Supporting Information

For

Design of a Highly Efficient and Wide pH E-Fenton Oxidation System with Molecular Oxygen Activated by Ferrous-Tetrapolyphosphate Complex

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The detection of H_2O_2 in the absence of iron electrode: The hydrogen peroxide concentrations in the absence of iron electrode were determined by triiodide method. 0.75 mL of chromogenic agent containing 0.4 mol L^{-1} potassium iodide, 0.06 mol L^{-1} sodium hydroxide, and 1×10^{-4} mol L^{-1} ammonium molybdate was mixed with 0.75 mL of 1,2-benzenedicarboxylic acid (0.1 mol L^{-1}), followed by the addition of 1.5 mL of sample solution. The mixed solutions were analyzed after 2 min, measuring the absorbance at 352 nm with a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan).

The detection of H_2O_2 in the presence of iron electrode: The fluorescence reagent containing 2.7 mg of para-hydroxyphenylacetic acid and 1 mg of horseradish peroxidase in 10 mL of 8.2 g L^{-1} potassium hydrogen phthalate buffer solution was prepared firstly. For the real-time H_2O_2 concentration detection, 50 μL of fluorescence reagent was mixed with 2 mL of the sample for 10 min, followed by the addition of 1 mL of NaOH (0.1 mol L^{-1}) to quench the reaction and maintain the reaction solution at pH 10.0 or higher. But for the measurement of accumulative H_2O_2 concentration, 10 mL of the fluorescence reagent was added to the reaction solution of different

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electrochemical system instead of atrazine solution, 2 mL of the samples were taken out at predetermined time intervals, and then 1 mL of 0.1 mol L^{-1} NaOH solution was added. The reaction product of H_2O_2 with POHPAA fluorescence reagent had a strong fluorescent emission at 409 nm when excited at 315 nm.

Pre-treatment process of the reaction mixture: 20 mL of sample was extracted with 20 mL dichloromethane for three times. The combined extracts were dried with anhydrous sodium sulfate and the dichloromethane was removed using a rotary evaporators. The residue was re-dissolved in 1 mL of acetone GC-MS analysis or acetonitrile for LC-MS detection.

Identification of degradation intermediates by GC-MS and LC-MS. The identification of degradation intermediates was first performed by GC-MS. The final acetone extract (1.0 μL) was automatically injected into GC-MS with splitless mode. The oven temperature program was as follows. The initial temperature was 50 °C and held for 3 min, then heat up to 260 °C with a rate of 7 °C min^{-1}, and held at 260 °C for 10 min. The possible degradation intermediates were then identified by LC-MS. The column was maintained at 30 °C; the injected volume was 10 μL. The mobile phase used for gradient elution consisted of (A) acetonitrile and (B) water containing 0.75% formic acid. The gradient was linear from 95 to 50% of B in 30 min, followed by 50 to 10% of B in 5 min, and then held for 5 min. the mass spectra were recorded across the range of 50-300 m/z with the positive scan mode.

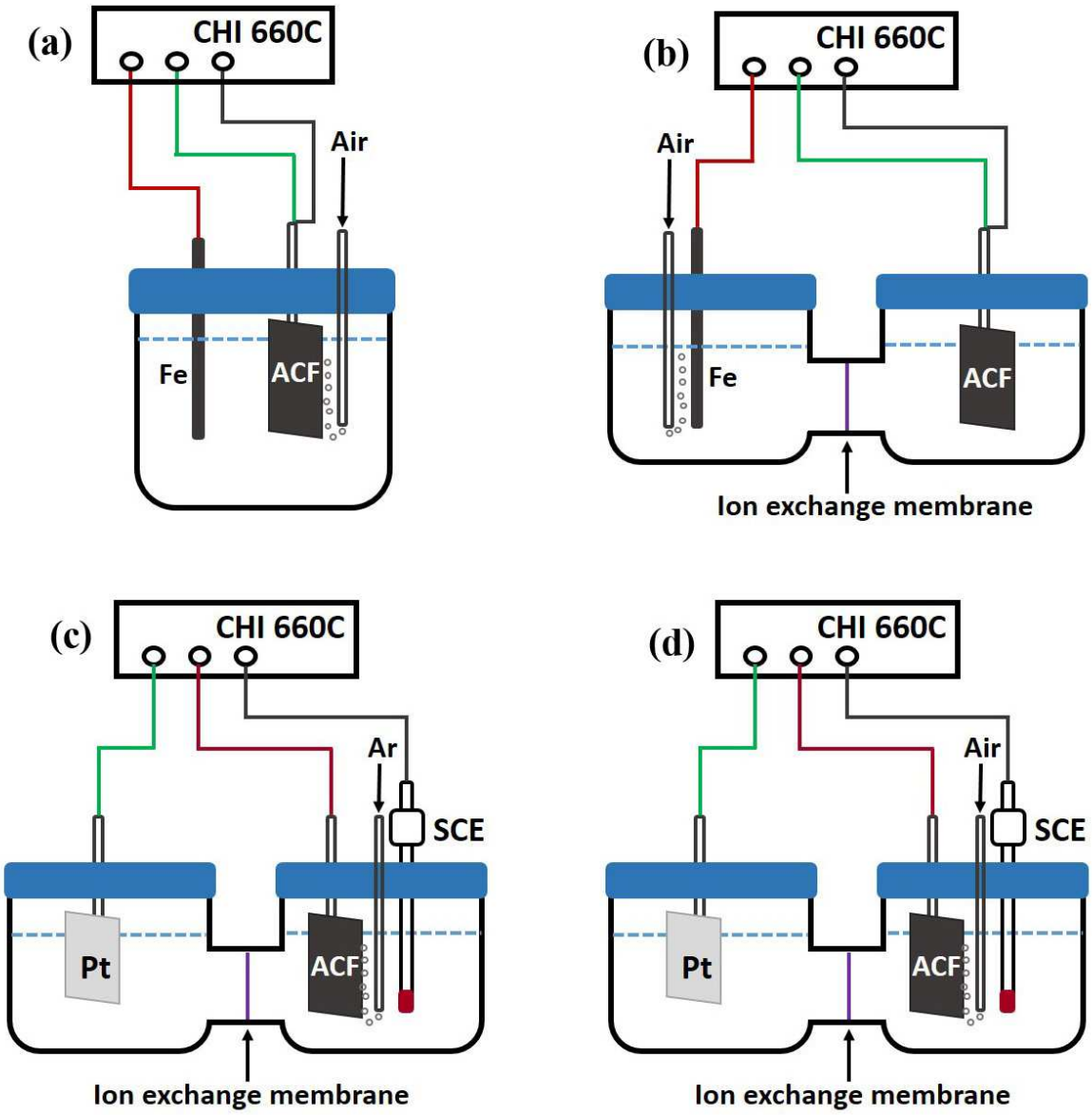


Figure S1. Configurations of the different electrochemical systems: (a) Na_6TPP-EF or Na_2SO_4-EF system (b) Na_6TPP-EC system (c) the separated dual-cell electrochemical system for the regeneration of Fe(II) by Fe(III) reduction on the ACF cathode (d) the separated dual-cell electrochemical system for atrazine degradation via the molecular oxygen activation process induced by the regenerated Fe(II).

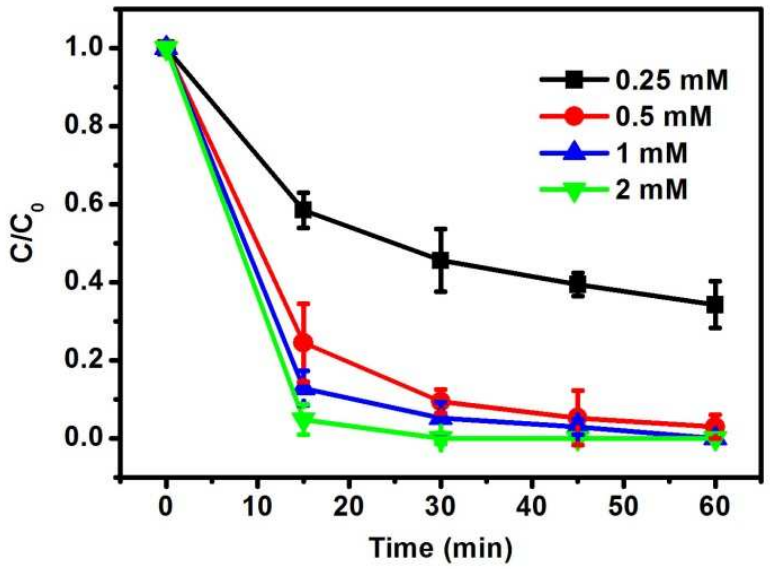


Figure S2. Effect of Na_6TPP concentration on the atrazine degradation in the Na_6TPP-EF system. The constant current was 0.5 mA, the concentration of atrazine was 10 mg L^{-1}, and the initial pH values were about 8.0.

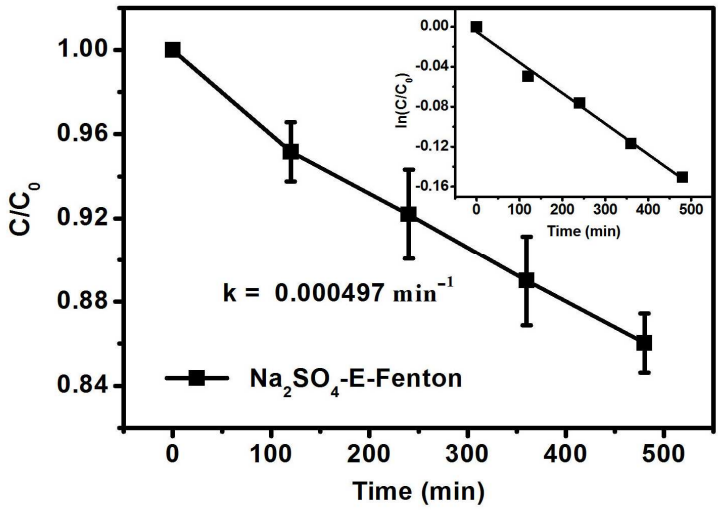


Figure S3. The atrazine degradation in the Na_2SO_4-EF system at pH 8.0. The constant current was 0.5 mA, the concentration of atrazine was 10 mg L^{-1}, and 0.5 mM of Na_2SO_4 was used as the electrolyte.

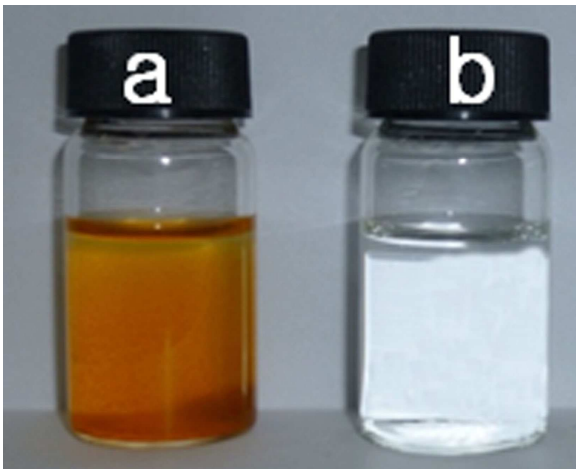


Figure S4. Pictures of the solutions of the Na_2SO_4-EF (a) and Na_6TPP-EF (b) systems after 180 min.

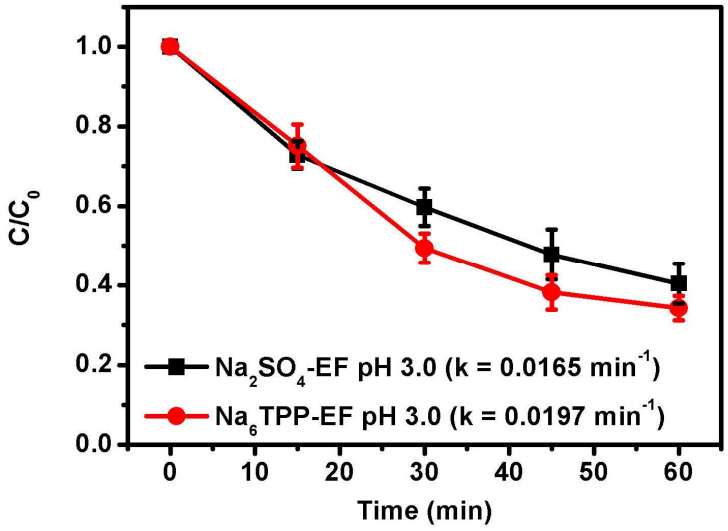


Figure S5. The atrazine degradation in the Na_2SO_4-EF and Na_6TPP-EF system at pH 3.0 with 0.5 mM of Na_6TPP or Na_2SO_4 as the electrolyte under a constant current of 0.5 mA. The initial concentration of atrazine was 10 mg L^{-1}.

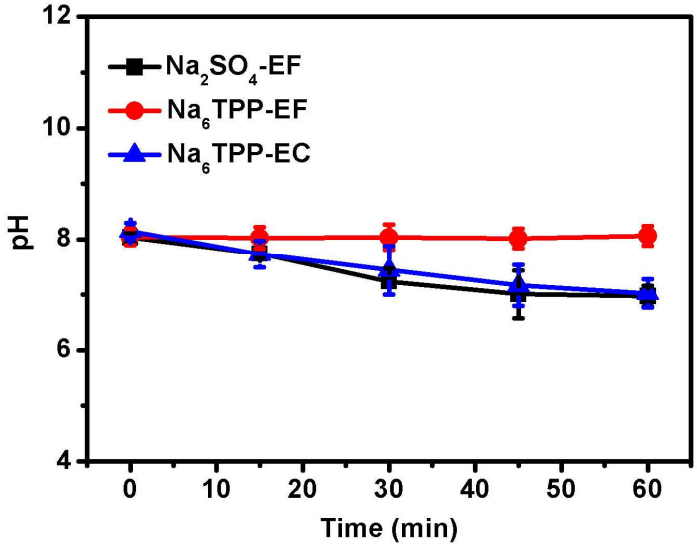


Figure S6. The pH value variations in different systems with 0.5 mM of Na_6TPP or Na_2SO_4 as the electrolyte under a constant current of 0.5 mA. The initial concentration of atrazine was 10 mg L^{-1}. The initial pH values were 8.0.

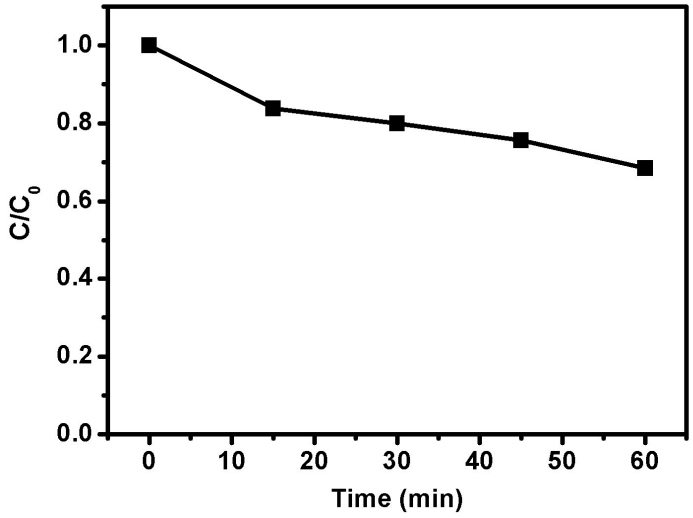


Figure S7. The atrazine degradation in the Na_6TPP-EF system without applied any current (0 mA). 0.5 mM of Na_6TPP was used as the electrolyte. The concentration of atrazine was 10 mg L^{-1}, and the initial pH value was about 8.0.

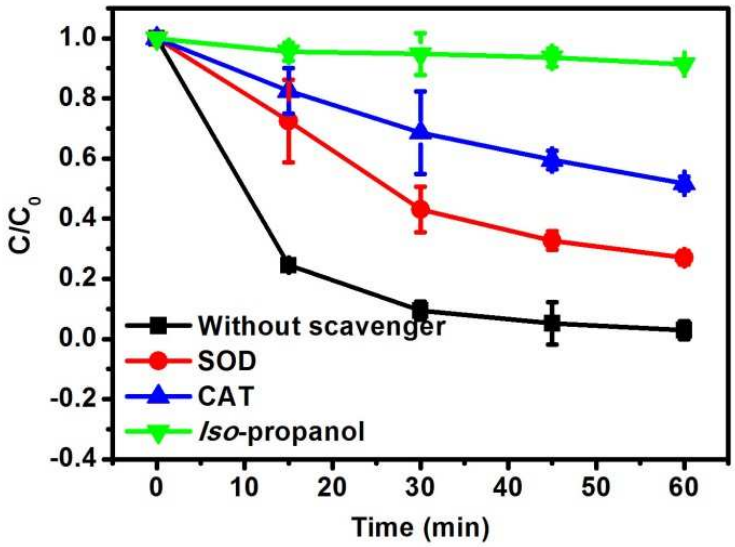


Figure S8. The atrazine degradation in the Na_6TPP-EF system with adding different scavengers. The constant current was 0.5 mA, the concentration of atrazine was 10 mg L^{-1}, 0.5 mM of Na_6TPP was used as electrolyte, and the initial pH values were about 8.0. The concentrations of SOD, CAT and *iso*-propanol were 250-700 U mL^{-1}, 400-1000 U mL^{-1} and 200 mM, respectively.

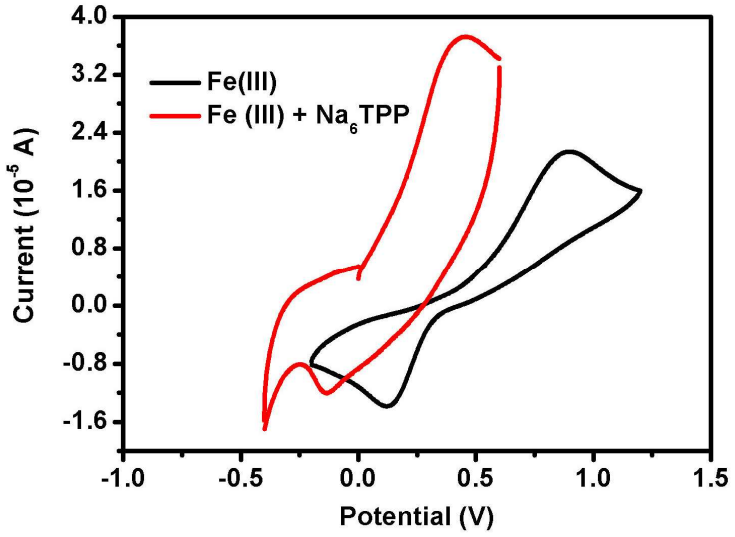


Figure S9. CV curves of Fe(III) and Fe(III) + Na_6TPP systems. Three electrode system, electrolyte: Na_2SO_4, 0.5 mol L^{-1}, scan rate: 5 mV s^{-1}. The concentrations of Fe(III) and Na_6TPP were 0.3 and 0.5 mM, respectively.

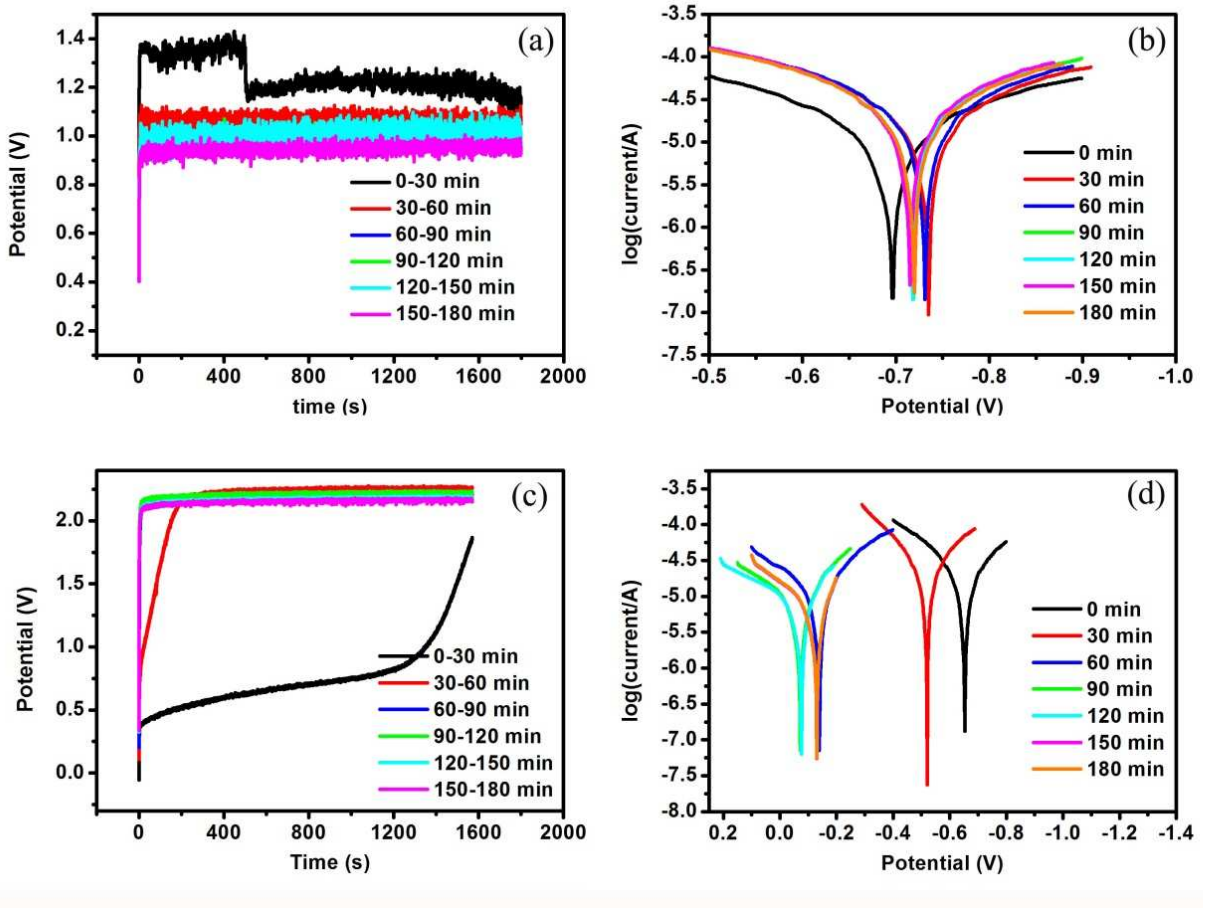


Figure S10. (a) and (c) Cell voltage verse time of the Na_2SO_4-EF and Na_6TPP-EF systems, respectively. (b) and (d) Tafel scans of iron electrode in the presence of 0.5 mM Na_2SO_4 and Na_6TPP, respectively.

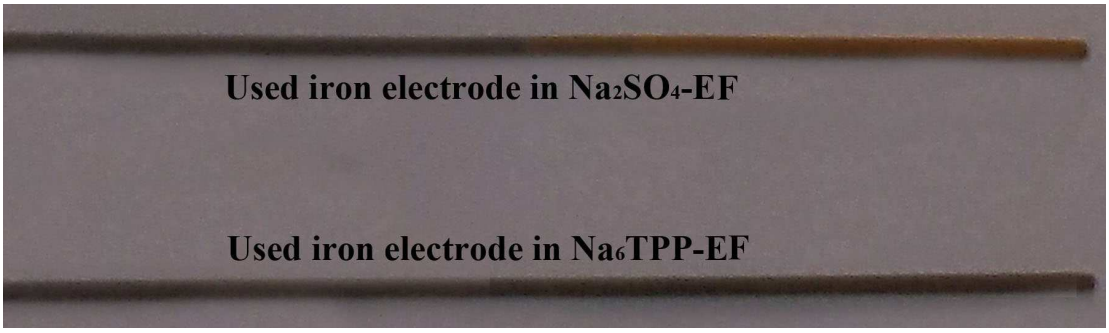


Figure S11. Pictures of the used iron electrodes in the Na_2SO_4-EF and Na_6TPP-EF systems after 180 min.

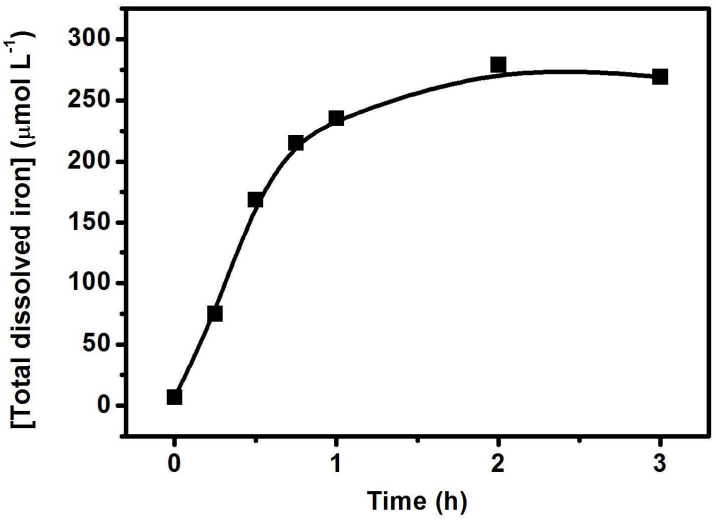


Figure S12. The concentration of total dissolved iron as a function of time during the degradation of 50 mL of a 20 mg L^{-1} atrazine solution with 0.5 mM Na_6TPP as the electrolyte at a constant current of 0.5 mA and pH 8.0.

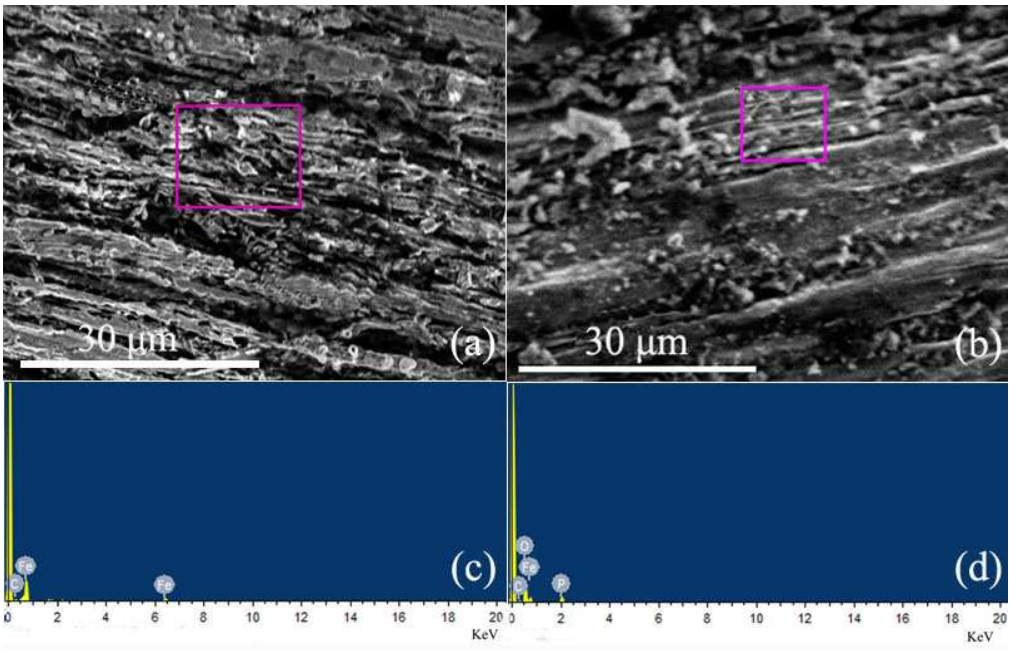


Figure S13. SEM images of the pristine iron electrode (a) and the used iron electrode in the Na_6TPP-EF system (b); EDS graphs of the pristine iron electrode (c) and the used iron electrode in the Na_6TPP-EF system (d).

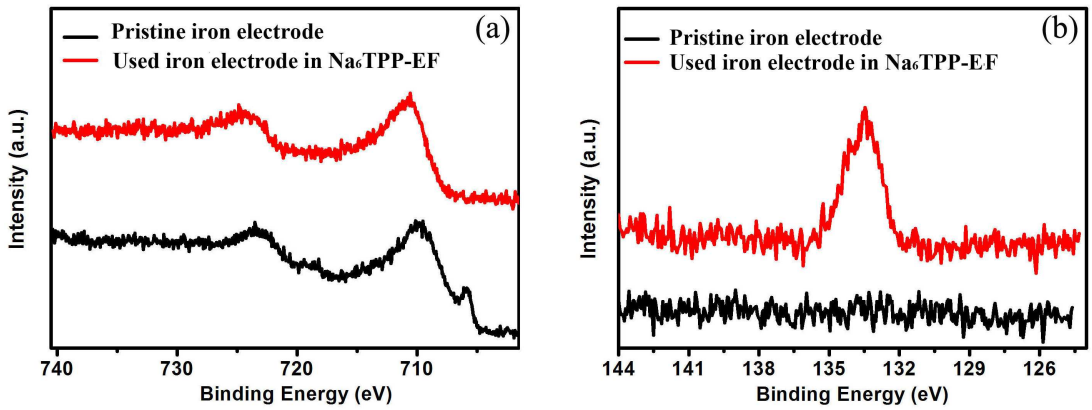


Figure S14. (a) High-resolution XPS of Fe 2p and Fe^0 of the pristine iron electrode and the used iron electrode in the Na_6TPP-EF system. (b) High-resolution XPS of P 2p of the pristine iron electrode and the used iron electrode in the Na_6TPP-EF system.

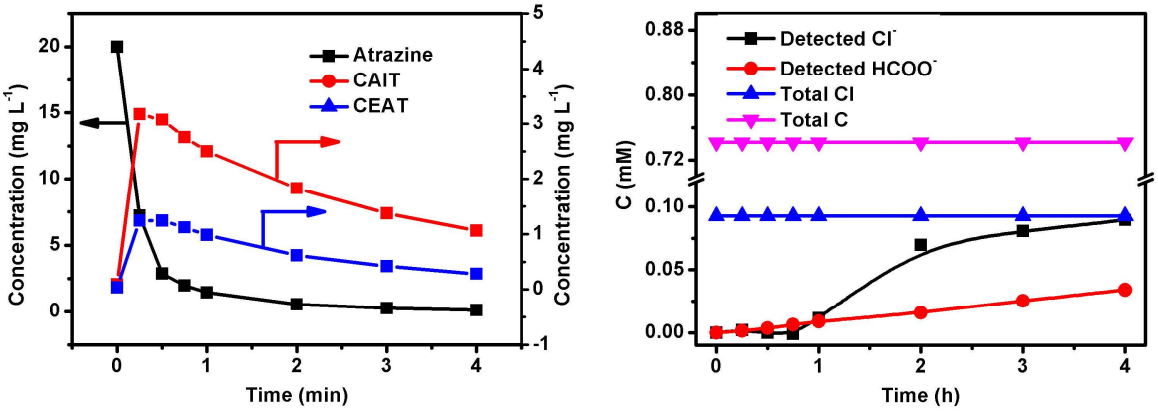
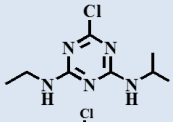
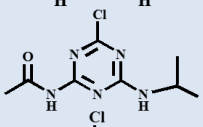
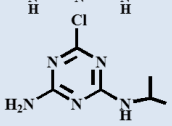
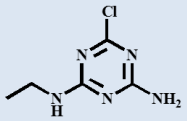
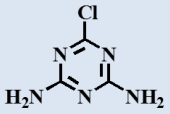
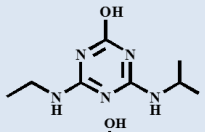
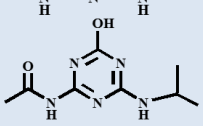
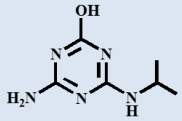
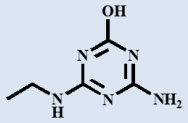
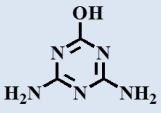
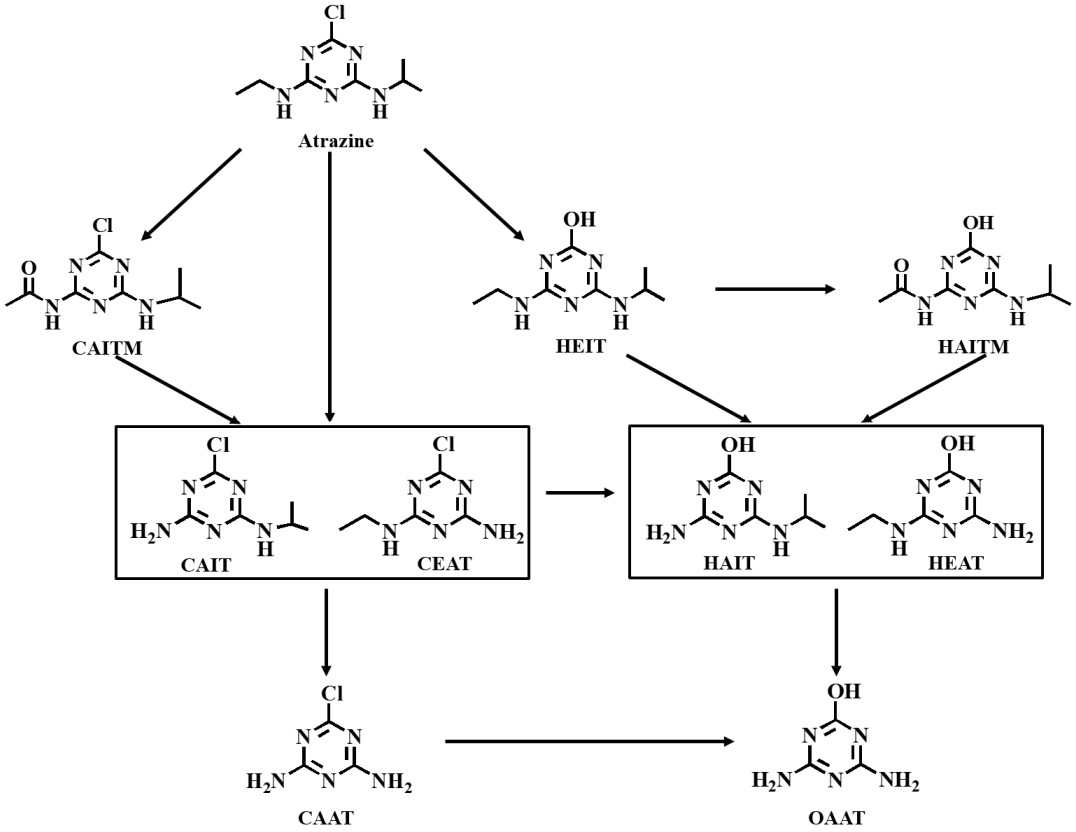


Figure S15. (a) Decay of atrazine concentration and evolution of the main aromatic intermediates (b) Evolution of chloride ions and formic acid during the degradation of 50 mL of a 20 mg L^{-1} atrazine solution with 0.5 mM Na_6TPP as the electrolyte at a constant current of 0.5 mA and pH 8.0.

Table S1. Chemical name, structural formula and abbreviation of atrazine and its degradation intermediates.

Chemical Name	Structural Formula	Abbreviation	Detected
2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine		Atrazine	HPLC GC-MS LC-MS
2-Chloro-4-acetamido-6-isopropylamino-1,3,5-triazine		CAITM	LC-MS
2-Chloro-4-amino-6-isopropylamino-1,3,5-triazine		CAIT	HPLC GC-MS LC-MS
2-Chloro-4-ethylamino-6-Amino-1,3,5-triazine		CEAT	HPLC GC-MS LC-MS
2-Chloro-4,6-diamino-1,3,5-triazine		CAAT	GC-MS
2-Hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine		HEIT	LC-MS
2-Hydroxy-4-acetamindo-6-isopropylamino-1,3,5-triazine		HAITM	LC-MS
2-Hydroxy-4-amino-6-isopropylamino-1,3,5-triazine		HAIT	LC-MS
2-Hydroxyl-4-ethylamino-6-amino-1,3,5-triazine		HEAT	LC-MS
2-Hydroxy-4,6-diamino-1,3,5-triazine		OAAT	LC-MS



Scheme S1. A possible degradation pathway of atrazine in the Na_6TPP-EF system.

Table S2. The TPP and Fe(III)-TPP complex recovery with anion exchange resin.

	TPP	Fe(III)+ TPP	
		TPP	Fe(III)
Before the treatment	**0.5 mM**	**0.5 mM**	**0.25 mM**
After the treatment	**0**	**0**	**0.052 mM**