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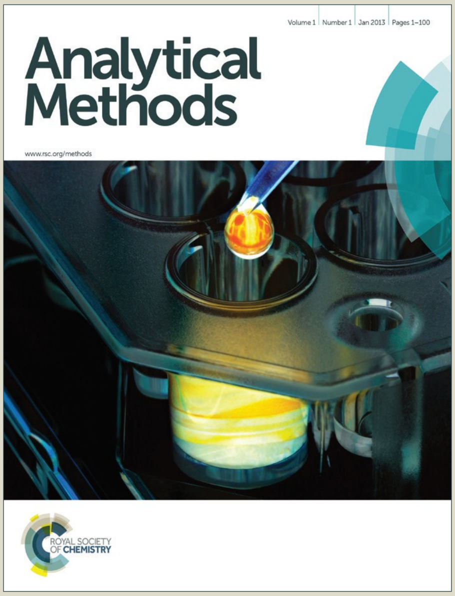

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A facile method for determining Fe(0) content and reactivity of zero valent iron

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Abstract

Zero valent iron (ZVI) is increasingly used in large quantities for water treatment. In large-scale application of ZVI, a common question that engineers encounter is ZVI selection or its quality assurance and quality control (QA/QC). A facile method for assessing ZVI quality is proposed and studied in this work. The method is based on Fe(III)-Fe(0) reaction that has fast reaction rate, known and simple stoichiometry, and easy-to-assay product. The method is conducted by mixing sample (e.g., testing ZVI) with concentrated Fe(III) solution (up to 3.0 g/L) for 3-4 hours. Metallic iron (Fe(0)) content of the sample is obtained by assaying the final increasing of total dissolved iron, and their reactivity are quantified using the observed dissolution rate constants. The method is experimentally validated using 23 iron-based materials. Studies with reference iron powder and iron oxide demonstrate that Fe(III) solution has satisfactory specificity in selecting Fe(0). Replicate experiments and *t*-tests evaluation show the complete dissolution of the Fe(0) content in micron-scale ZVI and the high reproducibility of the method for measuring Fe(0). The accuracy and reliability of the method are studied using 15 commercial ZVIs of known Fe(0) purity, in a series of experiments using Fe(III), Cu(II) or trichloroethylene. The experiments show that the results from the proposed method are accurate and reliable, and that the method is a strong tool more effective than conventional techniques such as X-ray diffraction and BET-N_2 adsorption. This work provides an easy and facile way for the quantitative assessment of the quality of metallic iron used for environmental clean-up, especially for the quick survey of large number of iron samples on site. The method may also serve as QA/QC procedure of ZVI in industrial-scale production.

1. Introduction

Zero valent iron (ZVI) is a solid reductant that is able to transform a wide array of recalcitrant and hazardous compounds, including chlorinated aliphatic hydrocarbons, chlorinated aromatics, nitro-aromatics, azo-dyes, carbon disulfides and heavy metals.[1-5] Owing to its low cost and environmentally-benign products (e.g., magnetite), ZVI is increasingly used in large quantity for groundwater remediation and industrial wastewater treatments.[1, 4-12] 900 tons of iron shaving were used in a single wastewater treatment plant in China,[13] and thousands kilos of ZVI nanoparticles (nZVI) may have been used in North America and Western Europe.[3, 4] The success of ZVI in large-scale application depends largely on ZVI quality, and demands a fast and reliable method for ZVI selection and its quality assurance and quality control (QA&QC).

ZVI family has a large number of iron materials, which are varied in size, shape, surface area, composition and are dissimilar in Fe(0) content and reactivity. Hundreds types of ZVIs and ZVI-embedded composites (e.g., with activate carbon, resin, clay and betonite) have been reported in the past two decades.[2, 3, 14-22] Iron has a large number of alloys, such as carbon/stainless steel and cast iron. These alloys may have different reducing power due to the difference in alloyed elements (e.g., C, Si, Cr, Ni or Ti).[16, 23-28] Iron shavings, by-products from metal cutting, often vary in size, shape and composition due to their difference in cutting methods and raw materials. Large disparities in Fe(0) purities and reactivity were observed among nZVIs synthesized via different routes, such as gas condensation, H_2 reduction or sodium borohydride reduction.[29-32] Metallic iron (Fe(0)) can be easily oxidized by water and O_2, resulting in the loss in Fe(0) content and reactivity, especially during long-term storage or shipping in large-scale application.

A common question that engineers encounter is the quick selection of high quality ZVI, or its QA&QC. Common techniques for ZVI characterization include scanning electron microscopy (SEM), BET-N_2 adsorption, X-ray diffraction (XRD), X-ray adsorption spectroscopy (XAS),[33] temperature programmed reduction (TPR)[30] and acid digestion,[14, 27, 34-36] which provide information on particle morphology, surface area and composition. However, these instruments are often not available on site and are not affordable for ordinary wastewater treatment plant, and require professional skills in operating or data analyses. More importantly, none of these methods provides quantitative results on ZVI reactivity.

ZVI reactions are mostly surface-mediated redox processes. ZVI reactivity has a complex cause-and-effect relationship with a number of physical properties of metallic iron, including surface area, Fe(0) content, crystallinity, composition and thickness of its oxide shell.[29, 36-38] Currently, the information from the ZVI supplier is basically physical properties, such as fabrication date, purity and particle size distribution. ZVI reactivity cannot be inferred directly from this information, and additional work is often required to determine reactivity. Various kinds of pollutants, such as trichloroethylene (TCE), 1,1,1,2-tetrachloroethane, methylene blue, nitrate and Cr(VI), were used as probing agent.[28, 37, 39, 40] As the chemistry of these probing reactions are inherently different and their rate constants vary as much as seven orders of magnitude,[41] these results provide limited guidance in the selection of ZVI from the large catalog of iron materials. Selecting probing agent is also controversial as hundreds of compounds could be reduced by ZVI. A standard probing reagent/method will facilitate the comparison and selection of ZVI materials.

In this work, we propose a facile method for the quick assessment of ZVI quality. The method is able to determine Fe(0) content and reactivity simultaneously. Twenty-three iron-based materials were used as testing agents for method validation. The precision and reproducibility of the method were studied with replicate tests. Its specificity, linearity and accuracy were examined using ZVIs with known purities. Results acquired using the proposed method were compared with those from conventional characterizations and then verified with experiments using model pollutants. The method offers an accurate and reliable way for the quantitative assessment of ZVI quality. The method is also time-saving, environmental friendly and simple in instrumentation. The work provides a reliable way to assess ZVI quality on site and for QA&QC in ZVI production. The method could also serve as standardization test for metallic iron used for water and wastewater treatment.

2. Experiment

2.1 Materials

Information of twenty-three iron-based materials used is provided in Table 1 and Figure 1. The high purity iron and iron oxides were purchased from Aladdin (Row A-E, Table 1). The commercial ZVIs (Row G-S, Table 1) were purchased from three different ZVI suppliers in China. nZVI (Row F) was synthesized via the reduction of ferric chloride ($FeCl_3$) using sodium borohydride ($NaBH_4$), following the procedure reported elsewhere.[42] Iron shaving (Row T) was from a mechanical cutting factory in Shanghai. $FeCl_3$ (99.9%, metal basis), $CuCl_2$ and TCE were from Aladdin, China. All materials were used as received.

Aged ZVIs (Row U-X) were prepared by mixing iron powder (400 mesh, Row E) with deionized water. Specifically, 200 g of fresh iron powder were mixed with 2-L DI water in four-necked flask at 200 rpm at extended periods (up to 12 days) at 30 °C. The flask was open to air and the samples were withdrawn at preset intervals, 1 d, 2 d, 10 d, 12 d, respectively. The samples were centrifuged; solid particles recovered were rinsed using ethyl alcohol 4 times and then kept in vacuum drier prior to analyses.

2.2 Experiment setup

Fe(III) solution were prepared using $FeCl_3$ (AR) and DI water. The experiments were conducted in 4-necked flask (Figure 2), which was placed at a water-bath set at 30 °C. The flask was agitated using a mixer at 600 rpm and purged with nitrogen throughout experiment. After ZVI addition, 10.0-ml solution samples were taken each time at the pre-determined intervals. Samples were filtered using 0.45-μm membrane filter (Millipore), diluted using DI water prior to analyses. Dissolved iron was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES Agilent 720ES). Calibration curve of ICP measurement covered a detection range of 0.5-20 mg/L, with the square of correlation co-efficiency (R^2) greater than 0.9996. The relative standard deviation (RSD) of ICP measurement is ~0.16% of measuring samples containing ~15 mg/L Fe(III).

2.3 Characterizations and analytic methods

ZVI samples were characterized using BET-N_2 adsorption, scanning electron microscope (SEM) and X-ray diffraction (XRD) respectively. BET-N_2 adsorptions were conducted using Micrometric 2010. Particle size and morphology were analyzed using

SEM (XL30, Holland Philips Corporation). Sample compositions were characterized using powder X-ray diffraction (XRD, D8 ADVANCE, Japan) equipped with a Rigaku diffraction meter and mono-chromatized Cu-K radiation. Diffractions were recorded from 10° to 80° with a step size of 0.01° and a count time of 0.07 s per step.

The oxidation-reduction potential (ORP) of ZVI slurry was measured using an experiment setup similar to Figure 2. Specifically, one gram ZVI were mixed with 1-L DI water in four-necked flask and solution ORP was obtained using an Ag/AgCl reference electrode fit into the ports. DI water was deoxygenated using nitrogen prior to use, and the solution in flask was purged with nitrogen during experiment. More information of Cu(II) and TCE experiments can be found elsewhere in our publications.[32, 43, 44]

3. Results and discussion

3.1 Characterization using XRD and SEM

Table 1 lists the information of twenty-three iron-based materials used in this work. The sizes of these samples range from nanometers to centimeters (Figure 1), and their Fe(0) purities range from 0 to 98%. We selected pure iron/iron oxide from chemical reagent supplier (Row A-E, Table 1), commercial iron powder from ZVI manufacturers (G-S), and iron shaving from a cutting factory in Shanghai (Row T). Aged ZVI and nZVI were lab-made (Row F, U-X).

The samples were first characterized using BET-N_2 adsorption, X-ray diffraction (XRD) and scanning electron microscope (SEM). ORPs of ZVI slurries were also measured to probe their reactivity. The results are presented in Table 1, Figure 1 and Figure S1.

These characterizations provide limited and insufficient information on ZVI quality. For example, XRD patterns (Figure S1) of most ZVIs are quite similar, all with Fe(0) peaks at the same place (e.g., 44.6°), in spite that they have a maximum 10% difference on Fe(0) purity (Table 1, D-S). SEM is not able to distinguish between iron and iron oxides. The particle morphology of (aged) ZVIs and iron oxide are quite similar in SEM images (Figure 1A-B, U-X). In brief, none of these techniques, alone or in combination, provides quantitative information about ZVI quality.

3.2 Fe(III) method

3.2.1 Principle

The proposed method for assaying Fe(0) and reactivity is based on the Fe(III)-Fe(0) reaction (Eq.1). The reason of selecting Fe(III) for the assay include:

1. The Fe(III)-Fe(0) reaction has a simple and known stoichiometry. In comparison, most other ZVI-pollutant reactions, such as those with chlorinated ethenes, have multiple intermediates and complex stoichiometry[45] that complicate mass-balance or quantitative analysis (Eq. 2)

$$2Fe^{3+}\,(l) + Fe^{0}\,(s) = 3\,Fe^{2+}\,(l) \qquad (1)$$

$$a\,Fe^{0} + TCE + (2a-b)\,H^{+} \rightarrow \text{products} + a\,Fe^{2+} + b\,Cl^{-} \qquad (2)$$

2. The reaction product (Fe(II)) is in dissolved form. The ferrous ion can be readily measured using ordinary spectrophotometer that is available in ordinary lab or wastewater treatment plant. The soluble Fe(II) also avoids the cementation of ZVI surface by reaction products. In comparison, other ZVI reactions, such as those with Cr(V), produce insoluble products that form a passive layer on ZVI surface (Eq. 3)[46-48].

$$2Fe^0(s) + 2H_2CrO_4 + 3H_2O \rightarrow 3(Cr_{0.67}Fe_{0.33})\,(OH)_3(s) + FeOOH\ (s) \quad (3)$$

3. The reaction has fast reaction rate, which reduce the time for the complete depletion of Fe(0) content in ZVI materials. As discussed below, the reaction rate of Fe(0) in Fe(III) solution is hundred times faster than that with TCE.

3.2.2 Feasibility of assessing ZVI quality

Feasibility of this Fe(III) method was first examined using standard reference materials with known purities (Row A-E, Table 1). The reference ZVI material was a high-purity ZVI powder (400-mesh, >98.0% Fe(0), wt) from lab reagent supplier (Aladdin, China). Three iron oxides powder (Row A-C, wt>99%), namely magnetite (Fe_3O_4), iron oxide (Fe_2O_3) and FeOOH, were also used to study the method specificity, as they are the most common impurities in ZVIs.[33, 35, 39]

ZVI dissolution and Fe(0) specificity

Figure 3a presents the dissolution of reference ZVI at five dosages in Fe(III) solution. The initial concentration of Fe(III) in the solution were 0.30, 1.50, 2.00, 2.50, 3.00 g-Fe(III)/L, for the ZVI dosages of 0.050, 0.250, 0.500, 0.750 and 1.000 g/L respectively, giving Fe(III)/ZVI ratios between 3:1~6:1. Solution pH was not adjusted. pH of the Fe(III) solutions was in narrow range of 1.8-2.4 as a result of Fe(III) hydrolysis.

Total dissolved iron in the solution increased quickly in the first few minutes (Figure 3a), indicating the rapid dissolution of metallic iron (Fe(0)). In less than 60 min, the increasing of total dissolved iron (C_3-C_0) approached the amounts of Fe(0) dosed into the solution, which are denoted by the dash lines and *theoretical value* in Figure 3a. Nearly 100% dissolution of Fe(0) content was observed after 4-hour reaction. The

Fe(III) solution remained acidic after reaction (pH=2.4-2.7) due to the excessive amount of Fe(III) used. For iron (hydro)oxides, the concentration of dissolved iron remained the same after hours of mixing, indicating that these oxides were insoluble in Fe(III) solution. Results suggested that the solution was able to differentiate Fe(0) from these common impurities in ZVIs.

Reproducibility and accuracy

Five replicate experiments were performed at each ZVI dosage (Figure 3b). The final increasing in total dissolved iron were 0.249 ± 0.005, 0.487 ± 0.011, 0.750 ± 0.017, 0.999 ± 0.017 g/L for ZVI dosages of 0.250, 0.500, 0.750, 1.000 g/L respectively.

1. The relative standard deviations (RSD) of the final increasing are all less than 2.5%, indicating satisfactory reproducibility of the results.

2. To find out whether the final increasing in dissolved iron agree with the amount of Fe(0) dosed, we evaluate the results following *t*-test procedure[49]:

$$t_{calculated} = \frac{\left|\bar{x} - known\ value\right|}{s}\sqrt{n} \quad (4)$$

where s is the measured standard deviation;

n is the number of replicate tests;

$\bar{x}$ is the average of the final increasing in total dissolved iron;

Known value is the Fe(0) content of the dosed ZVI.

The $t_{calculated}$ are compared with the t values at 95% confidence level at *Student's t-distribution*[49]. Because the $t_{calculated}$, 1.79, 0.70, 1.91 and 2.50, are all less than the t_{table} (2.78)[49], the increasing of total dissolved iron agrees well with the amount of Fe(0) dosed, indicating that all the Fe(0) contents in the ZVI samples were dissolved after reaction. The Fe(III) dissolution method thus has satisfactory accuracy in measuring

Fe(0) content of ZVIs.

Complete dissolution of reference ZVI

A calibration line was then plotted via the method of least squares (Figure 3b). The line shows perfect fit between the dosed ZVI and the final increasing in total dissolved iron (C_3-C_0), with the square of correlation co-efficiency (R^2) greater than 0.998. The magnitude of the line slope (1.01) is close to the known purity (>98%), providing additional evidence that the Fe(0) contents in samples are completely dissolved.

As the oxide impurities are inert and the Fe(0) contents in the ZVI samples are completely dissolved, its Fe(0) content (M) and purity (P) then can be calculated using the increasing of total dissolved iron (C_3 or C_{3t}),

$$\text{M (Fe(0), g)} = (C_3 - C_0) \times \text{V} \tag{5}$$

$$\text{P (g-Fe(0)/g)} = \frac{(C_3 - C_0) \times V}{M_0} \tag{6}$$

Experiments below show that most micron-scale ZVIs are dissolved completely at experimental conditions. The fast and complete dissolution benefited from some unique characteristics of Fe(III)-Fe(0) reaction.

1. Instead of cementing on ZVI surface and encapsulating the remaining Fe(0), the reaction product (Fe(II)) is highly soluble in water (e.g., the solubility of $FeCl_2$: 625 g/1000 g water at 20 °C). Fe(0) content embedded in the core zone is then accessible for reaction.

2. Fe(II) is able to depassivate the oxide shell of ZVI by increasing corrosion current

and decreasing polarization resistance.[50, 51]

3. The difference of standard potential between Fe(III)/Fe(II) couple and Fe(II)/Fe(0) couple is fairly large (∆E=1.18 V), the reaction has large reaction rate.

These characteristics allow the quick consumption of Fe(0) embedded in the core zone and make Fe(III) an idea analyte to probe Fe(0). In comparison, most other ZVI-pollutant reactions are not suitable for the assaying, due to the slow reaction rates or the formation of passive layer on ZVI surface.

Assessing reactivity

Figure 3c and 3d show the reaction of reference ZVI (400 mesh, Row E) at four different Fe(III) concentrations. The reaction rate (r) followed the first order of Fe(III) concentration (C_{1t}) well (Figure 3d), and can be expressed using the equation below.

$$r = -\frac{dC_t}{dt} = k_{Fe}C_{1t} \qquad (7)$$

$$\ln\frac{C_{1t}}{C_0} = -k_{Fe}t \qquad (8)$$

where C_{1t} is the Fe(III) concentration during reaction (mg/L);

k_{Fe} is the pseudo-first-order rate constant (min^{-1}).

The observed rate constants (k_{Fe}) are in a narrow range of 0.045-0.058 min^{-1} (Figure 3d). Because this Fe(III)-Fe(0) reaction is essentially a redox process as most other ZVI reactions, the observed reaction rate constant k_{Fe} could also serve to characterize ZVI reactivity. A number of experiments below provide evidence that k_{Fe} is reliable to quantify ZVI reactivity.

3.2.3 Suggested testing conditions

Standard testing conditions are then proposed for better comparison of the assay results.

1. ZVI dosage is suggested to be greater than 0.5 g/L, which will reduce the effects of random errors in sample weighing.
2. Solution pH of Fe(III) solution should not be adjusted, considering that the pH-adjusting regents (e.g., acid or NaOH) would react with ZVI or Fe(III) and bring errors to the measurement.
3. It is suggested that the initial Fe(III)/ZVI ratio be set at 3:1 to 6:1 for the fast dissolution of Fe(0) during assaying. The excessive amount of Fe(III) beyond the 2:1 ratio help to maintain fast dissolution rate throughout the test that shorten the dissolution time.

3.2.4 Method validation using commercial ZVIs

Reliability of measuring Fe(0)

Reliability of the method was examined using fifteen ZVIs with known Fe(0) purity (Row F-T, Table 1). The ZVIs are from five different sources, and their sizes range from nanometers to centimeters. According to the information from the vendor, the ZVIs have 4-15% difference in Fe(0) purities (Table 1). The same experimental condition was applied for better comparison of the results. Specifically, the ZVI dosages were 0.5 g/L and Fe(III)/Fe(0) ratios were kept at 4:1.The results are all summarized in Figure 4 and Table 1.

Figure 4a and 4b exemplify the dissolution processes of six ZVIs. Distinctive differences are found between these ZVIs in dissolution rates and in the increasing of total dissolved iron (C_{3t}-C_0), indicating that the method is an effective tool in distinguishing ZVIs. Figure 4c compares the measured Fe(0) purities and the known purities from the supplier. For most samples, the measured purities agree well with the information from the vendor. For example, the measured purities of the five 3 000-mesh ZVIs (Row G-K) are in the range of 96-99% and their average (97.8%) is quite close to the known purity (98%). The measured content of nZVI is 85% (w/w), consistent with the results (78-83% Fe^0, wt) from advanced techniques such as temperature programmed reduction and X-ray adsorption spectroscope.[30, 33]

Mixed ZVI samples were also measured to probe the method reliability (Figure S2). The mixtures were prepared by mixing 0.100 g high-purity ZVI (400 mesh, Row E, 98%) with 0.500 g 3000-mesh ZVI (Row H, 98%) and 0.500 g nZVI (Row F, 85%) respectively. Five replicate tests were conducted for each mixture. The measured Fe(0) contents were 0.588 ± 0.003 and 0.521 ± 0.002 g respectively (Figure S2), corresponding to the known values of 0.586 g and 0.521 g Fe(0) in the mixtures. *t*-test evaluation (Eq. 4) of the measured Fe(0) suggested that $t_{calculated}$ (2.14 and 0.37) are less than the t_{table} (2.776), indicating that the measured Fe(0) agree well with the known Fe(0) content.

For millimeter-scale ZVI such as 20-mesh ZVI (Figure 4c), the measured Fe^0 purity (~72%) is lower than its known purity (88-92%), indicating the sample was not completely dissolved in 4-hour reaction. However, the measured purity is more significant than its real value. The measured purity is based on the proportion of Fe(0) that is accessible to the reaction. The Fe(III) solution is in a favorable condition for the complete reaction of Fe(0), owing to the entirely soluble product (Fe(II)) and the strong oxidative conditions (pH~2.2, ORP~720 mV) created by the concentrated Fe(III) (up to 3.0 g/L). Fe(0) content that is not accessible under such extreme condition would also not be available in real world scenarios, of which conditions are much milder.[29] In most other ZVI reactions, cementation of ZVI surface by insoluble products deteriorates this issue of material efficiency.[12] For example, the accessible proportion of Fe(0) for reaction are lower in large ZVIs than that of fine ZVI powder in Cu(II) experiments below.

Reliability of k_{Fe} in reactivity assessment

The pseudo-first-order rate constants (k_{Fe}) of the fifteen ZVIs were also acquired during the Fe(0) assaying (Table 1). The reliability of k_{Fe} for reactivity assessment was evaluated by comparing their particle sizes and by measuring the ORPs of pure ZVI-DI water slurry. Figure 4d shows the correlation of the obtained k_{Fe} and their particle sizes. Generally, k_{Fe} value grows as particle size decreases, which is consistent with the general assumption that the fine ZVIs are often more reactive. Figure 4e summarizes the obtained k_{Fe} and the corresponding ORP values. The ORP data were taken at 30 min after ZVI addition. The graph shows a general trend that the k_{Fe} value increases as ORP decreases. As lower ORP value of ZVI slurry implicates stronger reductive reactivity, the trend suggests that k_{Fe} is a reliable parameter to assess ZVI reactivity.

The Fe(III) method is a powerful tool more sensitive than measuring particle size or ORP. For example, the k_{Fe} of five 3000-mesh ZVIs have maximum difference of nearly 7 times (G-K, Table 1). These five ZVIs would otherwise be considered to possess similar reactivity, because the differences of their ORP values are minor and they are from the same source, of the same size and of the close specific surface area (Table 1).

3.2.5 Method validation using Cu(II) and TCE

Cu(II) removal capacity

The accuracy of the method for assaying Fe(0) was experimentally verified using concentrated Cu(II) solution (1.0 g-Cu(II)/L). We examined six ZVI samples, plus one iron oxide sample and an aged ZVI sample. Their sizes range from nanometers to centimeters, and Fe(0) purities range from 0-98%.

Figure S3a shows XRD of the solids after ZVI-Cu(II) reaction: all the Fe(0) peaks disappear and the new peaks are all derived from Cu products (Cu^0 and Cu_2O), indicating that Fe(0) is almost consumed. Fe(0)-Cu(II) reactions are galvanic replacement reaction and the removal capacity of Cu(II) by ZVI correlates directly to the Fe(0) content of ZVI. The reactions were used to estimate the Fe(0) content in iron nanoparticles.[43]

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu \quad (9)$$

$$Fe^0 + 2Cu^{2+} + H_2O \rightarrow Fe^{2+} + Cu_2O + 2H^+ \quad (10)$$

Figure 5a and Table 1 summarized the Cu(II) removal capacities (mg-Cu(II)/g-ZVI) and the measured Fe(0) contents using Fe(III) method (mg-Fe^0/g-ZVI). The results demonstrate good agreement between the measured contents and their removal capacities. The contents and the capacities are in the same order: 400 mesh ≈ 3000 mesh > 150 mesh^{I} > nZVI ≈ 150 mesh^{II}> 20-mesh^{II} > aged ZVI ≈ iron oxide. It is interesting to note that the capacity of 20-mesh ZVI (O, Table 1) is exceptionally lower (610 mg-Cu(II)/Fe) compared to those of other ZVIs of the similar purity. The low capacity has been predicted by its low measured Fe(0) content (0.72 g-Fe^0/g-ZVI), suggesting that the Fe(III) method is more powder tool for the assessment of ZVI quality.

TCE degradation

Trichloroethylene (TCE) degradation experiments were conducted to validate the k_{Fe} for reactivity assessment. The rate of TCE degradation by ZVI follows the first-order of TCE concentration (C_{TCE}) (Figure S3b) and is often expressed using the following equation:

$$\frac{dC_{TCE}}{dt} = -k_{TCE}C_{TCE} \tag{11}$$

where k_{TCE} is the observed first-order rate constant (d^{-1}),

C_{TCE} is TCE concentration (mg/L) at certain time (t).

k_{TCE} was often used to characterize ZVI reactivity.[29, 50] Figure 5b summarizes k_{TCE} and k_{Fe} of seven ZVIs. The graph demonstrates strong correlation of the two coefficients. Generally, larger k_{Fe} corresponds to greater $k_{TCE.}$ nZVI and 3000-mesh ZVI (J) have the largest k_{TCE} (0.631 and 0.580 d^{-1} respectively) among the seven ZVIs, and these two ZVIs also have the largest k_{Fe}. The correlation suggests that the k_{Fe} could serve as a reliable parameter to predict ZVI reactivity.

Probing reactivity using Fe(III) takes much less time and effort in test preparation, reaction and product assay. k_{Fe} is about two orders of magnitude larger than k_{TCE}, indicating that Fe(III) experiment takes less reaction time. Sample pretreatment in measuring Fe(III) is also simple and the assaying can be conducted using one ordinary spectrometer. More importantly, the informative Fe(III) method measures Fe(0) content and reactivity of ZVI at the same time. A demonstration experiment shows that the method is a reliable tool for quality assessment of real iron samples (e.g., ZVIs of different aging time). More details can be found in supporting information (Figure S5).

4. Conclusion

In summary, the proposed Fe(III) method provides an accurate and reliable way to measure Fe(0) content in ZVI and to assess ZVI reactivity. The method is environmental friendly and doesn’t involve hazardous reagent. The experiment takes just a few hours, and can be easily conducted with ordinary instrument (e.g., a portable spectrophotometer). The method provides an easy and facile way to assess ZVI quality, especially for the quick survey of large quantities of ZVIs on site. The method could also be used to assess the quality of reacted ZVI in PRB after long-term operation. The method may also serve as a universal testing procedure in QA/QC for ZVI supplier and be applied to standardize ZVI materials for environmental application.

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Supplementary Material

More information on XRDs of ZVIs, replicate tests measuring Fe(0) contents of ZVI mixtures, results of method validation experiments using Cu(II) and TCE, demonstration experiments with aged ZVI is provided in the Supplementary Material.

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Table 1 ZVIs and iron oxides studied in this work

Items				Information from ZVI vendor				This work					
								Characterizations		Fe(III) method			
				Source	Purity	Size	Designation	BET-N_2 (m^2/g)	ORP* (mV)	Fe^0 content (Fe-g/g-ZVI)	k_{Fe} (min^{-1})	Cu(II) (g-Cu/g-ZVI)	k_{TCE} (d^{-1})
Standard Reference Material	A	Fe_2O_3		Aladdin	99%	30 nm	Fe_2O_3	--	--	0	0	0	--
	B	Fe_3O_4		Aladdin	99%	20 nm	Fe_3O_4	--	--	0	0	--	--
	C	FeOOH		Aladdin	99%		FeOOH	--	--	0	0	--	--
	D	ZVI	Fe^0	Aladdin	98%	100 mesh	100 mesh	0.13	-360	0.97	0.04	--	
	E				98%	400 mesh	400 mesh	0.20	-560	0.97	0.06	1.07	0.18
Testing ZVIs	F	nZVI		This work	83%	120 nm	nZVI	40	-630	0.85	0.15	0.86	0.63
	G	Commercial ZVI (I)		Zhejiang China	98%	3000 mesh	3000 mesh^1	4.25	-543	0.99	0.5	--	--
	H				98%	3000 mesh	3000 mesh^2	3.83	-550	0.98	0.6	--	--
	I				98%	3000 mesh	3000 mesh^3	4.97	-515	0.97	0.09	--	--
	J				98%	3000 mesh	3000 mesh^4	5.64	-582	0.96	0.63	1.01	0.58
	K				98%	3000 mesh	3000 mesh^5	4.50	-580	0.99	0.11	--	--
	L	Commercial ZVI (II)		Jiangsu China	92%	20 mesh	20 mesh^{I}	0.15	-410	0.72	0.006	--	--
	M				92%	100 mesh	100 mesh^{I}	5.73	-12	0.90	0.01	--	--
	N				92%	150 mesh	150 mesh^{I}	0.08	-438	0.93	0.01	0.91	0.08
	O	Commercial ZVI (III)		Shandong China	88%	20 mesh	20 mesh^{II}	1.34	-442	0.73	0.004	0.61	0.12
	P				88%	60 mesh	60 mesh^{II}	1.32	-492	0.90	0.006	--	--
	Q				88%	80 mesh	80 mesh^{II}	1.34	-473	0.89	0.008	--	--
	R				88%	100 mesh	100 mesh^{II}	2.66	-575	0.87	0.03	--	--
	S				88%	150 mesh	150 mesh^{II}	1.78	-581	0.85	0.04	0.80	0.18
	T	Iron shaving		Shanghai	95%	2 cm	Iron shaving	0.03	-56	0.78	0.004	--	--
	U	Aged ZVI (400 mesh)	1 d	Aladdin and this work	--	400 mesh	400 mesh^{1d}	6.03	-400	0.94	0.03	--	--
	V		2 d		--	400 mesh	400 mesh^{2d}	8.57	-350	0.91	0.01	--	--
	W		10 d		--	400 mesh	400 mesh^{10d}	12.10	-130	0.20	0.003	--	--
	X		12 d		--	400 mesh	400 mesh^{12d}	9.22	-40	0.19	0.003	0	0.04

Figure captions

Figure 1 SEM images of ZVIs studied in this work. XRDs of these ZVIs are provided in Supporting Information.

Figure 2 Principle and Schematics of experimental setup.

Figure 3 Feasibility study using standard reference materials.

(a) Dissolution of standard reference ZVI in Fe(III) solution. ZVI: 400 mesh (Row E, Table 1); Iron oxide (Row A-C); Fe(III) concentration: 0.3, 1.0, 1.5, 2.0, 3.0 g-Fe(III)/L for 0.050 g, 0.250 g, 0.500 g, 0.750, 1.000 g-ZVI/L respectively; Solution pH was not adjusted;

(b) Correlation of the increasing in total dissolved iron concentration (g/L) and ZVI dosages (g/L);

(c) Dissolution of standard reference ZVI at four different initial Fe(III) concentration;

(d) Reaction kinetics of the dissolution processes in Figure 2c. Embedded figure summarizes the first-order rate constants (k_{Fe}) at four different dosages.

Figure 4 Method validations using commercial ZVIs/ZVI mixtures with known purities: study of accuracy and reliability (Fe(III) concentration (C_0): 2.0 g-Fe(III)/L, 0.50 g/L).

(a) Dissolution of six different ZVIs in Fe(III) solution;

(b) Reaction kinetics of the dissolution processes in Figure 4(a);

(c) Measured Fe(0) contents in ZVIs with known purities; the fifteen ZVIs were from five different sources and ZVIs from the same source have the same purity;

(d) Correlation of k_{Fe} and ZVI particle sizes; ZVIs: Row D-T, Table 1;

(e) Correlation of k_{Fe} and ORP of ZVI slurry; ZVIs: Row D-X, Table 1.

Figure 5 Method validations.

(a) Validations of measured Fe(0) content using Cu(II) solution (1.0 g-Cu(II)/L, ZVI dosage: 0.50 g/L): correlation of the measured Fe(0) content and Cu(II) removal capacity;

(b) Validation of ZVI reactivity with TCE-degradation experiments (C_{0TCE}: 50 mg/L, ZVI dosage: 0.50 g/L): correlation of the two observed rate constants (k_{TCE} and k_{Fe}).

Figure 1

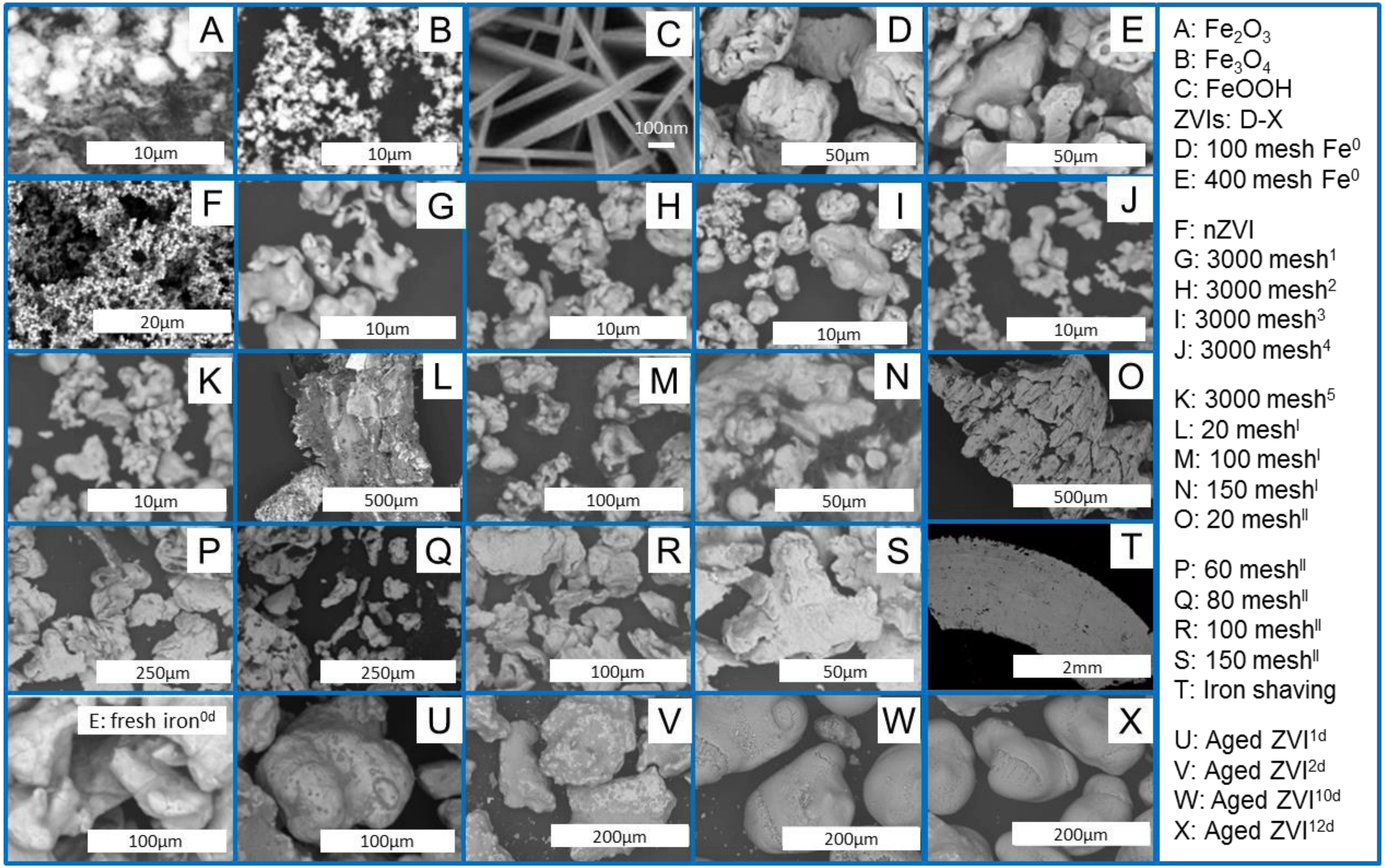
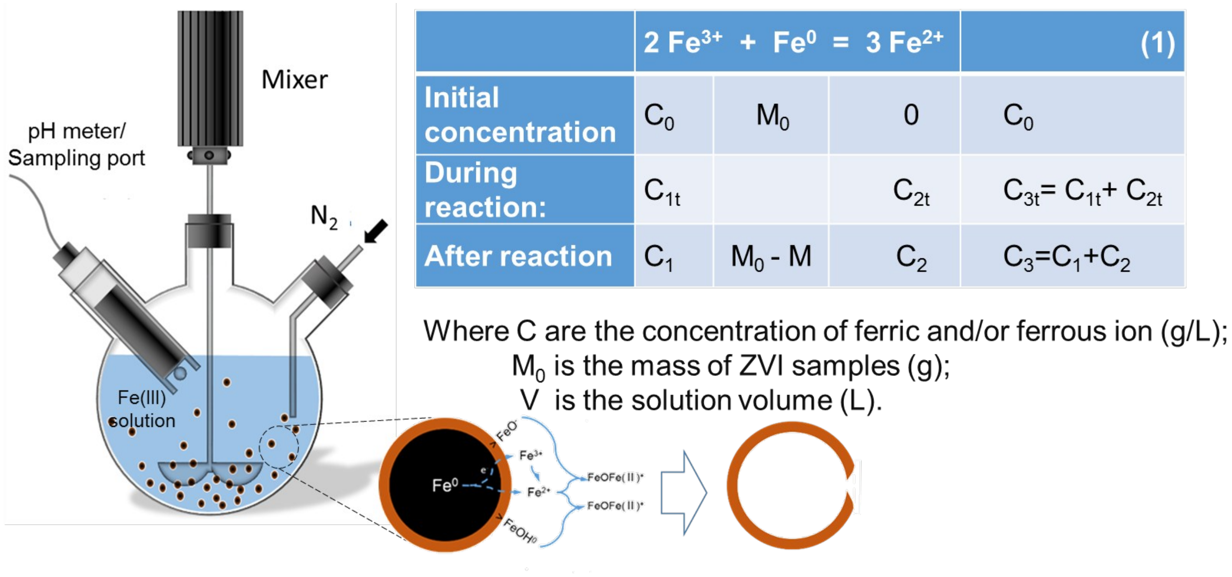

A
10µm
B
10µm
C
100nm
D
50µm
E
50µm
F
20µm
G
10µm
H
10µm
I
10µm
J
10µm
K
10µm
L
500µm
M
100µm
N
50µm
O
500µm
P
250µm
Q
250µm
R
100µm
S
50µm
T
2mm
E: fresh iron^{0d}
100µm
U
100µm
V
200µm
W
200µm
X
200µm
A: Fe_2O_3
B: Fe_3O_4
C: FeOOH
ZVIs: D-X
D: 100 mesh Fe^0
E: 400 mesh Fe^0
F: nZVI
G: 3000 mesh^1
H: 3000 mesh^2
I: 3000 mesh^3
J: 3000 mesh^4
K: 3000 mesh^5
L: 20 mesh^{I}
M: 100 mesh^{I}
N: 150 mesh^{I}
O: 20 mesh^{II}
P: 60 mesh^{II}
Q: 80 mesh^{II}
R: 100 mesh^{II}
S: 150 mesh^{II}
T: Iron shaving
U: Aged ZVI^{1d}
V: Aged ZVI^{2d}
W: Aged ZVI^{10d}
X: Aged ZVI^{12d}

Figure 2



	$2\ Fe^{3+}$ + Fe^0 = $3\ Fe^{2+}$			(1)
Initial concentration	C_0	M_0	0	C_0
During reaction:	C_{1t}		C_{2t}	$C_{3t}= C_{1t}+ C_{2t}$
After reaction	C_1	M_0 - M	C_2	$C_3=C_1+C_2$

Where C are the concentration of ferric and/or ferrous ion (g/L);
M_0 is the mass of ZVI samples (g);
V is the solution volume (L).

Figure 3a

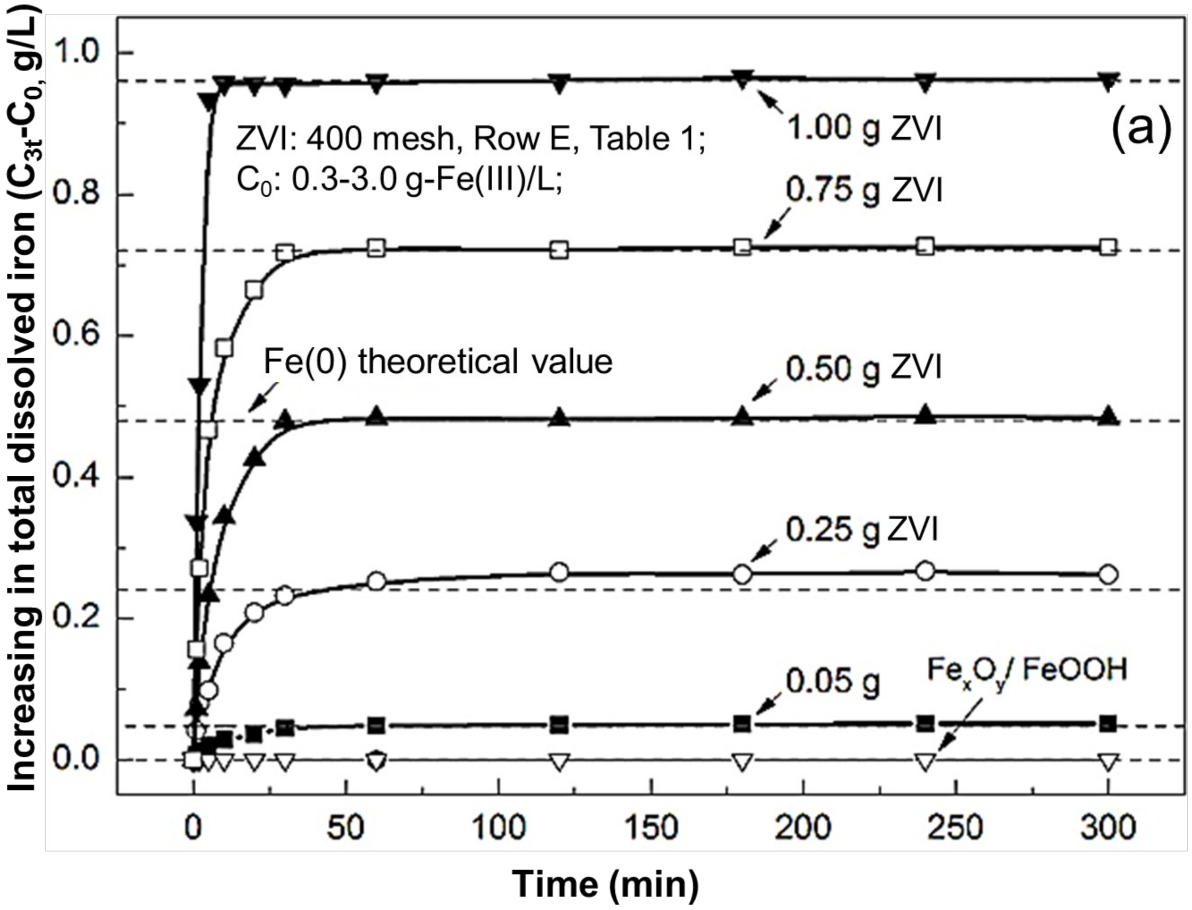

Increasing in total dissolved iron (C_{3t}-C_0, g/L)
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
Time (min)
ZVI: 400 mesh, Row E, Table 1;
C_0: 0.3-3.0 g-Fe(III)/L;
(a)
1.00 g ZVI
0.75 g ZVI
Fe(0) theoretical value
0.50 g ZVI
0.25 g ZVI
0.05 g
Fe_xO_y/ FeOOH

Figure 3b

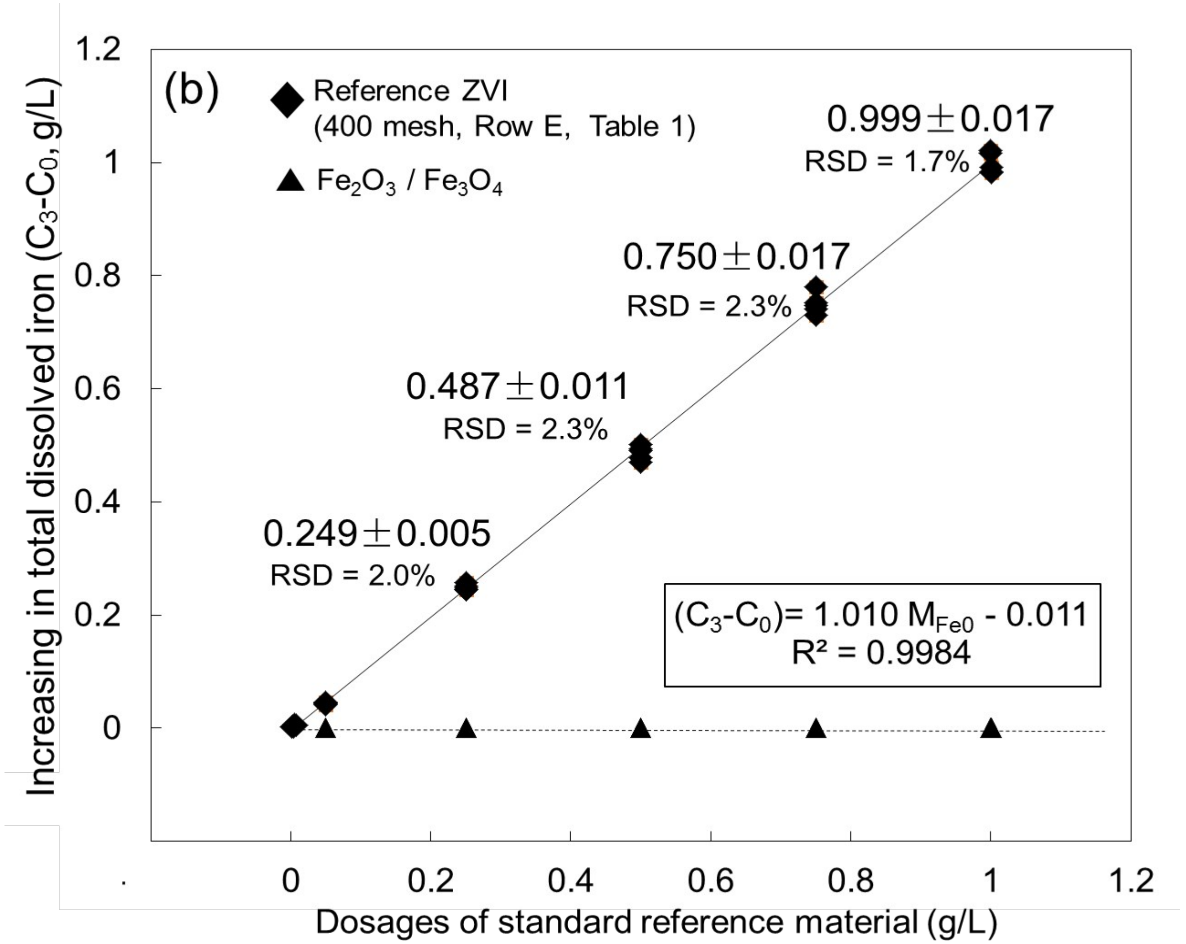

(b)
◆ Reference ZVI (400 mesh, Row E, Table 1)
▲ Fe_2O_3 / Fe_3O_4
0.999±0.017
RSD = 1.7%
0.750±0.017
RSD = 2.3%
0.487±0.011
RSD = 2.3%
0.249±0.005
RSD = 2.0%
$(C_3-C_0)= 1.010\ M_{Fe0} - 0.011$
$R^2 = 0.9984$
Increasing in total dissolved iron (C_3-C_0, g/L)
1.2
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
1.2
Dosages of standard reference material (g/L)

Figure 3c

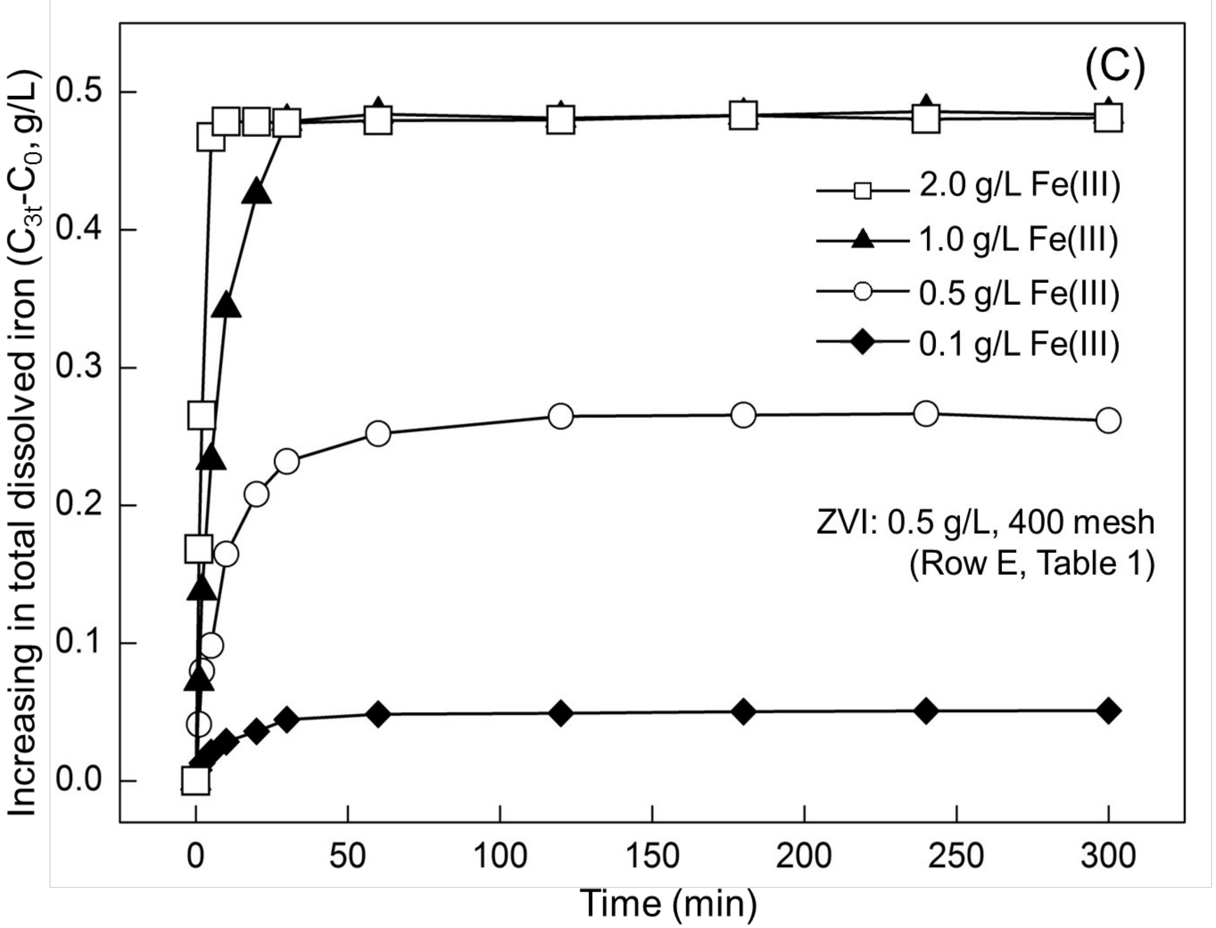

(C)
Increasing in total dissolved iron (C_{3t}-C_0, g/L)
0.0
0.1
0.2
0.3
0.4
0.5
Time (min)
0
50
100
150
200
250
300
2.0 g/L Fe(III)
1.0 g/L Fe(III)
0.5 g/L Fe(III)
0.1 g/L Fe(III)
ZVI: 0.5 g/L, 400 mesh
(Row E, Table 1)

Figure 3d

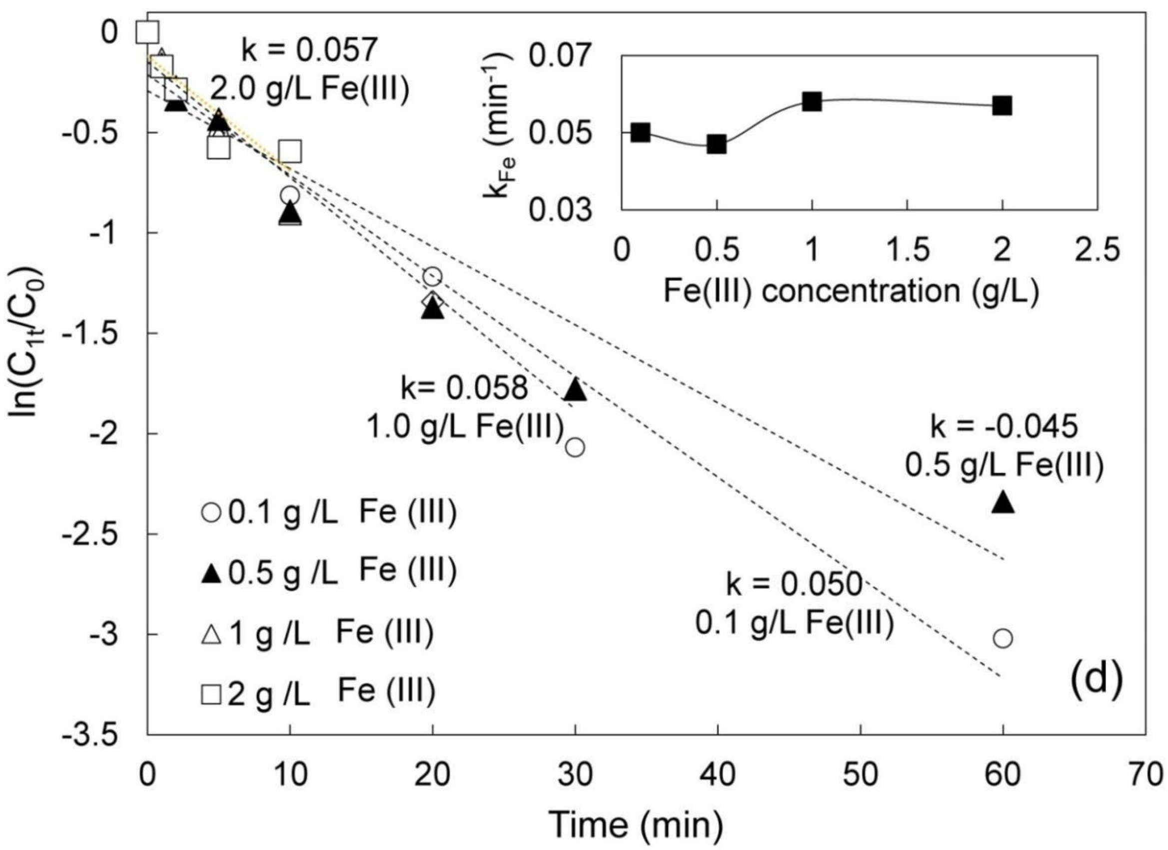

k = 0.057
2.0 g/L Fe(III)
k= 0.058
1.0 g/L Fe(III)
k = -0.045
0.5 g/L Fe(III)
k = 0.050
0.1 g/L Fe(III)
○ 0.1 g /L Fe (III)
▲ 0.5 g /L Fe (III)
△ 1 g /L Fe (III)
□ 2 g /L Fe (III)
(d)
ln(C1t/C0)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0
10
20
30
40
50
60
70
Time (min)
kFe (min-1)
0.07
0.05
0.03
0
0.5
1
1.5
2
2.5
Fe(III) concentration (g/L)

Figure 4a

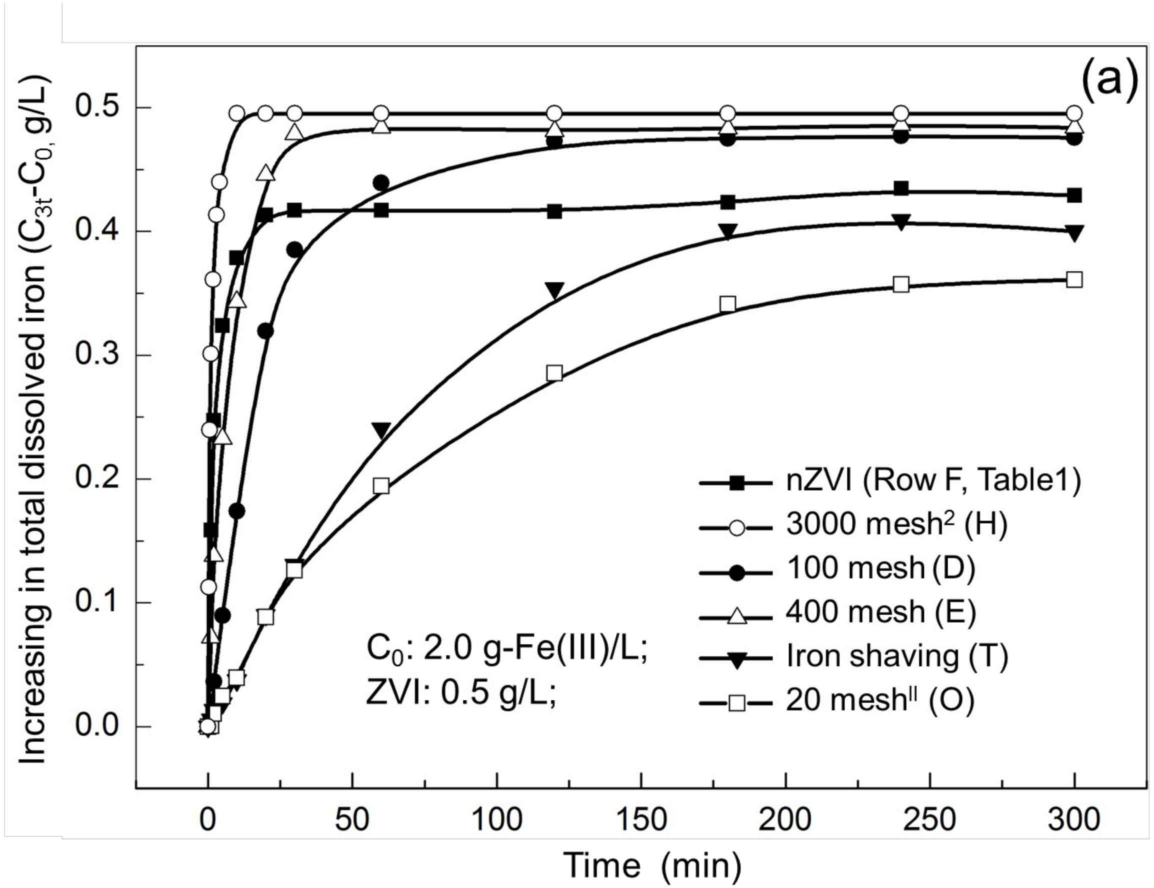

(a)
Increasing in total dissolved iron (C3t-C0, g/L)
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
300
Time (min)
C0: 2.0 g-Fe(III)/L;
ZVI: 0.5 g/L;
nZVI (Row F, Table1)
3000 mesh2 (H)
100 mesh (D)
400 mesh (E)
Iron shaving (T)
20 meshII (O)

Figure 4b

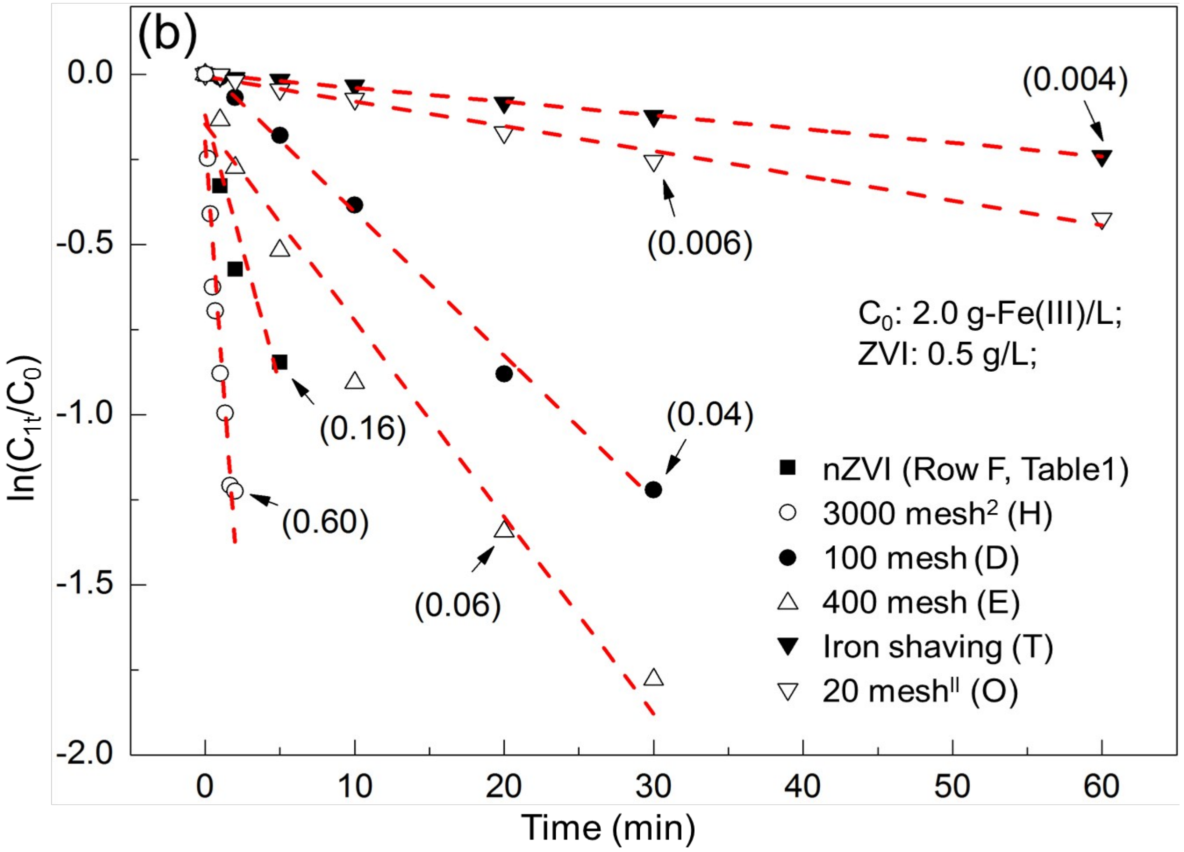

(b)
0.0
-0.5
-1.0
-1.5
-2.0
$\ln(C_{1t}/C_0)$
0
10
20
30
40
50
60
Time (min)
(0.004)
(0.006)
C_0: 2.0 g-Fe(III)/L;
ZVI: 0.5 g/L;
(0.16)
(0.04)
(0.60)
(0.06)
■ nZVI (Row F, Table1)
○ 3000 mesh² (H)
● 100 mesh (D)
△ 400 mesh (E)
▼ Iron shaving (T)
▽ 20 mesh^II (O)

Figure 4c

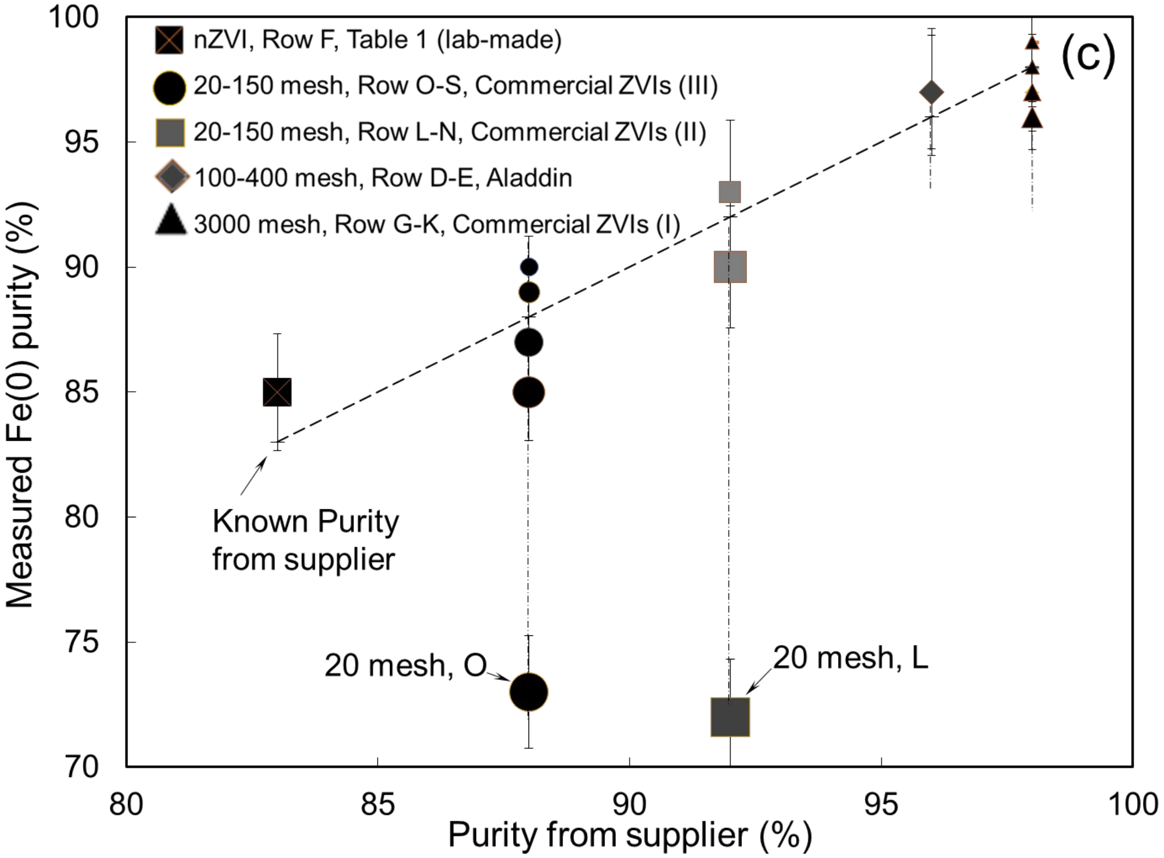

100
95
90
85
80
75
70
Measured Fe(0) purity (%)
80
85
90
95
100
Purity from supplier (%)
(c)
nZVI, Row F, Table 1 (lab-made)
20-150 mesh, Row O-S, Commercial ZVIs (III)
20-150 mesh, Row L-N, Commercial ZVIs (II)
100-400 mesh, Row D-E, Aladdin
3000 mesh, Row G-K, Commercial ZVIs (I)
Known Purity
from supplier
20 mesh, O
20 mesh, L

Figure 4d and 4e

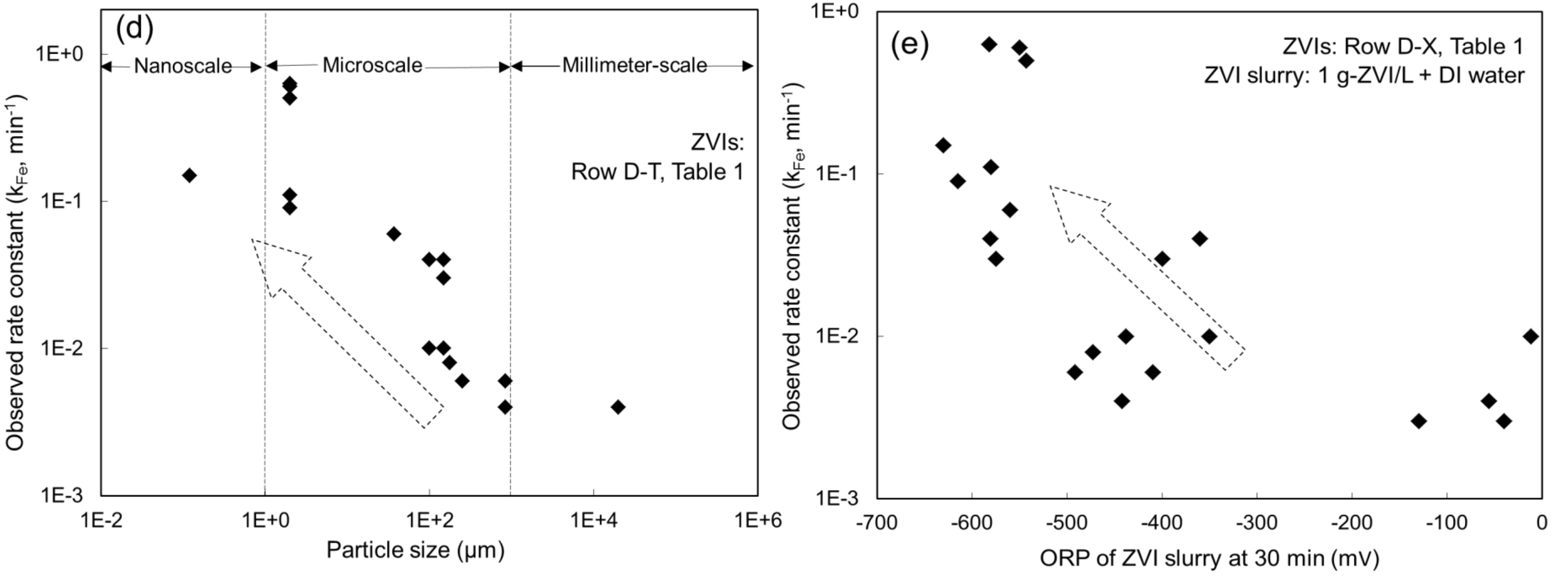
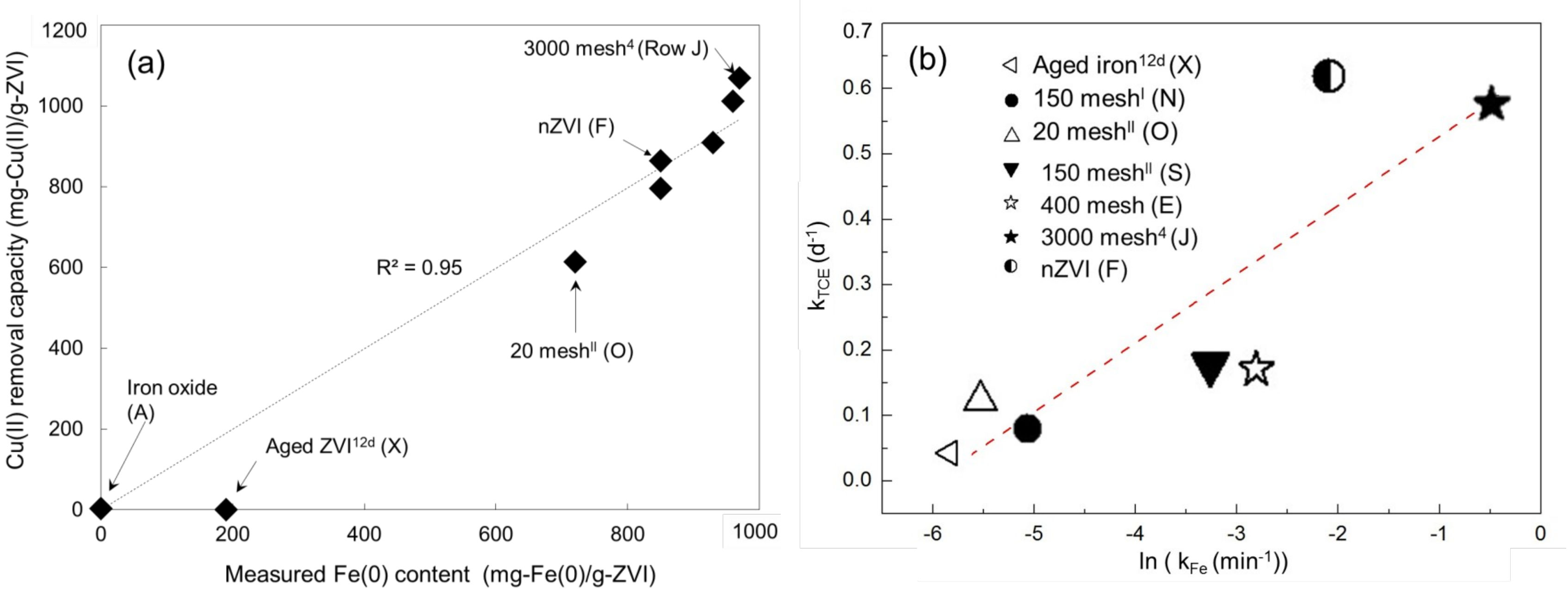


Figure 5a and Figure 5b



Graphical Abstract

This work provides a facile and reliable way to assess the quality of metallic iron used for environmental clean-up.