Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

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

Shaolin Li, Yangyang Ding, Wei Wang, Hong Lei*

State Key Laboratory for Pollution Control

School of Environmental Science and Engineering

Tongji University

Shanghai, 200092, China

*Corresponding author; Email: lishaolin@tongji.edu.cn; Fax: 86-21-65985885.

Figure captions

Figure S1 XRD of ZVIs studied in this work.

Figure S2 Measured Fe(0) content of two ZVI mixtures. Results from replicate tests were presented.

Figure S3 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): XRDs of solid products after reaction with Cu(II);

(b) Validation of ZVI reactivity with TCE-degradation experiments (C_{0TCE}: 50 mg/L, ZVI dosage: 0.50 g/L): reaction kinetics of TCE degradation using seven different ZVIs.

Figure S4 Determination of Fe(0) content and reactivity of aged ZVIs. ZVIs: Row E, U-X, Table 1.

(a) Reaction of aged ZVIs in Fe(III) solution. Fe(III) concentration (C_0): 2.00 g-Fe(III)/L; ZVI dosage: 0.50 g/L;

(b) Measured Fe(0) content and reactivity as a function of aging time.

Figure S1

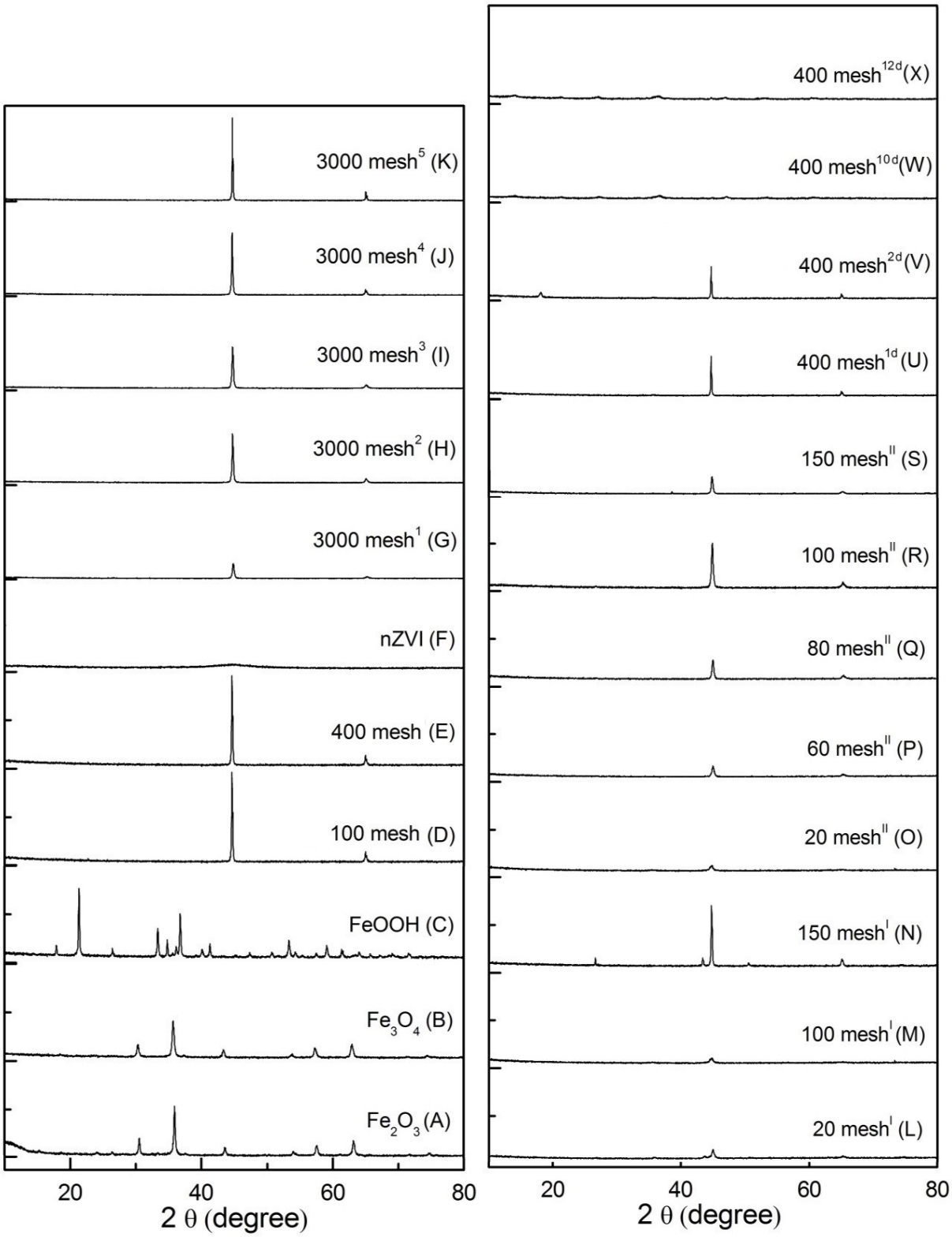

3000 mesh5 (K)
3000 mesh4 (J)
3000 mesh3 (I)
3000 mesh2 (H)
3000 mesh1 (G)
nZVI (F)
400 mesh (E)
100 mesh (D)
FeOOH (C)
Fe3O4 (B)
Fe2O3 (A)
20
40
60
80
2 θ (degree)
400 mesh12d(X)
400 mesh10d(W)
400 mesh2d(V)
400 mesh1d(U)
150 meshII (S)
100 meshII (R)
80 meshII (Q)
60 meshII (P)
20 meshII (O)
150 meshI (N)
100 meshI (M)
20 meshI (L)
20
40
60
80
2 θ (degree)

Figure S2

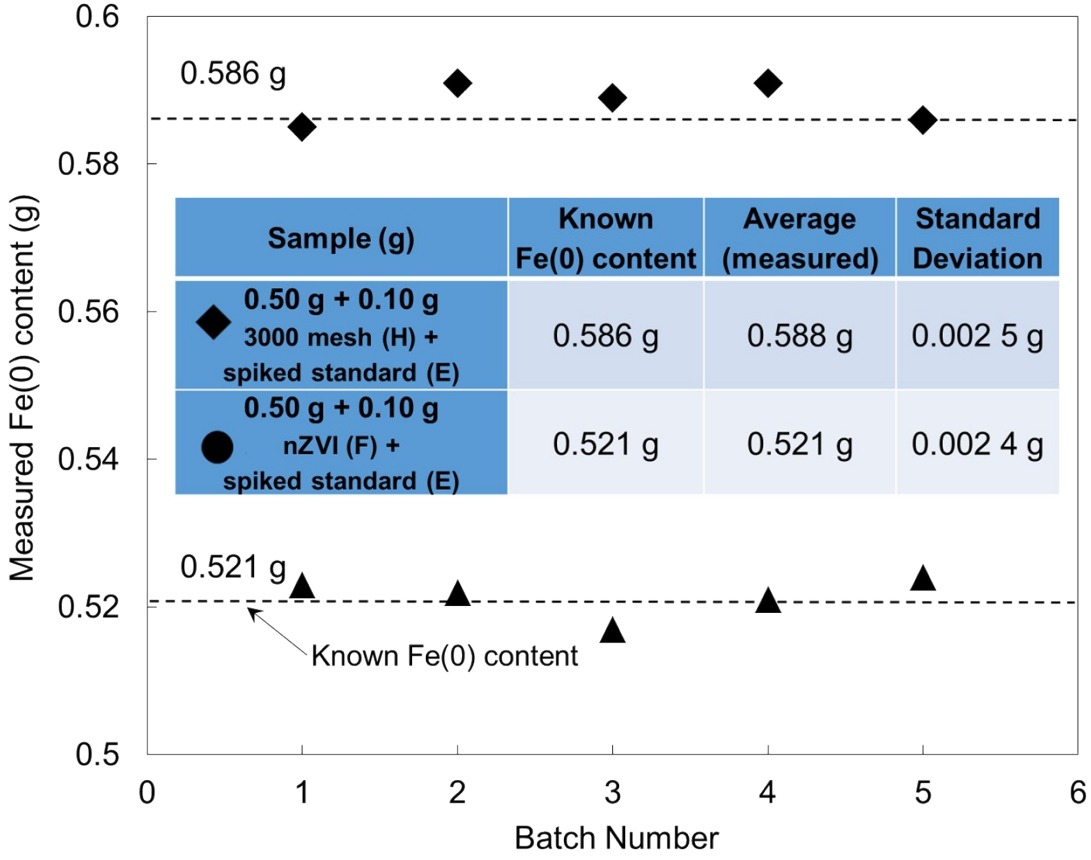

0.6
0.58
0.56
0.54
0.52
0.5
Measured Fe(0) content (g)
0.586 g
0.521 g
Known Fe(0) content
0
1
2
3
4
5
6
Batch Number
Sample (g)
Known Fe(0) content
Average (measured)
Standard Deviation
0.50 g + 0.10 g 3000 mesh (H) + spiked standard (E)
0.586 g
0.588 g
0.002 5 g
0.50 g + 0.10 g nZVI (F) + spiked standard (E)
0.521 g
0.521 g
0.002 4 g

Figure S3

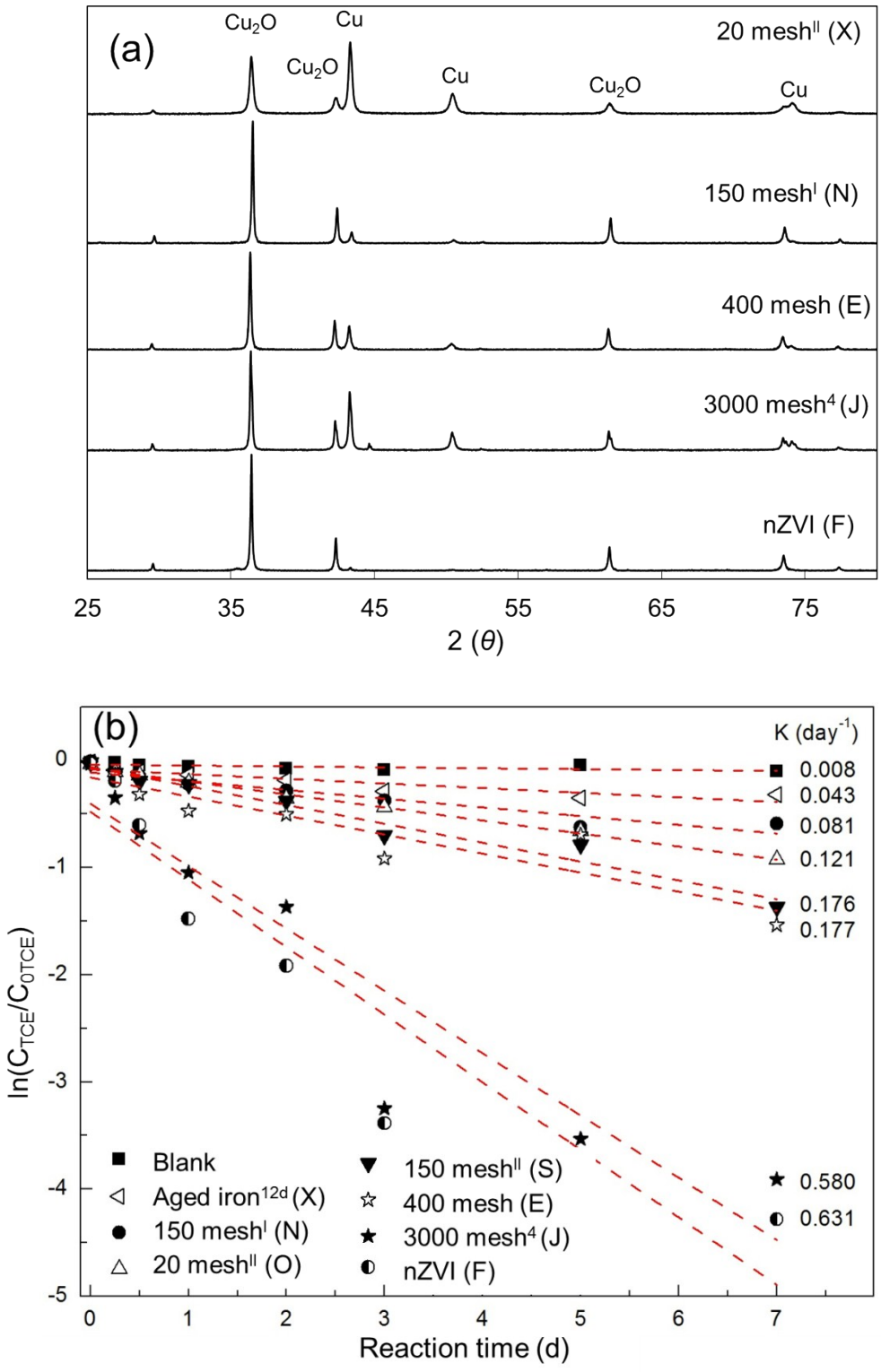
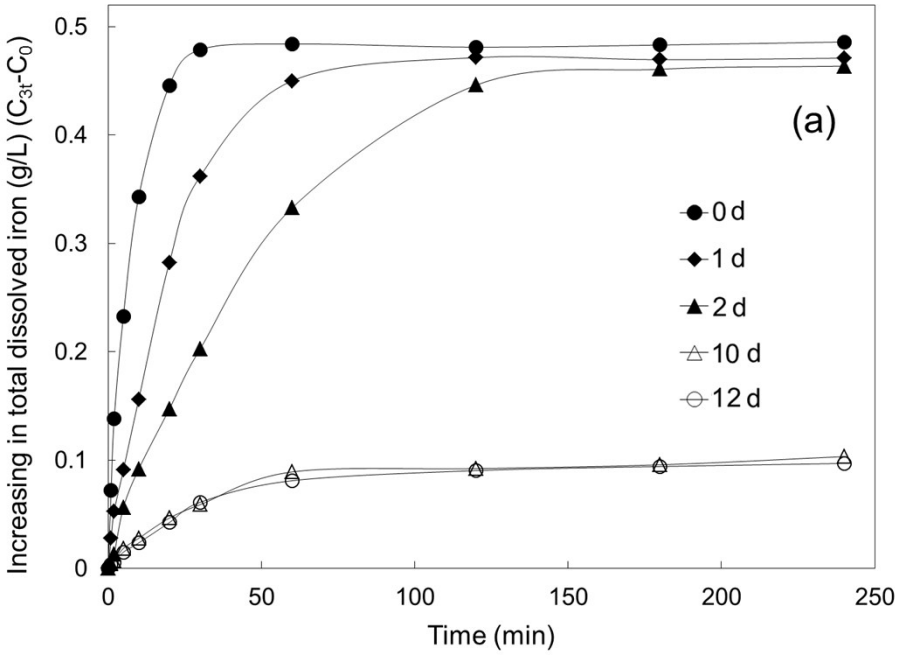
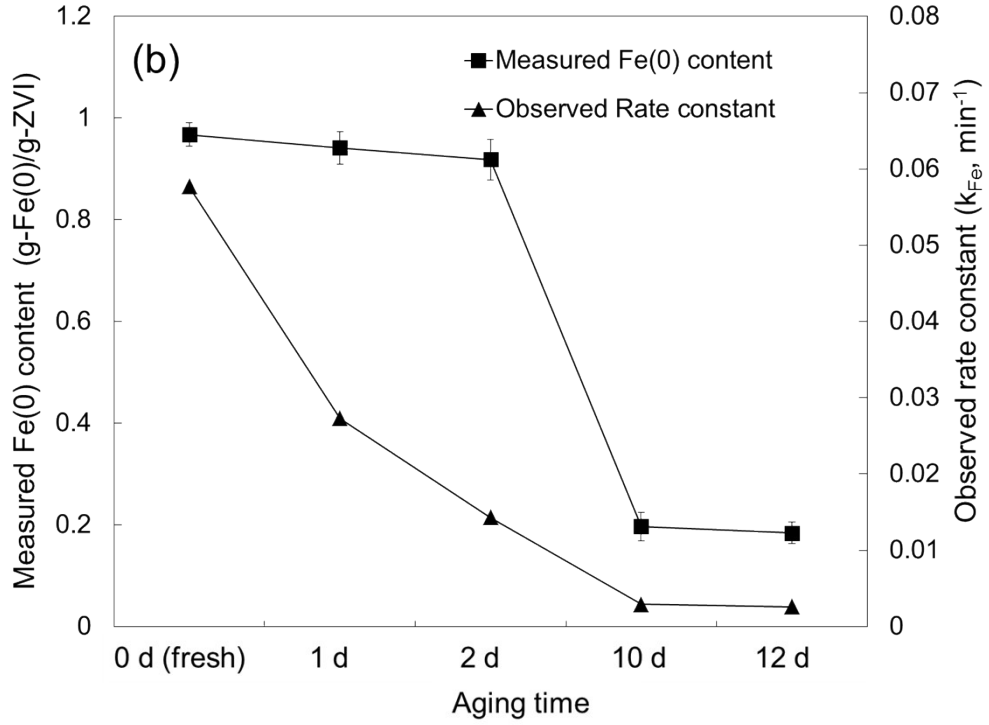

(a)
Cu2O
Cu
Cu2O
Cu
Cu2O
Cu
20 meshII (X)
150 meshI (N)
400 mesh (E)
3000 mesh4 (J)
nZVI (F)
25
35
45
55
65
75
2 (θ)
(b)
K (day-1)
0.008
0.043
0.081
0.121
0.176
0.177
0.580
0.631
Blank
Aged iron12d (X)
150 meshI (N)
20 meshII (O)
150 meshII (S)
400 mesh (E)
3000 mesh4 (J)
nZVI (F)
ln(CTCE/C0TCE)
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
7
Reaction time (d)

Figure S4


(a)
Increasing in total dissolved iron (g/L) (C_{3t}-C_0)
Time (min)
0 d
1 d
2 d
10 d
12 d


(b)
Measured Fe(0) content
Observed Rate constant
Measured Fe(0) content (g-Fe(0)/g-ZVI)
Observed rate constant (k_{Fe}, min^{-1})
0 d (fresh)
1 d
2 d
10 d
12 d
Aging time

Demonstration experiments using aged ZVIs

The aging or corrosion of iron material is almost inevitable due to the pervasive O_2 and moisture. This process could be significant in large-scale application of ZVI, in which ZVI may experience long-term aging during storage or shipping. Such aging process may go unnoticed because the change in physical appearance is minor. A quick, simple and reliable method is required for assessing the quality of ZVI after long-term storage, especially in large-scale application where hundreds iron sample needs to be analyzed.

Four aged ZVI samples were measured using the Fe(III) method to exemplify this possible application. The samples were prepared by mixing high-purity ZVI (Row E, Table 1) with water. Results suggest that both Fe(0) content and reactivity of ZVI lose gradually during aging (Figure S4a and S4b). More importantly, the method provides quantitative results in assessing the impact of aging on ZVI quality. For example, minor changes (~3%) in Fe(0) content was observed in the first few days of aging; the Fe(0) content and reactivity after 12-d aging were only 20% and 5% of the fresh ZVI. Such quantitative results or minor change could not be obtained using SEM, XRD or BET-N_2. XRDs and SEM images of aged ZVI (Figure 1 and S1) are quite similar. BET-N_2 adsorption even suggests the growth of their specific surface area (Table 1) during aging, which could be quite misleading in the judgment of their reactivity.