Concomitant Electro-Fenton Processes in Iron-based Electrocoagulation System for Sulfanilamide Degradation: Roles of Ca$^{2+}$ in Fe(II)/Fe(III) Complexation and Electron Transfer

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Summary

Number of Pages: 12; Page S1–Page S12
Number of Pages for Scheme: 1; Page S3
Number of Figures: 12; Figure S1–Figure S12 (Page S4–Page S12)
Text S1. Experimental Setup

All experiments were carried out in a cuboid plexiglas cell (110 mm×50 mm×100 mm). A direct current (DC) power supply (BK Precision, US) was used to perform the experiments. Two graphite plates (50 mm×100 mm×5 mm) were used as driving electrodes with the interspacing distance of 100 mm, fixed with two alligator clips and connected with DC power supply using copper wire. Iron plates (80 mm×40 mm×0.2 mm) were used as bipolar electrodes (BPEs). All electrode materials were cleaned by ultrasonic wave, and then washed with ethanol and DI-water before they were used as electrodes. During the HA-modified E-Fenton tests, the BPEs were placed at the center of the cell, fixed by the slots on the inner wall of the reactor. In each cycle of experiment, the cell was filled with 200 mL solution. We applied potentiometric operation rather than constant current operation to ensure preservation of the driving anode and driving cathode by not over-oxidizing or over-reducing them.

Scheme 1. Diagram of the setup based on the reaction system of WEC.
Figure S1. Time course of Fe$^{2+}$ concentration under voltage applied in a range of 3 to 10 V.
Figure S2. Time course of Fe$^{3+}$ concentration under voltage applied in a range of 3 to 10 V.
Figure S3. Time course of the ratio of Fe$^{2+}$: Fe$^{3+}$ under voltage applied in a range of 3 to 10 V.
Figure S4. Changes in the percentage of Fe$^{2+}$/Fe$^{3+}$ and in the ratio of Fe$^{2+}$:Fe$^{3+}$ under the condition of initial solution pH in a range of 4 to 9, electrolytic time of 100 mins.
**Figure S5.** The evolution of the ratio of Fe$^{2+}$ : Fe$^{3+}$ with electrolytic time. The experiments were carried out at 3 V of applied voltage, H$_2$O$_2$ concentration of 0.5 mM a), 1 mM b), 2 mM c) and 4 mM d).
**Figure S6.** Time course of SA removal rate in the absence and presence of 4 mM Ca\(^{2+}\). The experiments were carried out at 3 V of applied voltage, H\(_2\)O\(_2\) concentration of 2 mM.
**Figure S7.** The energy dispersive spectrometer (EDS) image of Ca(II)/Fe(II)/Fe(III)-HA precipitates generated after 120 minutes settlement in iron-EC system under the condition of Ca$^{2+}$ concentration of 0 ppm a), 2 ppm b), 4 ppm c), 8 ppm d).
**Figure S8.** LC-MS/MS chromatogram of SA (Retention time = 3.125 min)

**Figure S9.** Mass spectrum of m/z [M+H]+ = 174

**Figure S10.** Mass spectrum of m/z [M+H]+ = 189

**Figure S11.** Mass spectrum of m/z [M+H]+ = 202.2
Figure S12. Mass spectrum of m/z [M+H]+ = 108.0

Figure S13. Mass spectrum of m/z [M+H]+ = 114.1