Supporting Information

Sulfamethazine degradation in the VUV/PMS/Cu(II) System the critical role of VUV and reduction behavior of copper

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Figure S5. Mass spectrum of intermediate products of SMZ degraded by VUV/PMS/Cu(II) system

Text S1. Detection condition of UPLC

Waters ACQUITY UPLC®H-Class Ultra-Performance Liquid Chromatography (UPLC) system equipped is employed to ascertain the organic concentration with a diode array detector. The SMZ detection conditions are as follows: the mobile phase consisted of 0.1% acetic acid solution and acetonitrile (V1:V2 =80:20) at a flow rate of 0.35 mL min-1. The detection wavelength was set at λ=265 nm, with an injection volume of 10 μL. The column temperature was maintained at 30 °C.

Text S2. Detection condition of UPLC-MS

Methanol and 0.1% formic acid were used as the mobile phase (60%:40%), the flow rate was set to 0.3 mL/min, the column temperature was 40°C, and the sample injection volume was 10μL. Mass spectrometry (m/z 50-500) was performed with an electrospray ionization (ESI) source in positive and negative ion modes. The gas temperature and flow rate are 300°C and 8 L/min respectively.

Text S3. Kinetic fitting

the pseudo-first-order kinetic model was used to fit the oxidation process.

$$ln(\frac{C_t}{C_0}) = -k_{obs}t$$

where C_0 (mM) is the initial concentration of NOR, C_t (mM) represents the NOR concentration at reaction time t (min) after the introduction of calcite, k_{obs} (min^{-1}) is the reaction rate constants of pseudo-first order.

Table S1. Pseudo-first-order rate obtained under different reaction conditions

Conditions							
SMZ (mM)	PMS (mM)	Cu(II) (mM)	pH	Types	Impact factor	*k*	R^2
0.10	1.00	0.05	7	VUV	\	0.2767	0.9770
0.10	1.00	0.05	7	UVC	\	0.1388	0.9773
0.10	1.00	0.05	7	\	\	0.0638	0.9934
0.10	0	0	7	VUV	\	0.1460	0.9935
0.10	0	0	7	UVC	\	0.0643	0.9936
0.10	1.00	0	7	VUV	\		
0.10	1.00	0.01	7	VUV	\	0.1368	0.9928
0.10	1.00	0.02	7	VUV	\	0.1468	0.9934
0.10	1.00	0.03	7	VUV	\	0.1559	0.9944
0.10	1.00	0.04	7	VUV	\	0.1739	0.9892
0.10	1.00	0.05	7	VUV	\	0.2767	0.9770
0.10	0.25	0.05	7	VUV	\	0.0904	0.9933
0.10	0.50	0.05	7	VUV	\	0.1594	0.9863
0.10	0.75	0.05	7	VUV	\	0.1874	0.9859
0.10	1.00	0.05	7	VUV	\	0.2767	0.9770
0.05	1.00	0.05	7	VUV	\	0.8346	0.9566
0.10	1.00	0.05	7	VUV	\	0.2767	0.9770
0.15	1.00	0.05	7	VUV	\	0.1959	0.9282
0.20	1.00	0.05	7	VUV	\	0.0916	0.9836
0.10	1.00	0.05	3.2	VUV	\	0.2127	0.9593
0.10	1.00	0.05	5.2	VUV	\	0.2476	0.9147
0.10	1.00	0.05	7	VUV	\	0.2767	0.9770
0.10	1.00	0.05	8	VUV	\	0.1687	0.9586
0.10	1.00	0.05	9	VUV	\	0.1912	0.9426
0.10	1.00	0.05	7	VUV	1mM NO_3^-	0.2036	0.9908
0.10	1.00	0.05	7	VUV	3mM NO_3^-	0.1340	0.9921
0.10	1.00	0.05	7	VUV	5mM NO_3^-	0.1698	0.9905
0.10	1.00	0.05	7	VUV	1mM Cl^-	0.2241	0.9522
0.10	1.00	0.05	7	VUV	3mM Cl^-	0.1397	0.9705
0.10	1.00	0.05	7	VUV	5mM Cl^-	0.1284	0.9826
0.10	1.00	0.05	7	VUV	1mM SO_4^{2-}	0.2699	0.9226
0.10	1.00	0.05	7	VUV	3mM SO_4^{2-}	0.2582	0.9517
0.10	1.00	0.05	7	VUV	5mM SO_4^{2-}	0.2215	0.9284
0.10	1.00	0.05	7	VUV	1mM CO_3^{2-}	0.1878	0.9476
0.10	1.00	0.05	7	VUV	3mM CO_3^{2-}	0.3681	0.99394
0.10	1.00	0.05	7	VUV	5mM CO_3^{2-}	0.3679	0.9988
0.10	1.00	0.05	7	VUV	100mMMeOH	0.0878	0.9983
0.10	1.00	0.05	7	VUV	100mM TBA	0.1079	0.9875
0.10	1.00	0	7	VUV	100mMMeOH	0.0422	0.9626
0.10	1.00	0	7	VUV	100mM TBA	0.0901	0.9731

Table S2. Identification of SMZ intermediate products degraded by VUV/PMS/Cu(II) system

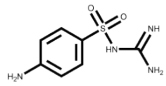
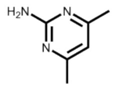
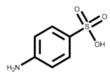
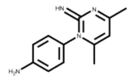
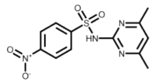
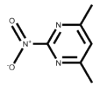
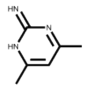
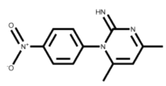
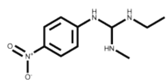
Product	Retention time	Molecular formula	$[M+H]^+$ m/z	Molecular structure
P1	8.43	$C_7H_{10}N_4O_2S$	214.04	
P2	0.98	$C_6H_9N_3$	123.91	
P3	3.69	$C_6H_7N_1O_3S$	173.83	
P4	3.66	$C_{12}H_{14}N_4$	214.92	
P5	6.24	$C_{12}H_{12}N_4O_4S$	308.85	
P6	3.82	$C_6H_7N_3O_2$	153.97	
P7	0.97	$C_6H_9N_3$	123.91	
P8	5.82	$C_{12}H_{12}N_4O_2$	244.98	
P9	8.46	$C_{10}H_{16}N_4O_2$	224.97	

Table S3. Predicted acute and chronic toxicity of SMZ and its degradation by ECOSAR

Compouund	Acute toxicity(mg/L)			Chronic toxicity(mg/L)		
	Fish (LC_{50})/96h	Daphnid (LC_{50})/48h	Green Algae (EC_{50})/96h	Fish	Daphnid	Green Algae
SMZ	195	6.02	19.5	3.26	**0.065**	8.88
P1-214.10	998000	142	1270	7060	1910	1390
P2-309.10	215	226	21.7	2.24	31	11
P3-245.10	1460000	558000	80500	89400	18000	8700
P4-225.10	466	46.3	54.8	47.4	3.18	15.9
P5-215.14	44800	43.5	271	3570	**0.331**	595
P6-124.13	19200000	6350000	501000	991000	137000	39100
P7-124.10	62.1	2.34	7.3	**0.951**	**0.026**	3.04
P8-174.13	119	3.74	12.1	155	65.3	87.2
P9-154.10	1350	689	331	116	50.1	68.5

Table S4. Toxicity classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Toxicity range (mg/L)	Class
$LC_{50}/EC_{50}/ChV \leqslant 1$	Very toxic
$1 \leqslant LC_{50}/EC_{50}/ChV \leqslant 10$	Toxic
$10 \leqslant LC_{50}/EC_{50}/ChV \leqslant 100$	Harmful
$LC_{50}/EC_{50}/ChV > 100$	Not Harmful

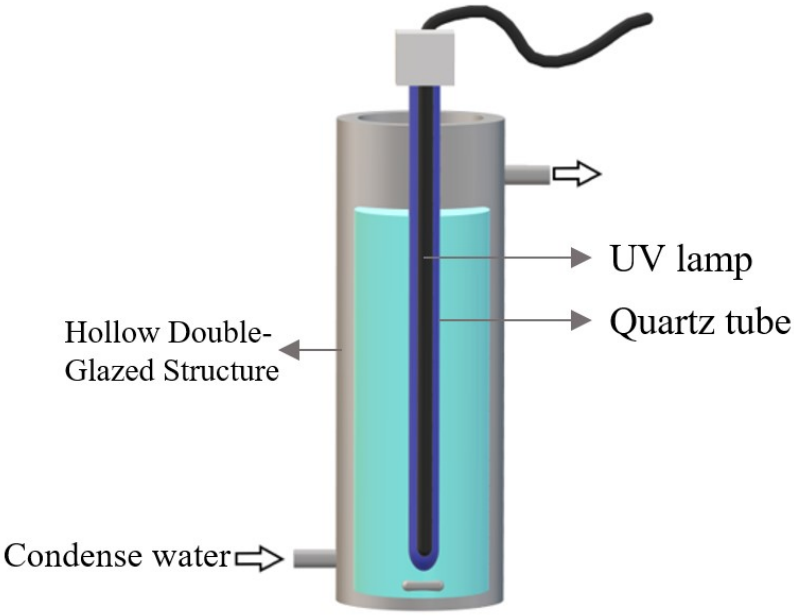


Figure S1 Experimental device diagram

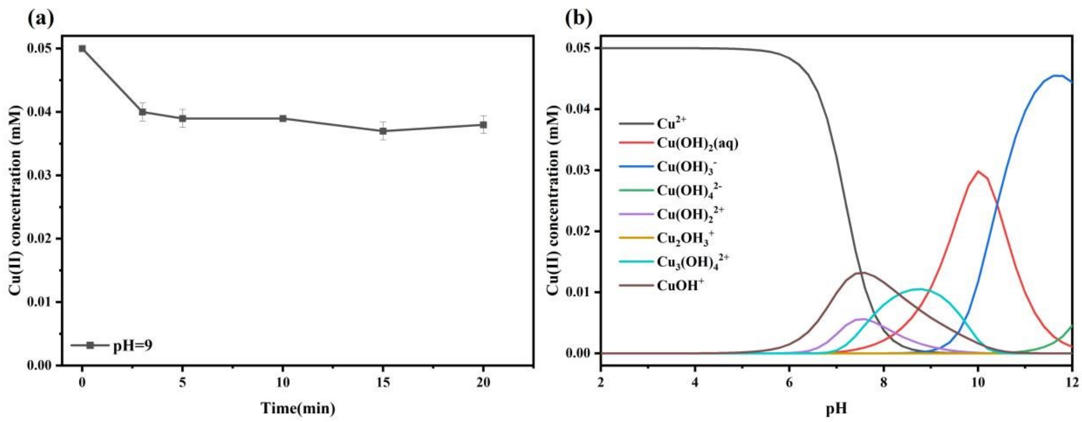


Figure S2 Concentration of Cu(II) at pH=9(a),Visual Minteq numerical simulation of Cu(II)(b).

Experimental conditions: $[Cu(II)]_0$ = 0.05 mM, $[SMZ]_0$ = 0.1 mM, $[PMS]_0$ = 1 mM, pH = 9.0.

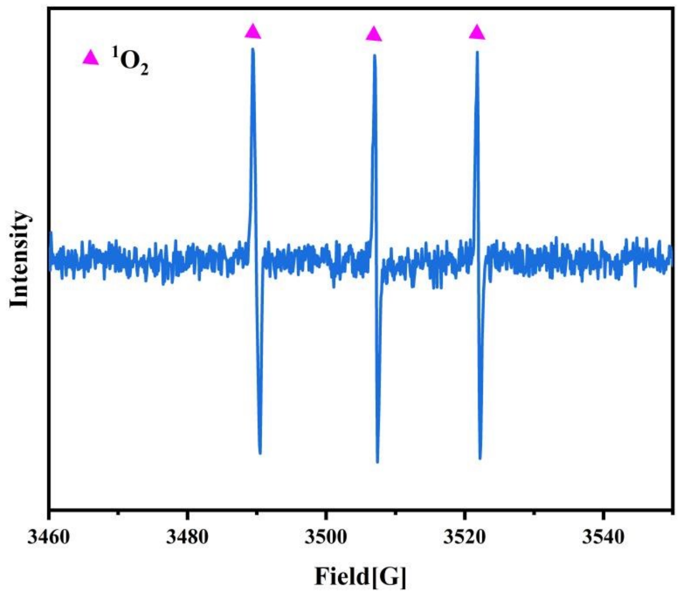


Figure S3 ESR spectra of $^1O_2$. Experimental conditions: $[Cu(II)]_0$ = 0.05 mM, $[SMZ]_0$ = 0.1 mM, [PMS]0 = 1 mM, pH = 7.0.

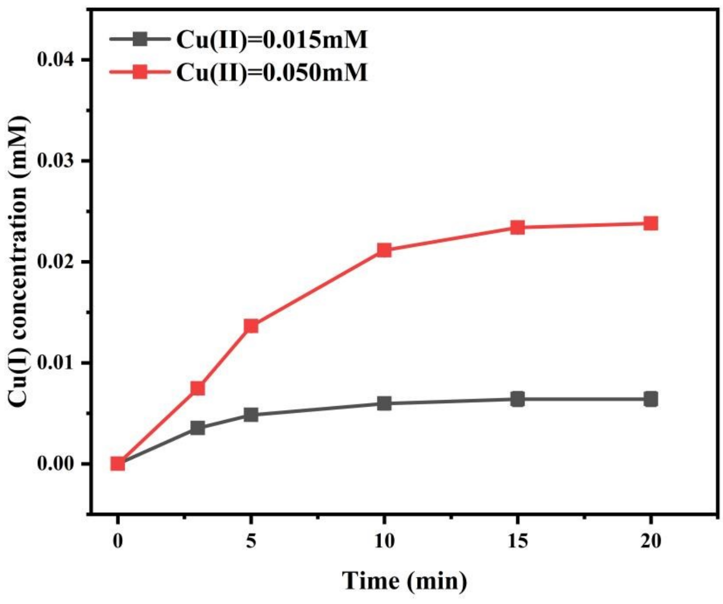


Figure S4 Cu(I) concentration change under different Cu(II) initial in VUV/PMS/Cu(II). Experimental conditions: $[SMZ]_0$ = 0.1 mM, $[PMS]_0$ = 1 mM, pH = 7.0.

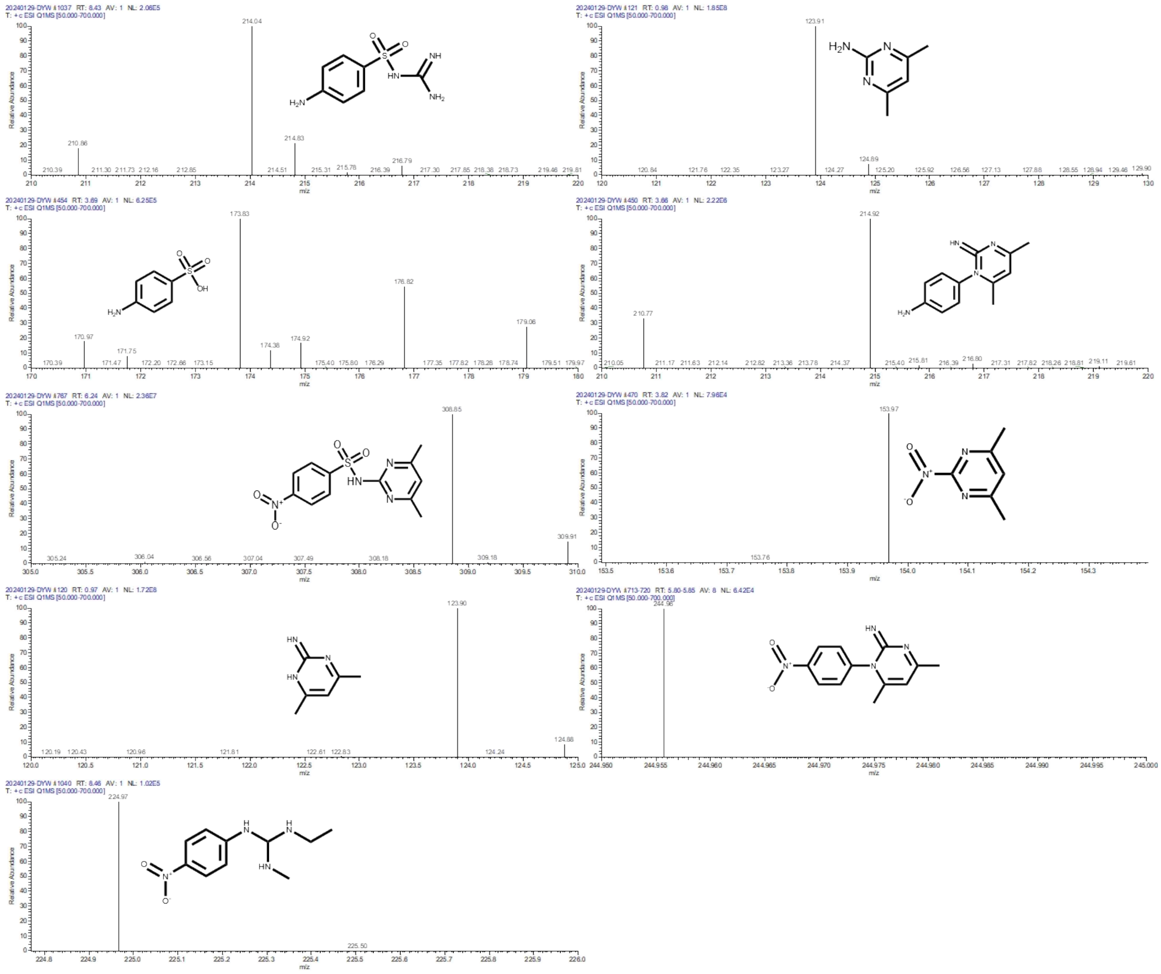


Figure S5. Mass spectrum of intermediate products of SMZ degraded by VUV/PMS/Cu(II) system