard test. It is also possible to adopt what could be termed a 'Phen index', which could characterize the extent of iron (0.1 g) dissolution in a 2 mM Phen solution for 24 or 48 h. A significant body of data is needed on k_{Phen} for many Fe^0 materials, including those already used in field applications to fine-tune the criteria for a standard test. On the other hand, it would be interesting to perform long-term parallel dynamic 'leaching' experiments [14] to deepen the information gained herein.

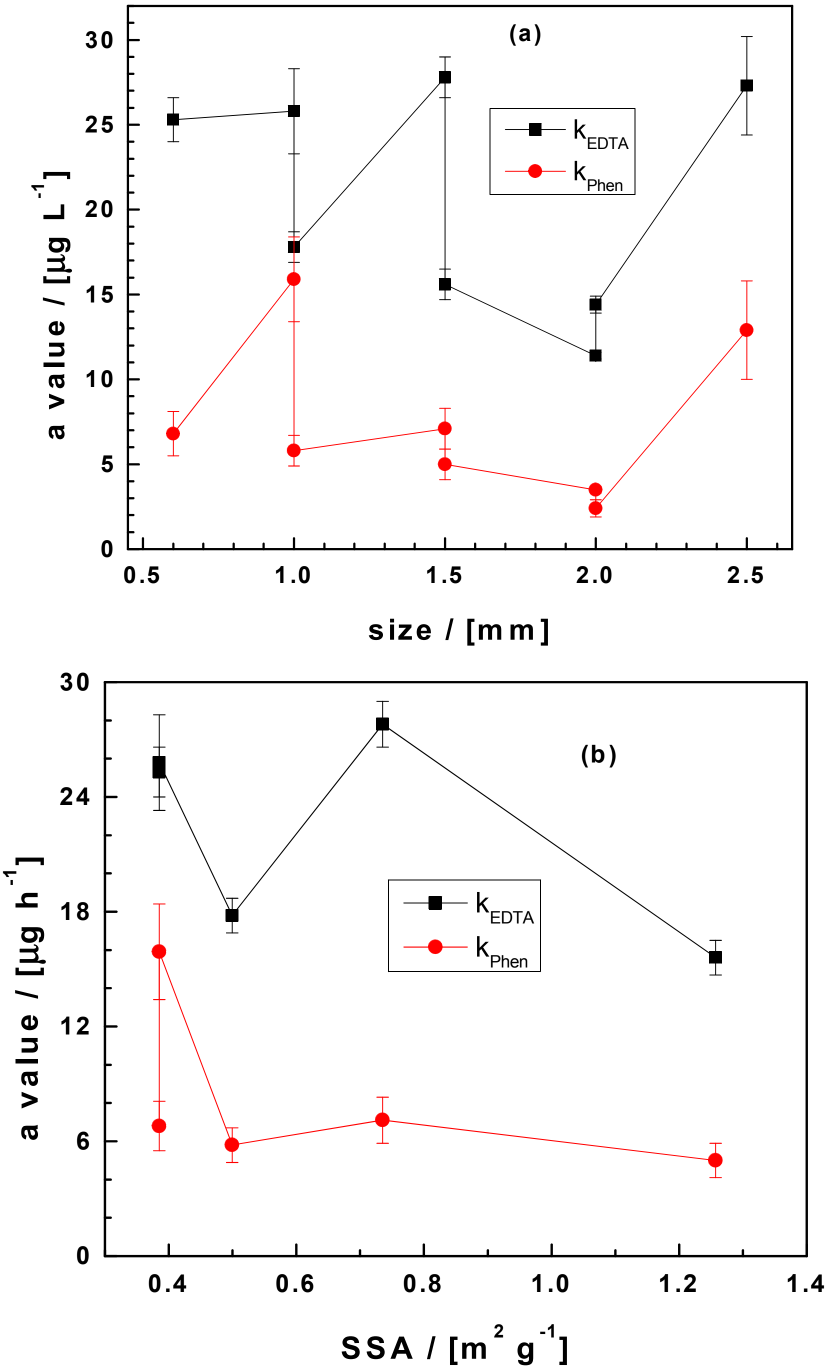


Figure 5. Changes of the 'a' value for both EDTA and Phen tests as influenced by: (**a**) the particle size, and (**b**) the specific surface area (SSA). Each sample is represented by its mean particle size or it is SSA (Table 1). Error bars denote the standard error for triplicate experimental results. Experimental conditions: V = 50 mL, m_{ZVI} = 0.1 g. The lines are not fitting functions, they simply connect points to facilitate visualization.

3.5. Significance of the Results

The present work aims at improving the understanding of the Fe^0/decontamination relationships which is essential to design efficient and sustainable remediation systems. Previous efforts, aiming at a complete physical Fe^0 characterization (surface chemistry, textural characterization) and extent of decontamination were proven less useful [6,14,17]. The rationale, therefore, is that adsorbents (FeCPs) are generated in-situ and transformed into a highly dynamic process [12,13,52–54]. For example, the point of zero charges or the specific surface area of individual iron oxides and hydroxides are different [55], and their relative amounts in a Fe^0/H_2O system is not known as a rule [56]. This inherent dynamism makes an accurate detailed characterization of the remediation system at any time very challenging. On the contrary, using pure adsorbents (e.g. activated carbon, bone char) as the starting materials, it suffices to characterize the porous texture, the nature of surface groups and their amount to predict the adsorption process [9,57]. Therefore, the characterization of Fe^0 dissolution is crucial for understanding the decontamination process, and thus properly design new remediation systems. It is also important to select Fe^0 materials with controlled properties.

There is still a controversial discussion in the literature on whether the Fe^0/H_2O system is an adsorbing or a reducing system [4,5,13], Fortunately, there is agreement on that Fe^0 is constantly shielded by an oxide-scale, possibly passivating the system (reactivity loss) [2,4]. Oxide-scale and contaminant reductive transformation both result from Fe^0 oxidative dissolution such that characterizing Fe^0 dissolution is a tool to assess Fe^0 intrinsic reactivity [40,41]. Fe^0 oxidative dissolution generates H_2 and Fe^{2+} (Equation (2)). Under ambient (oxic) conditions, Fe^{II} is further oxidized to very low soluble Fe^{III} species. The present work has used EDTA and Phen to delay the precipitation of Fe^{II}/Fe^{III} species for up to ten days. The results clearly show (Section 3.1) that the Phen test is not disturbed by dissolved O_2 and less sensitive to the presence of atmospheric FeCPs [39].

In essence, the Phen test is only comparable to the EDTA and is already discussed herein. The tri-iodide (I_3^-) test [19] and the Fe^{III} test [20] basically use an additive to induce Fe^0 corrosion, like hundreds of other works in the scientific literature [6,17]. On the contrary, the EDTA test and the Phen test characterize iron corrosion by water (Equation (2)). Another test using Eq. 2 is H_2 evolution introduced by Reardon [48,49] and independently considered by some research groups as discussed by Hu et al. [14]. However, the H_2 test needs longer experimental duration and larger Fe^0 amounts. Additionally, the experimental design to capture (and quantify) the generated H_2 can be regarded as complex and eventually not readily available in poorly equipped laboratories. On the contrary, the Phen test uses one single chemical and 0.3 g of each Fe^0 (triplicate a 0.1 g) in experiments using glass beakers and lasting for just 4 days. Iron determination can be undertaken by any available method. Therefore, the Phen test is an affordable, easy, reliable and reproducible method for characterizing Fe^0 reactivity for water treatment. These advantages make the Phen test a potential candidate for a standard Fe^0 characterization method.

4. Conclusions

This study has presented an affordable, easy, reliable, and reproducible method for routine characterization of the intrinsic reactivity of granular Fe^0 materials. The test uses 1,10 Phenanthroline to sustain iron corrosion by water. It is a further development of the EDTA test with the added advantage that no Fe^{III} species are produced nor dissolved in the system, thus nearly the forward oxidation of Fe^0 is quantified. The Phen test is regarded as a candidate rigorous protocol for standardization of methods for the routine characterization of the intrinsic reactivity of Fe^0 materials. Since Fe^0 is reactive under storage conditions, many of its properties may vary with time. Thus, the history of Fe^0, the particle size distribution and the time at which characterization is performed can significantly affect the extent of iron dissolution ([Fe] values). The protocol used herein suggests large variability (standard deviations from triplicates) for more reactive materials, exhibiting significant changes on relatively short time scales. Further efforts towards the establishment of unified standard protocols should carefully consider this variability as it could be more pronounced when different investigators and different ambient conditions are taken into consideration (e.g. inter-laboratories). Indeed, to be comparable, (Fe) data from Phen tests have to be collected precisely in the same manner, including the sample pre-treatment procedures. Given the extreme simplicity of the Phen test, it is even a candidate for automation. The way forward is the characterization of the full range of factors influencing the reliability and reproducibility of k_{Phen} values. Additional investigations focusing on developing or selecting a reference Fe^0 material will greatly improve comparability of independent data.

Author Contributions: R.H., X.C., M.X., P.Q., M.L., W.G. and C.N. contributed equally to manuscript compilation and revisions.

Funding: This work is supported by the Ministry of Science and Technology of China through the Program "Research on Mechanism of Groundwater Exploitation and Seawater Intrusion in Coastal Areas" (Project Code 20165037412) and by the Ministry of Education of China through "the Fundamental Research Funds for the Central Universities" (Project Code: 2015B29314). It is also supported by Jiangsu Provincial Department of Education (Project Code 2016B1203503) and Postgraduate Research & Practice Innovation Program of Jiangsu Province (Project Code: SJKY19_0519, 2019B60214).

Acknowledgments: The manuscript was improved thanks to the insightful comments of anonymous reviewers from Processes. We acknowledge support by the German Research Foundation and the Open Access Publication Funds of the Göttingen University.

Conflicts of Interest: The authors declare no conflict of interest.

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