

SUPPORTING INFORMATION

A Novel Strategy of Combined Pulsed Electro-oxidation and Electrolysis for Degradation of Sulfadiazine

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Test S1. Response surface methodology (RSM) analysis

According to the Box-Benhnken design prinSNDle, the response surface test results were fitted to the second-order model data, and the regression equation was obtained as follows:

$$\text{SND degradation rate} = 70.07 + 8.20A + 3.41B - 2.64C - 0.81AB + 0.26AC + 4.04BC - 14.28A^2 - 6.31B^2 - 5.21C^2$$

Test S2. EPR instrumental parameters

The center field of the spectrometer was 3897 G, resonance frequency (empty) of 9.81 GHz. The signal of free radicals that were trapped by 5,5-dimethyl-pyrroline-oxide (DMPO). The sample solution and 50 μ M DMPO solution were mixed quickly at a ratio of 2:1 (v/v) to get adducts. Operating parameters: Center field, 3385 G; Static field, 3285 G; sweep width, 200 G; Modulation frequency, 100 kHz; Modulation amplitude, 2.00 G; Microwave bridge frequency, 9.52 GHz; Power, 2.00 mW. Four equidistance and highly intense peaks with intensity ratio of approximately 1:2:2:1 and six low intensity peaks whose ratio was approximately 1:1:1:1:1:1 as signed to DMPO–OH and DMPO–OSO₃H, respectively. The hyperfine splitting constants for the modeled spectra were as follows: $a_H = a_N = 14.9$ G for DMPO–OH; $a_N = 12.2$ G, $a_H = 10.28$ G, 2.58 G and 0.1 G for DMPO–OSO₃H.

Test S3. Analytical methods of byproducts.

For characterization of SND degradation by HPLC-MC/MS (Agilent Technologies, USA), the Column - C18 (2.1×100 mm, $1.7 \mu\text{m}$) was used. The mass spectrometric analysis was conducted using positive/ negative electrospray ionization with a mass scan range of m/z 50-1000. The capillary voltage, cone voltage, desolvation temperature, and source temperature were set at 2000 V, 40 V, 450°C , and 115°C , respectively.

10 μL of the samples was injected into column with the mobile phases of 10mM ammonium acetate/methanol (10/90, v/v). The flow rate was set at 0.2 mL min^{-1} and the column temperature maintained at 30°C , operated with electro spray ionization (ESI) in negative mode.

Tables

Table S1 First order kinetics of SND degradation with different PMS concentration

PMS (g/L)	k/min ⁻¹	R ²
0.05	2.2×10 ⁻³	0.8414
0.1	6.02×10 ⁻³	0.9933
0.3	6.35×10 ⁻³	0.9761
0.5	8.01×10 ⁻³	0.9775
1	8.25×10 ⁻³	0.9589

Table S2 First order kinetics of SND degradation with different frequency

Frequency (Hz)	k/min ⁻¹	R ²
500	4.74×10 ⁻³	0.9744
1000	1×10 ⁻²	0.9881
3000	1.04×10 ⁻²	0.9958
5000	9.73×10 ⁻³	0.9941
20000	6.45×10 ⁻³	0.9782

Table S3 First order kinetics of SND degradation with different pH

pH	k/min ⁻¹	R ²
1	1.45×10 ⁻²	0.9906
3	1.04×10 ⁻²	0.9958
5	5.9×10 ⁻³	0.9965
7	5.13×10 ⁻³	0.9801
9	3.54×10 ⁻³	0.9497

Table S4 First order kinetics of SND degradation with different electrode inter distance

Electrode inter distance (cm)	k/min ⁻¹	R ²
2.1	3.79×10 ⁻³	0.9772
2.8	7.67×10 ⁻³	0.9984
3.5	1.04×10 ⁻²	0.9958
4.2	8.71×10 ⁻³	0.9929
4.9	9.49×10 ⁻³	0.9942

Table S5 First order kinetics of SND degradation with different voltage

Voltage (V)	k/min ⁻¹	R ²
4	5.36×10 ⁻³	0.9929
5	8.01×10 ⁻³	0.9775
6	8.3×10 ⁻³	0.9704
7	1×10 ⁻²	0.9877
8	1.06×10 ⁻²	0.9848

Table S6 First order kinetics of SND degradation with different duty cycle

Duty cycle (%)	k/min ⁻¹	R ²
10	5.14×10 ⁻³	0.9536
30	9.52×10 ⁻³	0.9994
50	1×10 ⁻²	0.9877
70	9.85×10 ⁻³	0.9693
90	1.02×10 ⁻²	0.9523

Table S7 First-order kinetics of SND degradation with different reaction systems

Reaction systems	k/min ⁻¹	R ²
PMS alone	2.72×10 ⁻³	0.9624
Direct alone	6.17×10 ⁻³	0.9724
Direct+PMS	6.6×10 ⁻³	0.9763
Pulse alone	6.97×10 ⁻³	0.9725
Pulse+PMS	1.04×10 ⁻²	0.9958

Table S8 Variance analysis for the established regression model

Sources of variation	Quadratic sum	Degree of freedom	Mean square	F	P	Clinical significance
Model	1995.20	9	221.69	381.89	<0.0001	**
A	537.59	1	537.59	926.08	<0.0001	**
B	92.75	1	92.75	159.78	<0.0001	**
C	55.76	1	55.76	96.05	<0.0001	**
AB	2.59	1	2.59	4.47	0.0725	
AC	0.26	1	0.26	0.45	0.5247	
BC	65.45	1	65.45	112.74	<0.0001	**
A ²	859.08	1	859.08	1479.89	<0.0001	**
B ²	167.59	1	167.59	288.70	<0.0001	**
C ²	114.47	1	114.47	197.18	<0.0001	**
Residual error	4.06	7	0.58			
Lack of fit	1.90	3	0.63	1.17	0.4255	
Pure error	2.17	4	0.54			
Total variation	1999.26	16				
R ²					0.9980	
R ² _{Adj}					0.9954	
R ² _{Pred}					0.9831	

**P≤0.01 means factors have a significant impact on the response value.

Table S9 Reaction rate of radical inhibitors with hydroxyl and sulfate radicals

Radical inhibitors	Rate constants/ ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$)	
	$\cdot\text{OH}$	$\text{SO}_4\cdot^-$
SND	8.78×10^9	4.16×10^{10}
MeOH	9.7×10^8	3.2×10^6
Ethanol	$(1.2\sim 2.8)\times 10^9$	$(1.6\sim 7.7)\times 10^7$
TBA	$(3.8\sim 7.6)\times 10^9$	$(4\sim 9.1)\times 10^5$
Nitrobenzene	$(3\sim 3.9)\times 10^9$	1.2×10^5

Table S10 Chemical and physical character of SND.

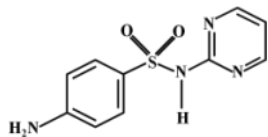
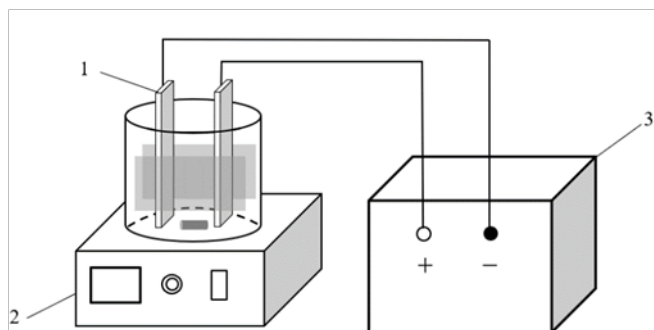
Characters	Value
Molecule structure	 <chem>Nc1ccc(cc1)S(=O)(=O)Nc2ccncc2</chem>
	C ₁₀ H ₁₀ N ₄ O ₂ S
Molar mass	250.28
pK _{a1}	2.49
pK _{a2}	6.48

Table S11 Contribution rate of active species oxidized substance degradation by PMS activated

	by different electric fields	
	$\text{SO}_4^{\bullet-}$	$\bullet\text{OH}$
PEF/PMS	12	30
CEF/PMS	4	10

Figures



1. Graphite electrode; 2. Magnetic stirring controller; 3. Power supply.

Figure S1. Diagram of experimental device.

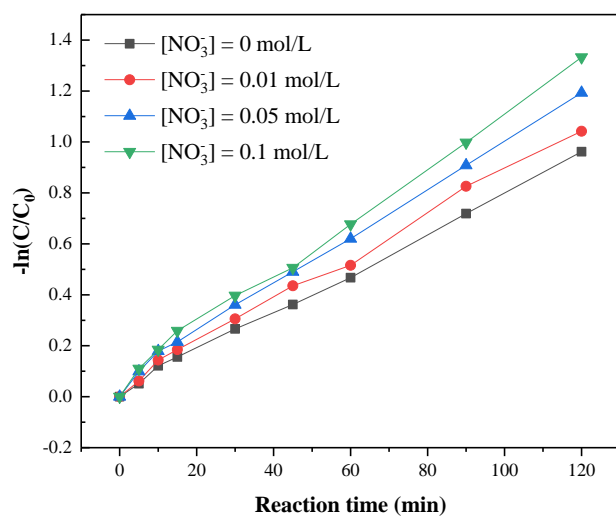
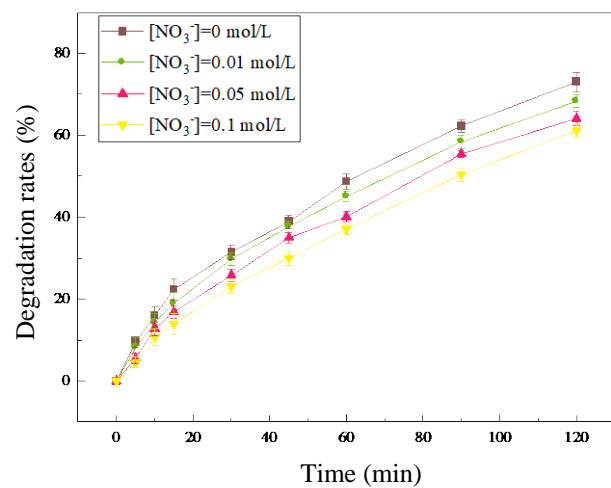


Figure. S2 Effect of NO_3^- concentration on SND degradation

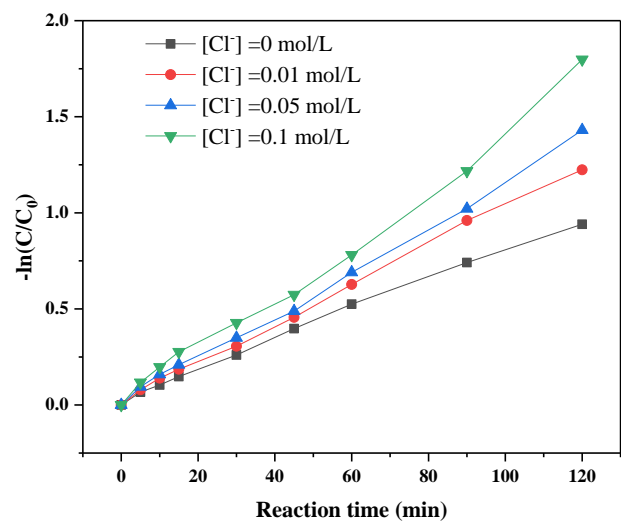
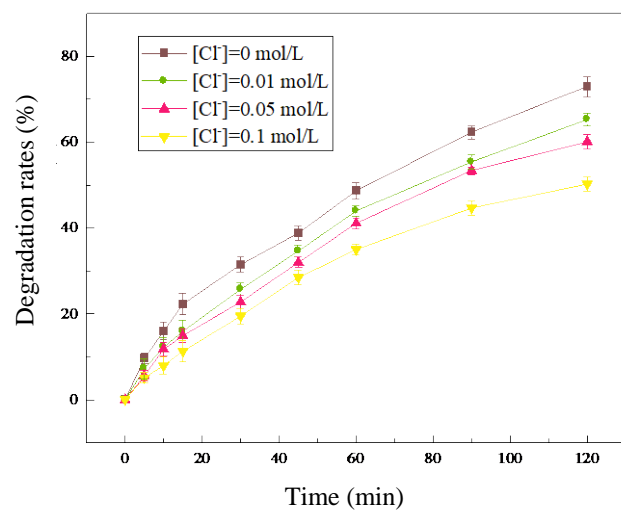


Figure. S3 Effect of Cl^- concentration on SND degradation

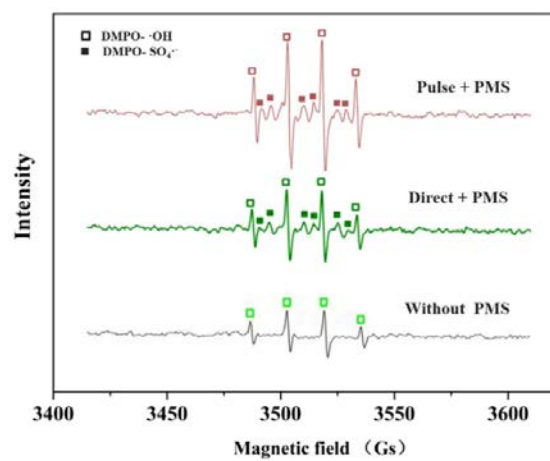


Figure S4. ESR spectra at three reaction systems

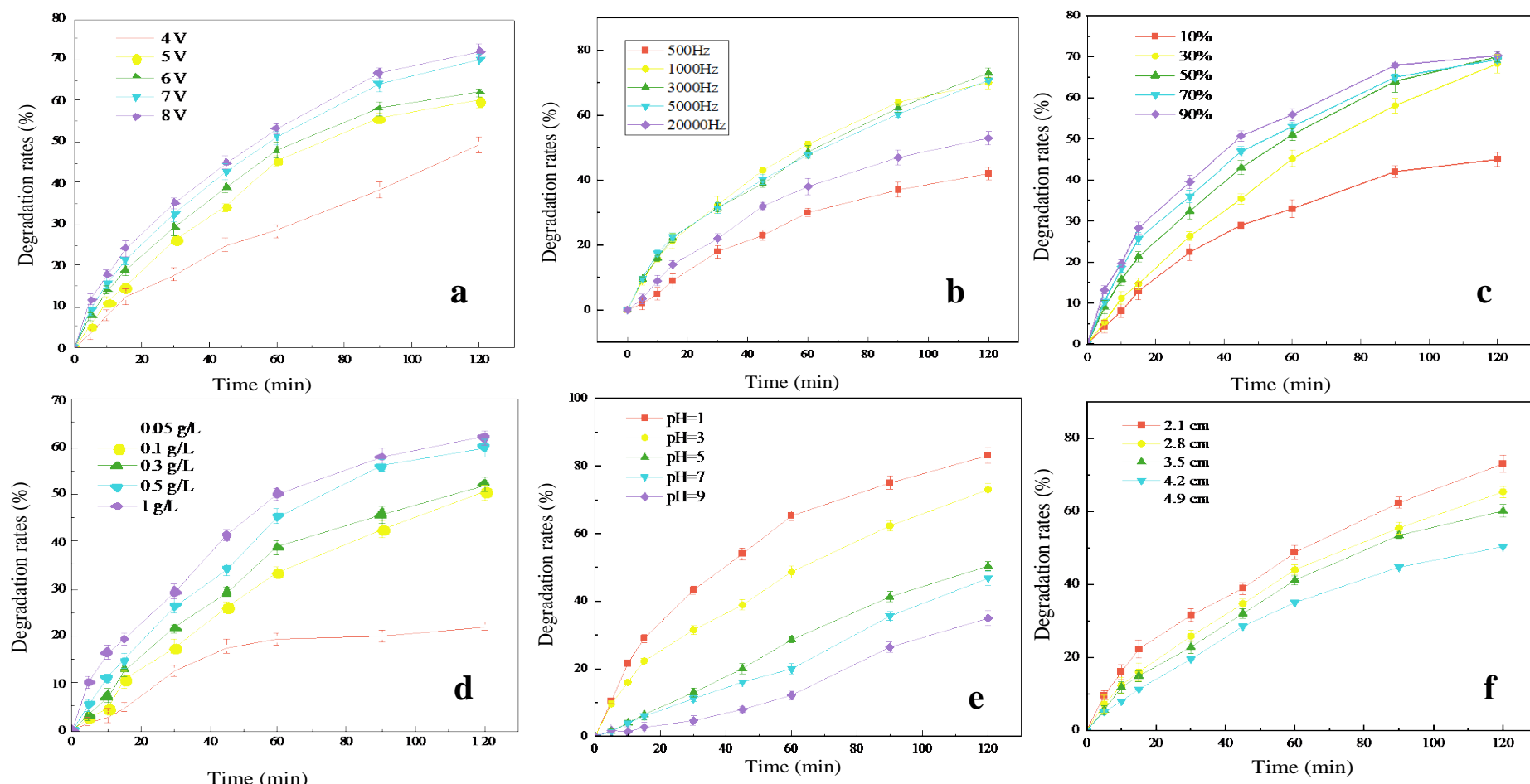


Figure S5. Effect of operation parameters on degradation rate of SND. (a) Initial PMS concentration; (b) Voltage of PEF; (c) Frequency of PEF; (d) Duty cycle of PEF; (e) Initial pH value; (f) Electrode inter distance