Supporting Information

Insights into the potential applications of permanganate/peroxymonosulfate systems: Enhancement by amorphous MnO_2, effects of water matrices, optimization by response surface methodology

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Supplementary Catalogue

FIGURES

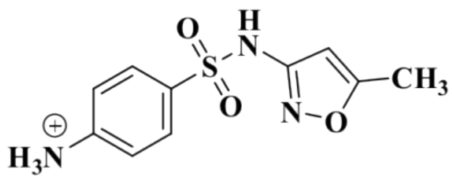


Fig. S1. The chemical structure of SMX（m/z=254）

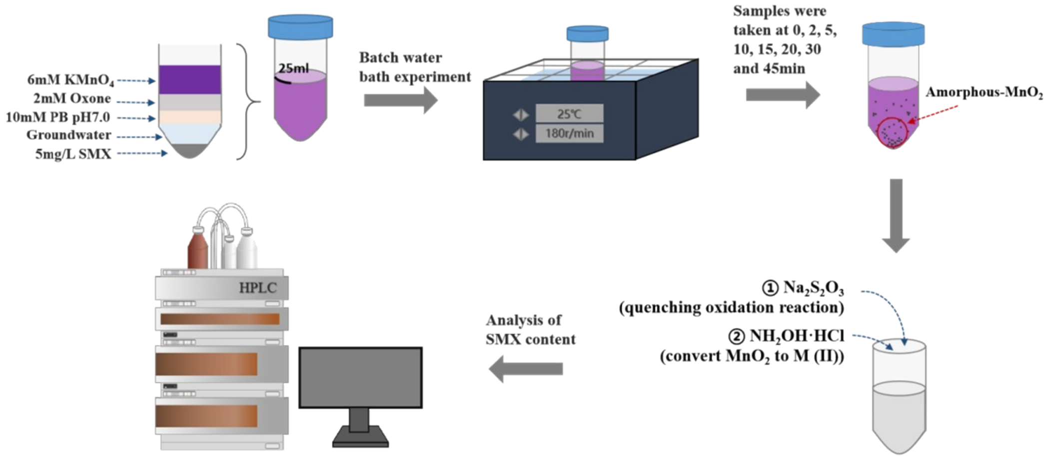


Fig. S2. Batch oxidation experiment operating procedure

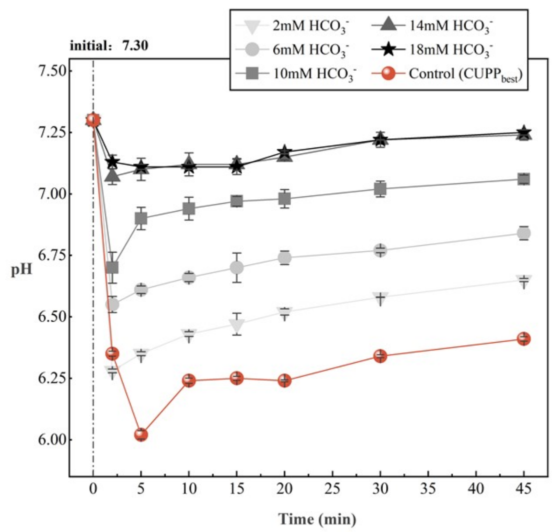
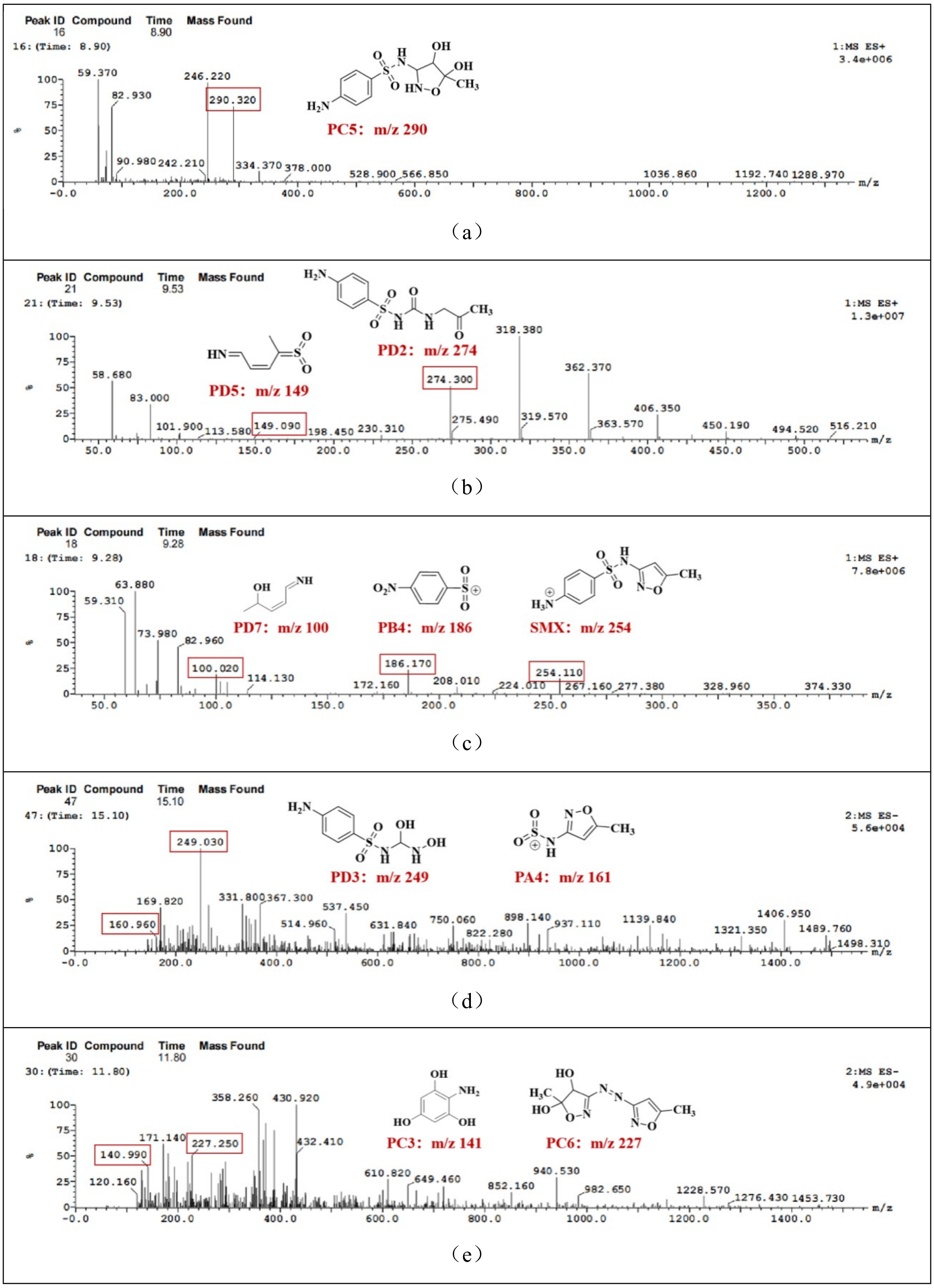
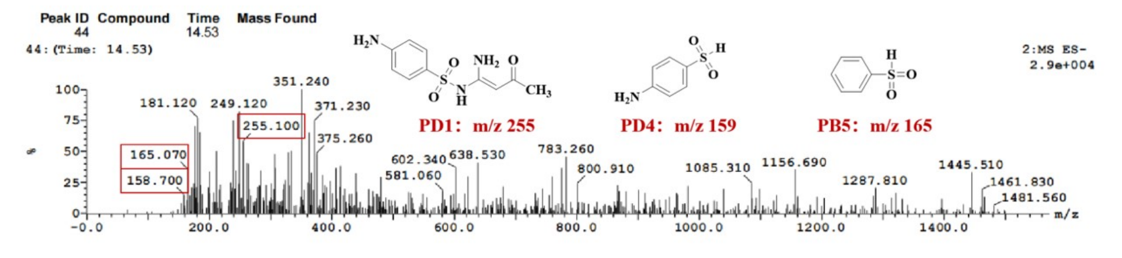


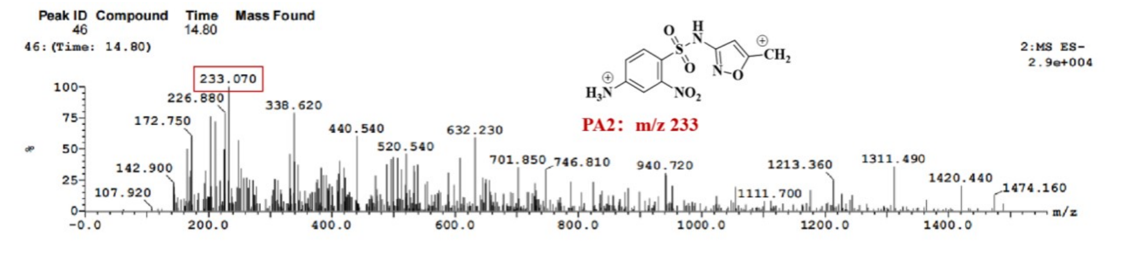
Fig. S3. Effect of bicarbonate addition on pH Changes in CUPP system degradation of SMX



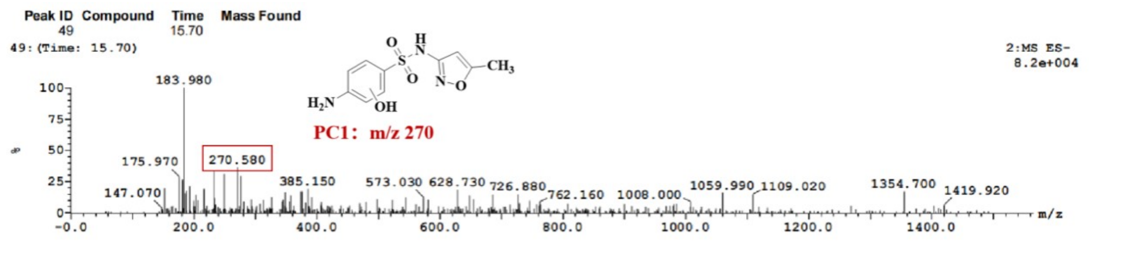
Peak ID Compound Time Mass Found
16 8.90
16: (Time: 8.90)
1:MS ES+ 3.4e+006
PC5：m/z 290
59.370
82.930
246.220
290.320
90.980
242.210
334.370
378.000
528.900
566.850
1036.860
1192.740
1288.970
m/z
(a)
Peak ID Compound Time Mass Found
21 9.53
21: (Time: 9.53)
1:MS ES+ 1.3e+007
PD2：m/z 274
PD5：m/z 149
58.680
83.000
101.900
113.580
149.090
198.450
230.310
274.300
275.490
318.380
319.570
362.370
363.570
406.350
450.190
494.520
516.210
(b)
Peak ID Compound Time Mass Found
18 9.28
18: (Time: 9.28)
1:MS ES+ 7.8e+006
PD7：m/z 100
PB4：m/z 186
SMX：m/z 254
63.880
59.310
73.980
82.960
100.020
114.130
172.160
186.170
208.010
224.010
254.110
267.160
277.380
328.960
374.330
(c)
Peak ID Compound Time Mass Found
47 15.10
47: (Time: 15.10)
2:MS ES- 5.6e+004
PD3：m/z 249
PA4：m/z 161
249.030
169.820
160.960
331.800
367.300
537.450
514.960
631.840
750.060
822.280
898.140
937.110
1139.840
1321.350
1406.950
1489.760
1498.310
(d)
Peak ID Compound Time Mass Found
30 11.80
30: (Time: 11.80)
2:MS ES- 4.9e+004
PC3：m/z 141
PC6：m/z 227
358.260
430.920
171.140
227.250
140.990
432.410
120.160
610.820
649.460
852.160
940.530
982.650
1228.570
1276.430
1453.730
(e)


Peak ID 44 Compound Time 14.53 Mass Found
44: (Time: 14.53)
2:MS ES-
2.9e+004
PD1: m/z 255
PD4: m/z 159
PB5: m/z 165
351.240
181.120
249.120
371.230
255.100
375.260
165.070
158.700
602.340
638.530
581.060
783.260
800.910
1085.310
1156.690
1287.810
1445.510
1461.830
1481.560
m/z

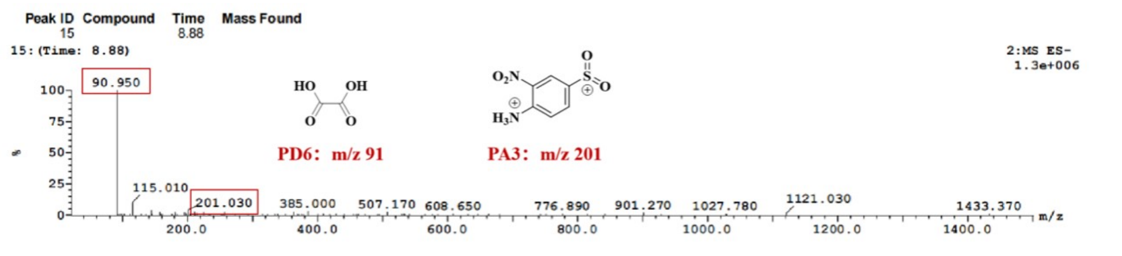
（f）


Peak ID 46 Compound Time 14.80 Mass Found
46: (Time: 14.80)
2:MS ES-
2.9e+004
PA2: m/z 233
233.070
226.880
338.620
172.750
440.540
632.230
520.540
701.850
746.810
940.720
1213.360
1311.490
142.900
1420.440
107.920
1111.700
1474.160
m/z

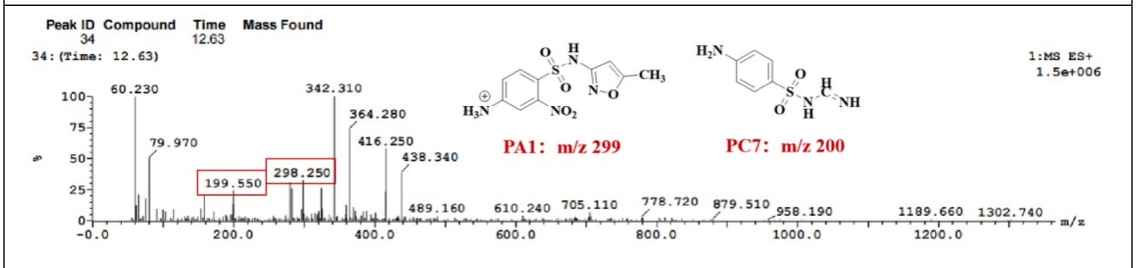
（g）


Peak ID 49 Compound Time 15.70 Mass Found
49: (Time: 15.70)
2:MS ES-
8.2e+004
PC1: m/z 270
183.980
175.970
270.580
385.150
573.030
628.730
726.880
147.070
762.160
1008.000
1059.990
1109.020
1354.700
1419.920
m/z

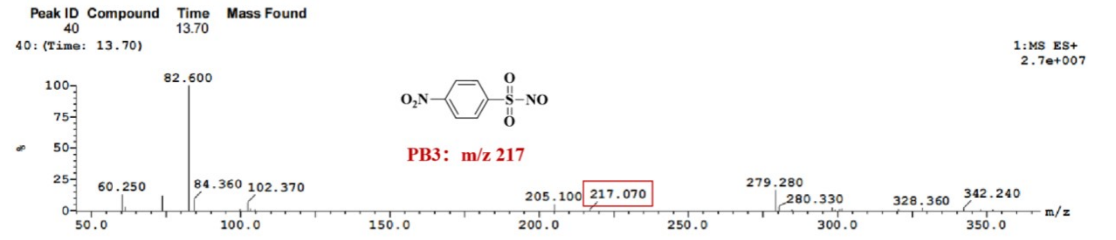
（h）


Peak ID 15 Compound Time 8.88 Mass Found
15: (Time: 8.88)
2:MS ES-
1.3e+006
PD6: m/z 91
PA3: m/z 201
90.950
115.010
201.030
385.000
507.170
608.650
776.890
901.270
1027.780
1121.030
1433.370
m/z

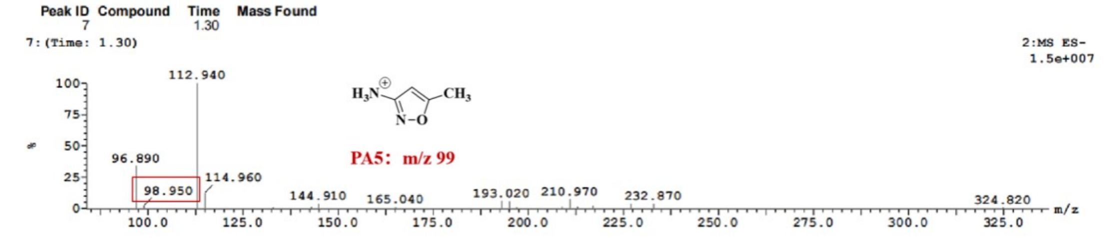
（i）


Peak ID 34 Compound Time 12.63 Mass Found
34: (Time: 12.63)
1:MS ES+
1.5e+006
PA1: m/z 299
PC7: m/z 200
60.230
342.310
364.280
79.970
416.250
438.340
298.250
199.550
489.160
610.240
705.110
778.720
879.510
958.190
1189.660
1302.740
m/z

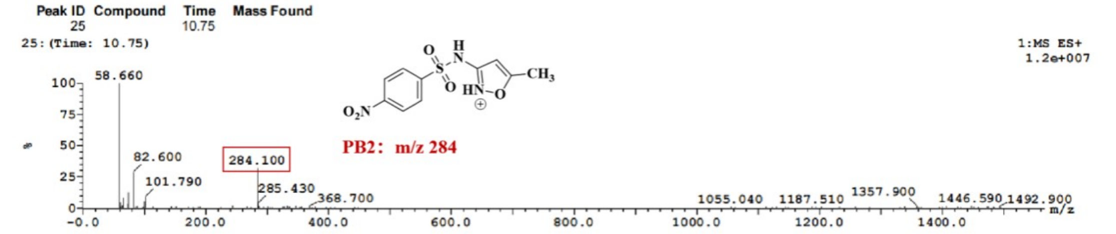
（j）


Peak ID Compound Time Mass Found
40 13.70
40: (Time: 13.70)
1:MS ES+
2.7e+007
82.600
60.250
84.360
102.370
205.100
217.070
279.280
280.330
328.360
342.240
PB3: m/z 217
m/z

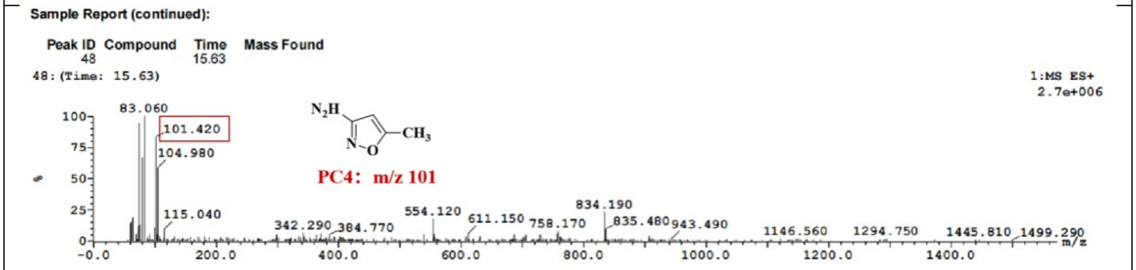
（k）


Peak ID Compound Time Mass Found
7 1.30
7: (Time: 1.30)
2:MS ES-
1.5e+007
112.940
96.890
98.950
114.960
144.910
165.040
193.020
210.970
232.870
324.820
PA5: m/z 99
m/z

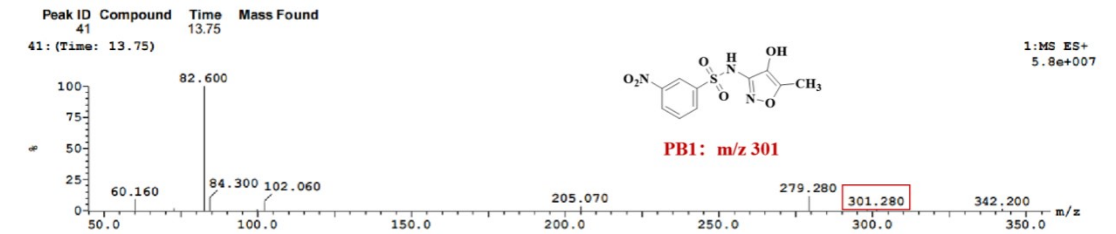
（l）


Peak ID Compound Time Mass Found
25 10.75
25: (Time: 10.75)
1:MS ES+
1.2e+007
58.660
82.600
101.790
284.100
285.430
368.700
1055.040
1187.510
1357.900
1446.590
1492.900
PB2: m/z 284
m/z

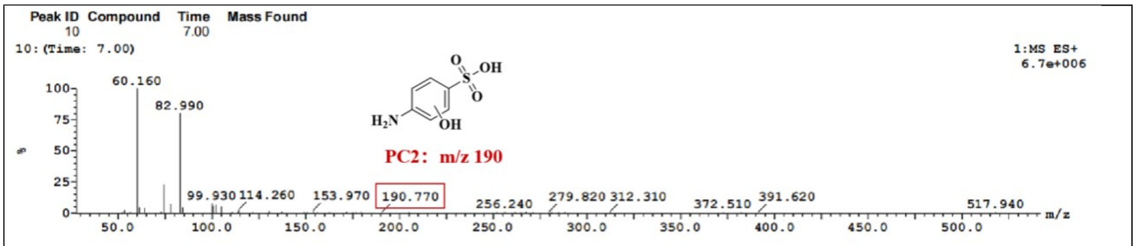
（m）


Sample Report (continued):
Peak ID Compound Time Mass Found
48 15.63
48: (Time: 15.63)
1:MS ES+
2.7e+006
83.060
101.420
104.980
115.040
342.290
384.770
554.120
611.150
758.170
834.190
835.480
943.490
1146.560
1294.750
1445.810
1499.290
PC4: m/z 101
m/z

（n）


Peak ID Compound Time Mass Found
41 13.75
41: (Time: 13.75)
1:MS ES+
5.8e+007
82.600
60.160
84.300
102.060
205.070
279.280
301.280
342.200
PB1: m/z 301
m/z

（o）



（p）

Fig. S4. (a)~(p): The retention time of each degradation intermediate, fragment ion and corresponding mass spectrometry of SMX

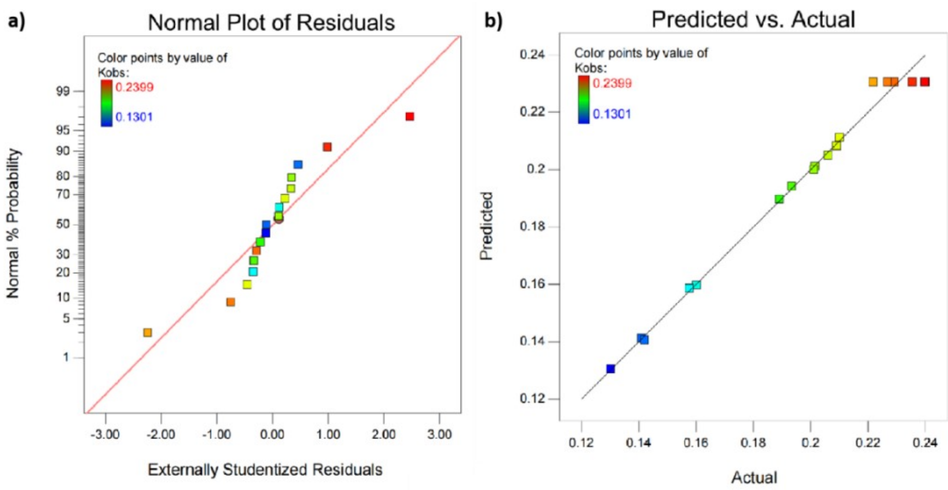
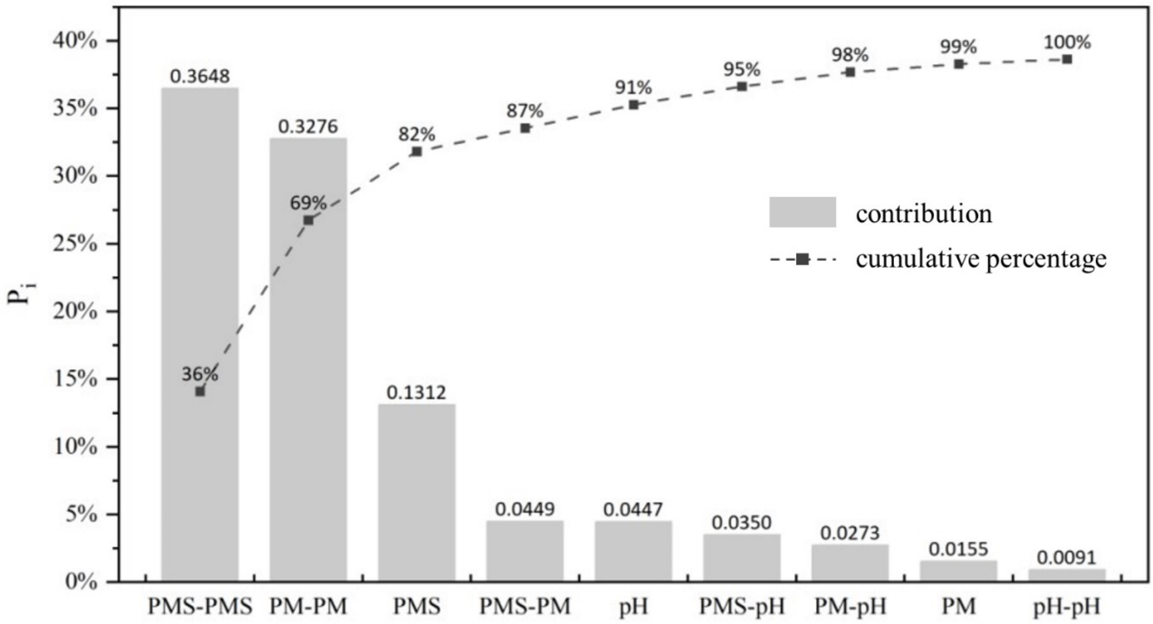


Fig. S5. a) Residual distribution map; b) The degree to which the predicted value of the response value is close to the actual value



（Note：P_i represents the contribution value of each factors）

Fig. S6. Contribution of each influence factor to response (Pareto chart)

TABLES

Table S1. List of materials and reagents

Reagent name	Chemical formula	Purity	Company
Sulfonamethoxazole (SMX)	$C_{10}H_{11}N_3O_3S$	≥98%	PTSRTI
Permanganate	$KMnO_4$	AR	CHENGDU SHUDU Chemical Reagent
Peroxymonosulfate (Oxone)	$KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$	≥42%	
Sodium Carbonate	Na_2CO_3	AR	
Sodium Bicarbonate	$NaHCO_3$	AR	
Hyposulphite	$Na_2S_2O_3$	AR	
Potassium Sulphate	K_2SO_4	GR	
Potassium Nitrate	KNO_3	AR	
L-tryptophan	$C_{11}H_{12}N_2O_2$	AR	
tert-Butyl Alcohol (TBA)	C_4H_9OH	AR	Chengdu Kelong Chemical Co., Ltd
Sodium Hydroxide	NaOH	AR	
Ethanol Absolute (EtOH)	C_2H_6O	AR	Chengdu Jinshan Chemical Reagent Co., Ltd
Hydroxyamine Hydrochloride	$HONH_3Cl$	AR	
Trichloromethane	$CHCl_3$	AR	Xilong Chemical Co., Ltd
Natural Organic Matter (NOM)	Humic Acid (HA)	AR	Tianjin kwangfu Fine Chemical Industry Research Institute
Methanol	CH_4O	HPLC	Hubei Futon Science and Technology Co., Ltd
Acetonitrile	CH_3CN	HPLC	CINC High Purity Solvents Co., Ltd

Table S2. Results of Full-scale Analysis on Background Indicators of Natural Groundwater Body

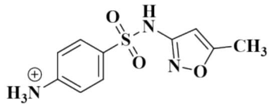
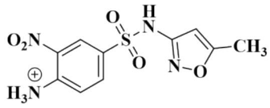
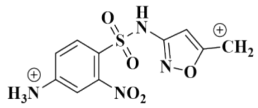
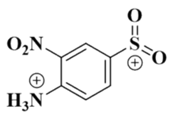
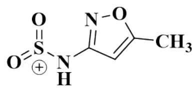
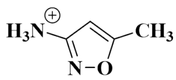
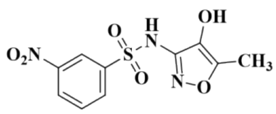
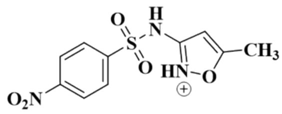
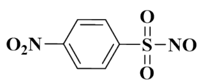
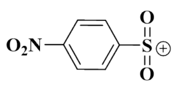
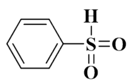
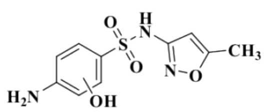
Index	pH	NTU	TH (mg/L)	Alkalinity (mg/L)	TDS (mg/L)	Sulfate (mg/L)	Nitrate (mg/L)	Chlorides (mg/L)	Ammonia nitrogenm (g/L)	UV254 cm-1	TOC (mg/L)
Actual measured value	7.92	0.8	288	285	490	185	0.023	49.4	0.10	0.007	1.6615
Quality standard	Ⅰ	Ⅰ	Ⅱ	-	Ⅱ	Ⅰ	Ⅰ	Ⅰ	Ⅱ	-	-

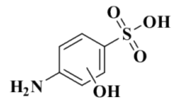
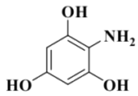
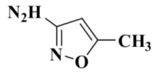
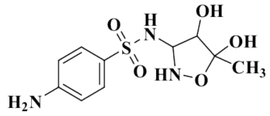
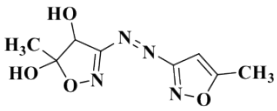
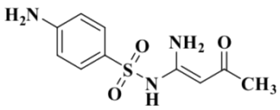
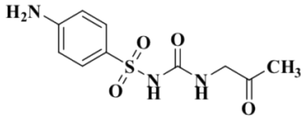
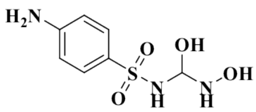
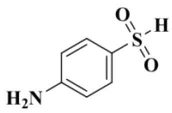
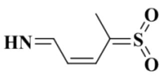
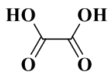
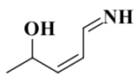
ps. TH：Total Hardness，TDS：Total dissolved solids; The Quality standard is based on groundwater specification (GBT14848-2017)

Table S3. Indirect identification of free radicals: Relationship between Kobs and inhibition rate

MeOH/TBA/$CHCl_3$: PMS (Molar ratio)	K_{obs} (min^{-1})			Inhibition ratio (%)		
	MeOH	TBA	$CHCl_3$	MeOH	TBA	$CHCl_3$
Control ($CUPP_{best}$)		0.2291		-	-	-
50:1	0.1138	0.1124	0.1318	50.34%	50.94%	42.48%
100:1	0.1031	0.0963	0.1349	54.98%	57.96%	41.12%
200:1	0.0979	0.0671	0.1344	57.26%	70.71%	41.34%

Table S4. Details of SMX degradation intermediates and fragments（HPLC/MS）

No.	Product number	Molecular formula	Molecular structure	Mass-charge ratio（m/z）	Retention time（min）
1	SMX	$C_{10}H_{12}O_3N_3S$		254	9.28
2	PA1	$C_{10}H_{11}O_5N_4S$		299	12.63
3	PA2	$C_{10}H_9O_3N_4$		233	14.80
4	PA3	$C_6H_5O_4N_2S$		201	8.88
5	PA4	$C_4H_5O_3N_2S$		161	15.10
6	PA5	$C_4H_7ON_2$		99	1.30
7	PB1	$C_9H_9O_6N_3S$		301	13.75
8	PB2	$C_{10}H_{10}O_5N_3S$		284	10.75
9	PB3	$C_6H_4O_4N_2S$		217	13.70
10	PB4	$C_6H_4O_3NS$		186	9.28
11	PB5	$C_6H_6O_2S$		165	14.53
12	PC1	$C_{10}H_{11}O_4N_3S$		270	15.70

13	PC2	$C_6H_8O_4S$		190	7.00
14	PC3	$C_6H_7O_3N$		141	11.80
15	PC4	$C_4H_6ON_2$		101	15.63
16	PC5	$C_{10}H_{15}N_3SO_5$		290	8.90
17	PC6	$C_8H_{10}O_4N_4$		227	11.80
18	PD1	$C_{10}H_{11}O_3N_3S$		255	14.53
19	PD2	$C_{10}H_{13}O_4N_3S$		274	9.53
20	PD3	$C_7H_{10}O_4N_3S$		249	15.10
21	PD4	$C_7H_9O_2N_3S$		200	12.63
22	PD5	$C_6H_7O_2NS$		159	14.53
23	PD6	$C_5H_7O_2NS$		149	9.53
24	PD7	C_5H_9ON		100	9.28

(ps: The product numbers A, B, C, etc. represent the different degradation paths, while the Arabic numerals represent the intermediates and fragment ions within each degradation path.)

Table S5. Kinetic parameters of SMX degradation in CUPP system with Cl^-, HCO_3^-, HA added

Added substances	Concentration	K_{obs} (min^{-1})	Kinetic equation	$t_{1/2}$ (min)	R^2
Control	0	0.2219	y=-0.142x-0.475	4.36	0.954
	1	0.1470	y=-0.147x-0.199	5.58	0.945
	3	0.2110	y=-0.211x-0.075	3.81	0.968
Cl^- (mM)	5	0.2810	y=-0.281x-0.030	2.69	0.985
	7	0.2770	y=-0.277x-0.213	2.62	0.924
	9	0.3710	y=-0.371x-0.017	2.53	0.998
	2	0.1748	y=0.143+4.723e^(-x/5.721)	5.72	0.996
	6	0.1652	y=0.153+4.704e^(-x/6.054)	6.05	0.996
HCO_3^- (mM)	10	0.1693	y=0.162+4.702e^(-x/5.905)	5.91	0.996
	14	0.1640	y=0.100+4.818e^(-x/6.098)	6.10	0.999
	18	0.1710	y=0.125+4.756e^(-x/5.848)	5.85	0.998
	50	0.1689	y=0.117+4.728e^(-x/5.919)	5.92	0.995
	100	0.1748	y=0.124+4.725e^(-x/5.722)	5.72	0.995
HA (mg/L)	150	0.1703	y=0.086+4.718e^(-x/5.873)	5.87	0.994
	200	0.1667	y=0.097+4.710e^(-x/6.000)	6.00	0.992
	250	0.1943	y=0.149+4.637e^(-x/5.147)	5.15	0.986

Table S6. Response surface experimental design scheme and response value

Standard order	Run sequence	PMS（mM）	PM（mM）	pH	K_{obs}（min^{-1}）
6	1	8	2	5	0.2090
7	2	4	2	9	0.1891
17	3	6	2	7	0.2355
4	4	8	2.4	7	0.2015
10	5	6	2.4	5	0.1933
16	6	6	2	7	0.2399
11	7	6	1.6	9	0.2060
14	8	6	2	7	0.2268
1	9	4	1.6	7	0.1409
3	10	4	2.4	7	0.1301
9	11	6	1.6	5	0.1576
15	12	6	2	7	0.2218
8	13	8	2	9	0.2100
5	14	4	2	5	0.1420
13	15	6	2	7	0.2291
2	16	8	1.6	7	0.1601
12	17	6	2.4	9	0.2010

Table S7. Response surface model ANOVA results

Source	Quadratic sum	Degree of Freedom	Mean sum of square	F-value	P-value（Prob >F）
Model	0.02	9	2.17E-03	71.14	<0.0001**
Residual error	2.14E-04	7	3.05E-05		
Loss of fit	8.91E-06	3	2.97E-06	0.058	0.9792
Pure error	2.05E-04	4	5.12E-05		
Total deviation	0.02	16			

Table S8. Regression model fitting results

Statistical data	Abbreviation	Value
Standard deviation	Std.Dev.	0.005523
Mean value	Mean	0.19
Variable coefficient	C.V.%	2.85
Determination coefficient	R^2	0.9892
Correction coefficient of determination	R^2_{Adj}	0.9753
Adeq Precision	Adeq Precision	23.647

Table S9. Degradation efficiency of the CUPP system

PMS concentration	PM concentration	Pollutant and concentration	removal efficiency	reference
2.4mM	1.8mM	aqueous mixture of 0.3 mM benzene and TCE	>85%	22
3.9mM	5.8mM	50mg/L acid orange 7	89.5%	28
4mM	2mM	100uM p-chlorobenzoic acid	＞98%	29
6mM	2mM	5mg/L SMX	≈100%	the study

TEXTS

Text S1. Sample testing methods

a. pH Detection:

The pH meter should undergo daily calibration, employing a two-point calibration approach with buffer solutions of pH 4.00 and 9.18. When in use, the pH meter probe is immersed in the reaction solution, ensuring that the liquid level remains below the height of the electrolyte within the electrode. To ensure accurate readings, a stable measurement for at least 15 seconds is required, confirming the recorded data as the pH value of the solution.

b. SMX Content Determination (HPLC):

The alteration in SMX concentration was assessed using HPLC. The HPLC system was equipped with a Sapphiresil C18 column (150 mm×4.6 mm, 5 μm, Follie) and a UV-visible light detector set at a wavelength of 264 nm. The analysis employed a mobile phase consisting of 0.1% acetic acid water (60%) as Mobile Phase A and acetonitrile (40%) as Mobile Phase B, with a flow rate of 1 mL/min. The column temperature was maintained at 30 ℃, and an injection volume of 50 μL was used. The retention time was observed at 6.5 min.

c. Analysis of SMX Degradation Intermediates (HPLC/MS):

The degradation intermediates of SMX in the CUPP system were analyzed using the Waters E2695 Alliance HPLC coupled with the Waters ZQ2000 single quadrupole MS. The following detection conditions were utilized: a Water 2695 C18 chromatographic column (250×4.6 mm, 3 μm) was employed, with mobile phase A containing 0.1% ammonium formate and mobile phase B consisting of acetonitrile. The flow rate was set at 0.2 mL/min, and the injection volume was 20 nL. The analysis was conducted using the electrospray ionization (ESI) ion source, operating in the positive ion mode. The specific elution mode parameters can be found in the table below:

Gradient sequence	Total time	Velocity of flow (mL/min)	A phase (%)	B phase (%)
1	0.1	0.2	90	10
2	10	0.2	40	60
3	17	0.2	40	60
4	17.1	0.2	90	10
5	24	0.2	90	10

d. Surface Morphology Analysis of AMO:

The external morphology and chemical composition of the sample were examined using the Apreo 2 scanning electron microscope (SEM) with an accompanying energy dispersion spectrometer (EDS). Prior to observation, the sample was coated with a thin layer of gold.

FORMULAS

	$SO_4^{-}\cdot + TBA \rightarrow product\ k = 4.0 \times 10^5\ L \cdot mol \cdot s^{-1}$	(S1)
	$SO_4^{-}\cdot + MeOH \rightarrow product\ k = 1.1 \times 10^7\ L \cdot mol \cdot s^{-1}$	(S2)
	$\cdot OH + TBA \rightarrow product\ k = 6.0 \times 10^8\ L \cdot mol \cdot s^{-1}$	(S3)
	$\cdot OH + MeOH \rightarrow product\ k = 9.7 \times 10^8\ L \cdot mol \cdot s^{-1}$	(S4)
	$\cdot OH + MeOH \rightarrow product\ k = 9.7 \times 10^8\ L \cdot mol \cdot s^{-1}$	(S5)
	$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	(S6)
	$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$	(S7)