Supporting Information

Interaction of pyrite with zerovalent iron with superior reductive ability via Fe(II) regeneration

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Table S4. Intrinsic properties of FeS$_2$/ZVI (molar ratio 9:1).
Cr(VI) removal kinetics

Pseudo first-order model:

\[
\frac{dQ_t}{dt} = k_1(Q_e - Q_t)
\]  

(1)

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t
\]  

(2)

Pseudo second-order model:

\[
\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2
\]  

(3)

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}
\]  

(4)

where \( k \) is the rate constant of Cr(VI) removal by mixed FeS₂-ZVI and ball milled FeS₂/ZVI, \( Q_e \) is the amount of adsorbate at equilibrium (mg g⁻¹); \( Q_t \) is the amount of adsorbate (mg g⁻¹) at time \( t \) (min); and \( k_1 \) (min⁻¹) and \( k_2 \) (g·mg⁻¹·min⁻¹) are the rate constants for the pseudo first- and second-order adsorption, respectively.

Electrochemical characterizations

All electrochemical experiments were conducted in a conventional three-electrode electrochemical cell. The three-electrode electrochemical cell consisted of a calomel electrode reference electrode, a platinum counter electrode, and a modified glassy carbon working electrode. 0.2 mmol L⁻¹ NaCl was selected as the electrolyte solution.

Preparation of modified working electrode

The Nafion solution with a mass fraction of 5 % was dissolved in a 1:1 isopropanol-water solution to prepare a Nafion solution with a mass fraction of 0.5 %. Then 2 mg of the material was added to 100 μL of 0.5 wt% solution. 5 μL of the
suspension was dropped onto the surface of the disc electrode, which was air-dried for further use. Tafel polarization curve, open circuit potential (OCP), and electrochemical impedance spectroscopic (EIS) were performed by the CHI760E electrochemical workstation to elevate the electrochemical behavior of the materials. The electrochemical parameters are present as follow.

(1) Tafel polarization curve

The voltage range was -1.0V~ -0.5V (10 mV S⁻¹), and the corrosion potential was scanned twice.

(2) Electrochemical impedance spectroscopy (EIS)

EIS was carried out at the open-circuit voltage in the frequency range of 0.01 Hz to 100 kHz.

(3) Open circuit potential (OCP) curves

The OCP test time was 1500 s, sample interval 0.1 s. After the baseline was stable, the first solution was added at 300 s, and the second solution was added at 1100 s.
Fig. S1. SEM-EDS images of pristine FeS$_2$. 

<table>
<thead>
<tr>
<th>element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>85.28</td>
<td>92.99</td>
</tr>
<tr>
<td>S</td>
<td>10.41</td>
<td>5.66</td>
</tr>
<tr>
<td>Fe</td>
<td>4.31</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Total amount: 100.00%
Fig. S2. SEM images of pristine ZVI.
Fig. S3. (a) N\textsubscript{2} adsorption-desorption isotherm and (b) pore size distribution image of FeS\textsubscript{2}/ZVI (molar ratio 9:1).
Fig. S4. EDS elemental mapping images of FeS$_2$/ZVI (molar ratio:9:1).
Fig. S5. SEM-EDS images of FeS$_2$/ZVI (molar ratio 9:1).
Fig. S6. D-spacing intensity profiles of the different regions of FeS$_2$/ZVI sample.
Fig. S7. S 2p XPS spectra of FeS₂/ZVI (molar ratio 9:1).
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Fig. S9. (a) $^{57}$Fe Mossbauer spectra of FeS$_2$/ZVI, (b) FTIR spectra of FeS$_2$, ZVI and FeS$_2$/ZVI before and after reaction with Cr(VI); (Particle dosage: 1 g L$^{-1}$, [Cr(VI)]$_0$ = 50.0 mg L$^{-1}$, pH$_0$ = 5.20, air atmosphere).
Fig. S10. The concentration of total Cr, Cr(VI) and Cr(III) during Cr(VI) removal by Mixed FeS$_2$-ZVI. (Particle dosage: 1 g L$^{-1}$, [Cr(VI)]$_0$ = 50.0 mg L$^{-1}$, pH$_0$ = 5.20, air atmosphere).
Fig. S11. SEM images of (a) mixed FeS$_2$-ZVI and (b) FeS$_2$/ZVI after Cr(VI) removal.

(Particle dosage: 1 g L$^{-1}$, [Cr(VI)]$_0$ = 50.0 mg L$^{-1}$, pH$_0$ = 5.20, air atmosphere).
Fig. S12. (a) Cr(VI) removal by FeS$_2$/ZVI and mix FeS$_2$-ZVI, the fitting plots of (b) Pseudo first-order kinetic modeling and (c) pseudo-second-order by FeS$_2$/ZVI and mixed FeS$_2$-ZVI. (Particle dosage: 1 g L$^{-1}$, [Cr(VI)]$_0$ = 50.0 mg L$^{-1}$, pH$_0$ = 5.20, air atmosphere).
Fig. S13. XPS survey spectrum of FeS$_2$/ZVI after Cr(VI) removal.
Fig. S14. The concentration of (a) Fe$^{3+}$ and (b) SO$_4^{2-}$ in the mixed FeS$_2$-ZVI system and FeS$_2$/ZVI system. (Particle dosage: 1 g L$^{-1}$, [Cr(VI)]$_0$ = 50.0 mg L$^{-1}$, pH$_0$ = 5.20, air atmosphere).
Fig. S15. (a) Cr(VI) removal by mixed FeS$_2$-ZVI and FeS$_2$/ZVI in the absence or presence of 1,10-phenanthroline. (Particle dosage: 1 g L$^{-1}$, [Cr(VI)]$_0$ = 50.0 mg L$^{-1}$, NaAc-HAc buffer solution, pH$_0$ = 3.93, air atmosphere).
Fig. S16. Dissolution of Fe from mixed FeS$_2$-ZVI and FeS$_2$/ZVI in pure water system.

(Particle dosage: 1 g L$^{-1}$, air atmosphere).
Fig. S17. Effect of different amount of Fe$^{2+}$ added on Cr(VI) removal. ([Cr(VI)]$_0$ = 50.0 mg L$^{-1}$, pH$_0$ = 5.20, air atmosphere).
Fig. S18. XRD patterns of FeS$_2$/ZVI, FeS/ZVI and S/ZVI.
Fig. S19. Lattice constants of Fe BCC structure according to XRD Rietveld refinement
Fig. S20. Water contact angle images of FeS2/ZVI, FeS/ZVI, and S/ZVI.
Fig. S21. The influence of S precursors on hydrophobicity and Cr(VI) removal.

(Particle dosage: 1 g L\(^{-1}\), \([\text{Cr(VI)}]_0 = 50.0 \text{ mg L}^{-1}\), pH\(_0 = 5.20\), air atmosphere).
Fig. S22. The reusability of FeS$_2$/ZVI at initial pH 5.20 for Cr(VI) removal and rejuvenation of FeS$_2$/ZVI by BM again.
Fig. S23. Image of the magnetic separation after the Cr(VI) removal by FeS₂/ZVI.
Table S1. The $^{57}$Fe Mossbauer parameters\(^a\) of FeS\(_2\)/ZVI.

<table>
<thead>
<tr>
<th>Component</th>
<th>H  (KOE)</th>
<th>IS (mm s(^{-1}))</th>
<th>QS (mm s(^{-1}))</th>
<th>Г/2 (mm s(^{-1}))</th>
<th>Fe%</th>
<th>Identified state of iron</th>
</tr>
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<tbody>
<tr>
<td>Doublet 1</td>
<td>0.32</td>
<td>0.59</td>
<td>0.16</td>
<td>61.2</td>
<td>Fe(^{2+})</td>
<td></td>
</tr>
<tr>
<td>Doublet 2</td>
<td>1.24</td>
<td>2.73</td>
<td>0.15</td>
<td>25.7</td>
<td>Fe(^{3+})</td>
<td></td>
</tr>
<tr>
<td>Sextet 1</td>
<td>329.48</td>
<td>-0.02</td>
<td>0.05</td>
<td>0.16</td>
<td>13.1</td>
<td>Fe(^0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar ratio (FeS₂:ZVI)</th>
<th>9:1</th>
<th>10:1</th>
<th>11:1</th>
<th>10:0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI) removal rate (%)</td>
<td>99.9</td>
<td>92.71</td>
<td>79.48</td>
<td>26.8</td>
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Table S3. Linear regression analysis of mixed FeS$_2$-ZVI and FeS$_2$/ZVI for the kinetics of Cr(VI) removal.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FeS$_2$-ZVI</th>
<th>FeS$_2$/Fe$^0$</th>
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</thead>
<tbody>
<tr>
<td>Pseudo first-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$ (min$^{-1}$)</td>
<td>0.01</td>
<td>0.0254</td>
</tr>
<tr>
<td>$Q_e$ (mg g$^{-1}$)</td>
<td>13.92</td>
<td>49.93</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9355</td>
<td>0.9405</td>
</tr>
<tr>
<td>Pseudo second-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>0.006544</td>
<td>0.002137</td>
</tr>
<tr>
<td>$Q_e$ (mg g$^{-1}$)</td>
<td>11.95</td>
<td>52.08</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9939</td>
<td>0.9986</td>
</tr>
</tbody>
</table>
**Table S4.** Intrinsic properties of FeS$_2$/ZVI (molar ratio 9:1).

<table>
<thead>
<tr>
<th>Name</th>
<th>Content (mg g$^{-1}$)</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>S speciation (%)</th>
<th>Lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>S</td>
<td>SO$_4^{2-}$</td>
<td>S$^0$</td>
</tr>
<tr>
<td>FeS$_2$/ZVI</td>
<td>770</td>
<td>175</td>
<td>10.9</td>
<td>50.0</td>
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