Supplementary Materials for

Role of Dissolved Oxygen in Metal(loid)s Removal by Zerovalent Iron at Different pH: Its Dependence on the Removal Mechanisms

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Figure S1. Basic properties of pristine ZVI used in this study, including morphological appearances, particle size and mineral on the surface. (a) The scanning electron microscopy image; (b) The particle size distribution; (c) The Raman spectra. Morphological analysis was performed using a Hitachi 4700 microscope (at 15 kV). The size distribution of the Pri-ZVI particles was examined by Bettersize 2000 (Dandong Bettersize instruments Ltd., China). Raman spectra was collected using a DXR Raman Microscope (Thermo Fisher Scientific, Inc., China) with a 532 nm argon ion laser (2.0 mW), scanning from 100 cm$^{-1}$ to 1700 cm$^{-1}$ at room temperature. It should be noted that though the Raman spectroscopy identified FeOOH (goethite) in unreacted ZVI sample, it can be ignored for the very low quantity.
### Table S1. Half reactions, the corresponding standard reduction potential, and conditional reduction potential for the redox species involved in this study.

<table>
<thead>
<tr>
<th>Ox/Red</th>
<th>Half reaction</th>
<th>Standard reduction potential /V</th>
<th>Conditional reduction potential/V</th>
<th>pH 4.0</th>
<th>pH 6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(IV)/Se(0)</td>
<td>$\text{HSeO}_3^- + 5\text{H}^+ + 4\text{e}^- \rightarrow \text{Se} + 3\text{H}_2\text{O}$</td>
<td>0.74</td>
<td></td>
<td>0.444</td>
<td>0.296</td>
</tr>
<tr>
<td>Cr(VI)/Cr(III)</td>
<td>$\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$ (pH 4.0)</td>
<td>1.195</td>
<td></td>
<td>0.879</td>
<td>0.844</td>
</tr>
<tr>
<td></td>
<td>$\text{HCrO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{Cr(OH)}_3^+ + \text{H}_2\text{O}$ (pH 6.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)/Cu(0)</td>
<td>$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$</td>
<td>0.34</td>
<td></td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>Pb(II)/Pb(0)</td>
<td>$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$</td>
<td>-0.127</td>
<td></td>
<td>-0.127</td>
<td>-0.127</td>
</tr>
<tr>
<td>O$_2$/O(-II)</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.229</td>
<td></td>
<td>0.993</td>
<td>0.875</td>
</tr>
<tr>
<td>Fe(III)/Fe(II)</td>
<td>$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$</td>
<td>0.769</td>
<td></td>
<td>0.769</td>
<td>0.769</td>
</tr>
<tr>
<td>Fe(II)/Fe(0)</td>
<td>$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$</td>
<td>-0.44</td>
<td></td>
<td>-0.44</td>
<td>-0.44</td>
</tr>
<tr>
<td>Fe(OH)$_3$/Fe$^{2+}$</td>
<td>$\text{Fe(OH)}_3^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 3\text{OH}^-$</td>
<td>-1.51</td>
<td></td>
<td>0.26</td>
<td>-0.1</td>
</tr>
</tbody>
</table>
Figure S2. Eh–pH diagrams for species involved in this study (As(V) = 0.05 mM; Cr(VI) = 0.05 mM; Cu(II) = 0.2 mM; Pb(II) = 0.2 mM; Se(IV) = 0.2 mM; Temperature = 298 K; Suppressed iron phases: pyrite, pyrrhotite, and troilite.)
Figure S3. Schematic diagram of the experimental setup used in this study.
Figure S4. Kinetics of Fe(II) accumulation in the ZVI/H$_2$O systems without contaminant at pH 4.0 and 6.0. Reaction conditions: [Fe$^{0}$]$_0$ = 0.5 g/L, [NaCl] = 0.01 M.

Figure S5. Fractions of different Fe species in reacted ZVI samples collected in the process of removal by ZVI at pH 6.0, which were derived from the LCF of Fe $k^3$-weighted EXAFS spectra (reaction time: 3 h).
Figure S6. Concentration of total Fe in the ZVI/H$_2$O systems with As(V) at pH 4.0 and 6.0 (controlled).