

Supplementary Materials

This material contains 6 figures and 4 tables and 1 text.

Captions:

Text S1. Method for the incident light intensity measure	2
Figure S1. Variation of pH values in systems under different concentrations of HCO_3^-	3
Figure S2. Molecular structure diagram of deltamethrin	4
Figure S3. Bitmap of Vulnerable Points of Deltamethrin Molecules	5
Figure S4. Inferred degradation pathway of deltamethrin	6
Figure S5. Variation of COD concentration during reaction in secondary effluent.....	7
Figure S6. The change of Br^- and formation of BrO_3^- during the degradation of deltamethrin by Fe(III)/sulfite system in the presence of Br^- (20 μM).....	8
Table S1. NBO charge calculation of deltamethrin molecules	9
Table S2. Fukui function table of deltamethrin molecules.....	11
Table S3. Degradation products detected by GC-MS	12
Table S4. The characteristics of the secondary effluent used in this experiment.....	12

Text S1. Method for the incident light intensity measure

The light intensity was assessed using a digital UV and white light intensity meter (Spectroline, USA), which was validated by the potassium iron(III) oxalate method. 0.01 mol/L solution of $\text{KFe}(\text{C}_2\text{O}_4)_2$ was meticulously prepared and 10 mL of this solution was introduced into reaction reactor. Monochromatic light at 300 nm and 365 nm segregated from the simulated sunlight by the LOT Oriel grating monochromator was used for photolysis. Exposure durations were set at 2, 3, 4, 5, 10, 15, and 20 mins. After exposure, 2 mL of the solution was extracted and transferred to a 20 mL brown volumetric flask. Subsequently, 2 mL of o-phenanthroline (0.1% aqueous solution) and 2.5 mL of buffer solution were introduced, followed by dilution and thorough mixing. The absorbance of the Fe(II)-o-phenanthroline complex was measured at 510 nm after incubation for 0.5 h in a dark environment [1, 2, 3]. The incident light intensity of the photosensitive reaction device used in this study is calculated to be 100 mW/cm².

Reference:

1. He J, Zhang Y, Guo Y, et al. Photocatalytic degradation of cephalexin by ZnO nanowires under simulated sunlight: Kinetics, influencing factors, and mechanisms[J]. *Environ. Int.*, **2019**, 132: 105105.
2. Birkigt J, Gilevska T, Ricken B, et al. Carbon stable isotope fractionation of sulfamethoxazole during biodegradation by *Microbacterium* sp. strain BR1 and upon direct photolysis[J]. *Environ. Sci. Tech.*, **2015**, 49(10): 6029-6036.
3. Méndez-Díaz J D, Shimabuku K K, Ma J, et al. Sunlight-driven photochemical halogenation of dissolved organic matter in seawater: a natural abiotic source of organobromine and organoiodine[J]. *Environ. Sci. Tech.*, **2014**, 48(13): 7418-7427.

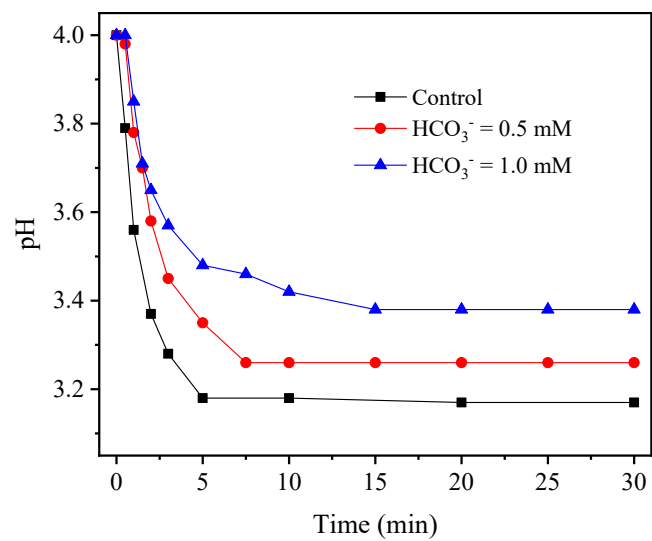


Figure S1. Variation of pH values in systems under different concentrations of HCO_3^-

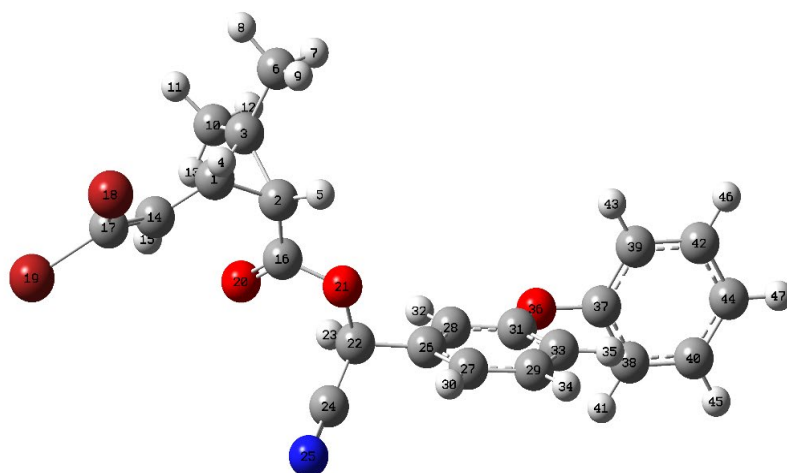


Figure S2. Molecular structure diagram of deltamethrin

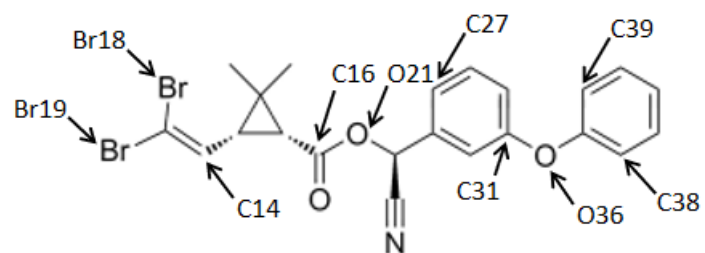


Figure S3. Bitmap of Vulnerable Points of Deltamethrin Molecules

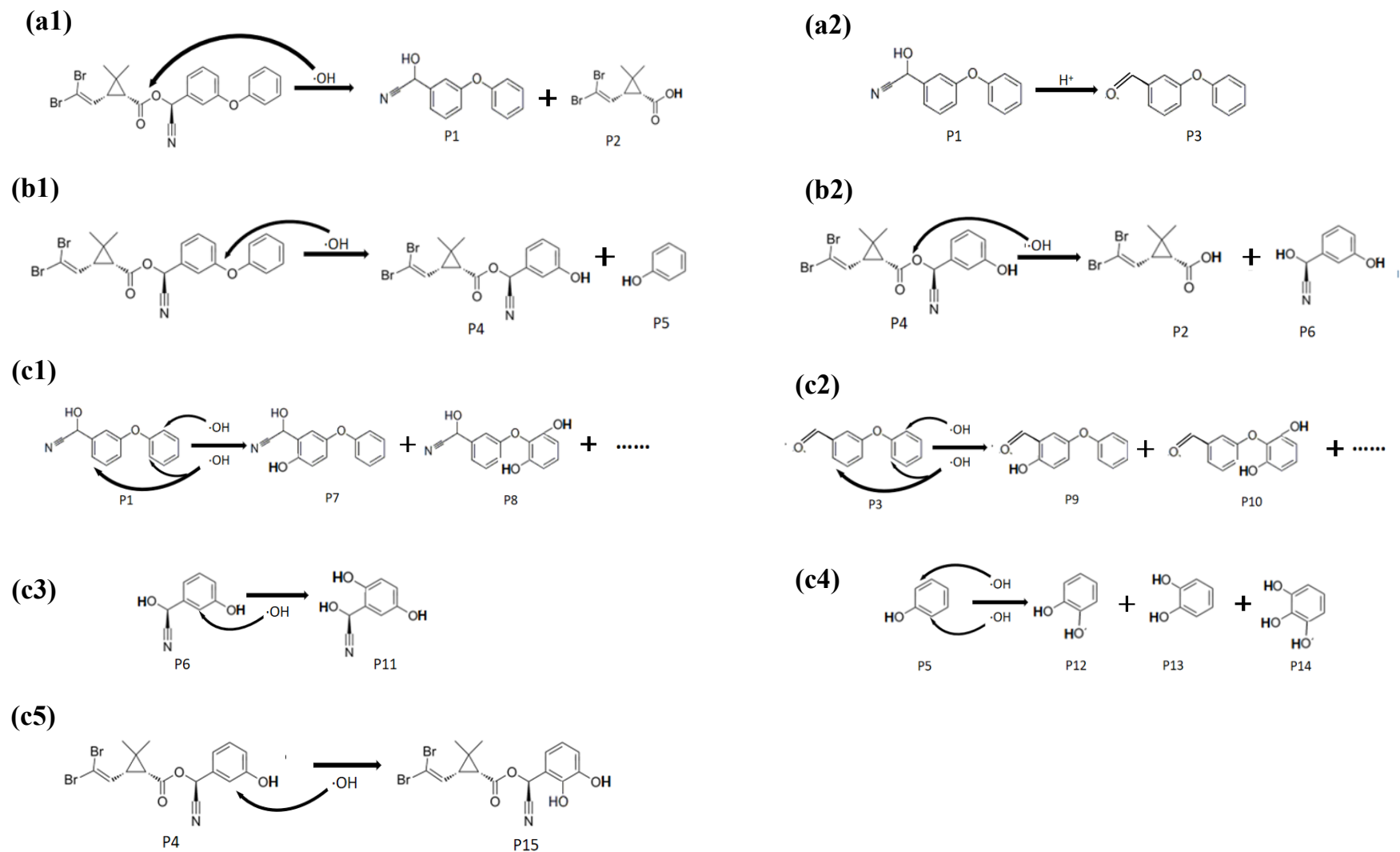


Figure S4. Inferred degradation pathway of deltamethrin

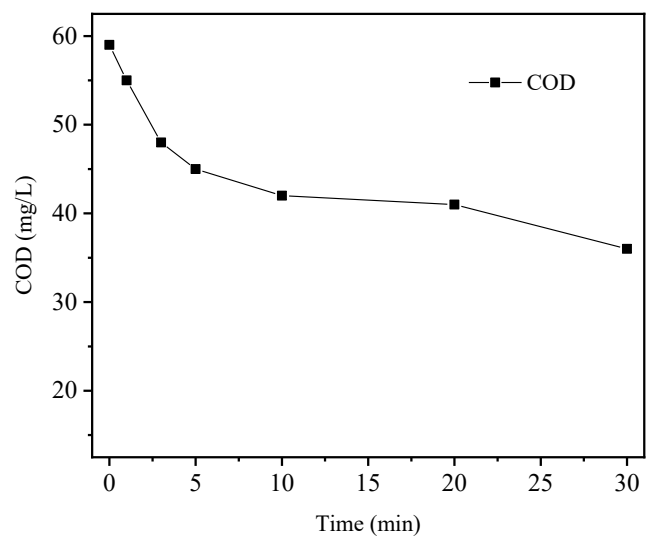


Figure S5. Variation of COD concentration during reaction in secondary effluent

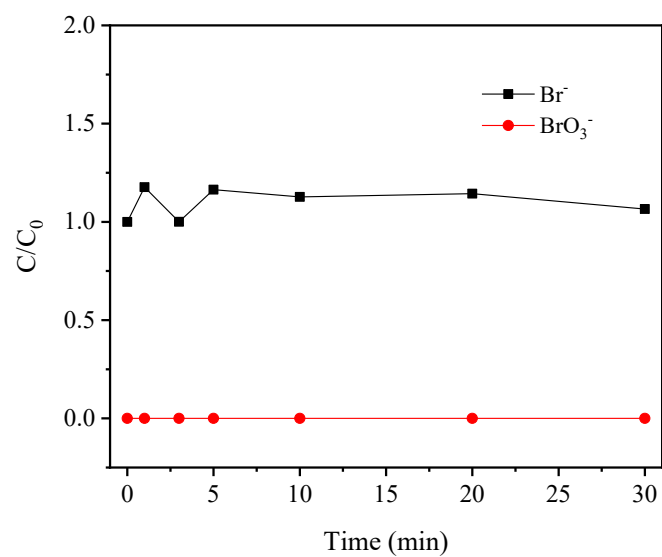


Figure S6. The change of Br^- and formation of BrO_3^- during the degradation of deltamethrin by Fe(III)/sulfite system in the presence of Br^- (20 μM)

Table S1. NBO charge calculation of deltamethrin molecules

	B3LYP			M06		
	N	N+1(obtained)	N-1(loose)	N	N+1(obtained)	N-1(loose)
C1	-0.25641	-0.24664	-0.2537	-0.27	-0.25633	-0.26812
C2	-0.35232	-0.3633	-0.34921	-0.36518	-0.37906	-0.36863
C3	-0.03214	-0.04381	-0.02508	-0.04143	-0.05291	-0.03963
H4	0.28379	0.27381	0.28736	0.29157	0.28225	0.29261
H5	0.29324	0.28515	0.29698	0.30171	0.29341	0.30292
C6	-0.68163	-0.67957	-0.68283	-0.68985	-0.68746	-0.69017
H7	0.25212	0.24649	0.25492	0.2564	0.2507	0.25677
H8	0.25345	0.24983	0.25575	0.25763	0.25387	0.25861
H9	0.2488	0.24611	0.25018	0.25216	0.24954	0.2525
C10	-0.69669	-0.69379	-0.69773	-0.70803	-0.70482	-0.70817
H11	0.25488	0.2506	0.25739	0.25972	0.25526	0.26085
H12	0.25376	0.24795	0.25632	0.25897	0.25296	0.25949
H13	0.25788	0.25777	0.25829	0.26203	0.26213	0.26184
C14	-0.24938	-0.36374	-0.23497	-0.253	-0.37313	-0.25422
H15	0.29051	0.27241	0.29297	0.29679	0.27909	0.2966
C16	0.8359	0.83363	0.8373	0.86598	0.86478	0.86769
C17	-0.27818	-0.37116	-0.26919	-0.30224	-0.38302	-0.30094
Br18	0.10306	-0.23654	0.12426	0.11524	-0.22349	0.11641
Br19	0.10248	-0.26657	0.12607	0.11582	-0.26833	0.11715
O20	-0.63787	-0.64333	-0.6276	-0.64375	-0.64709	-0.63586
O21	-0.54083	-0.54465	-0.53787	-0.55658	-0.55973	-0.55658
C22	-0.03292	-0.03333	-0.03795	-0.02432	-0.02447	-0.02977
H23	0.30855	0.30748	0.31923	0.31056	0.30944	0.32364

Continued Table S1. NBO charge calculation of deltamethrin molecules

	B3LYP			M06		
	N	N+1(obtained)	N-1(loose)	N	N+1(obtained)	N-1(loose)
C24	0.31142	0.31228	0.29912	0.30144	0.30254	0.28686
N25	-0.36088	-0.36378	-0.33076	-0.35151	-0.35404	-0.31887
C26	-0.0629	-0.06177	-0.04181	-0.06384	-0.06279	-0.05569
C27	-0.24902	-0.24941	-0.06632	-0.25794	-0.25811	-0.02545
C28	-0.25568	-0.25636	-0.16494	-0.26504	-0.26561	-0.15786
C29	-0.2191	-0.21935	-0.19736	-0.22198	-0.22217	-0.20798
H30	0.26208	0.26195	0.288	0.26903	0.26902	0.29869
C31	0.32078	0.3206	0.41892	0.32807	0.32788	0.45012
H32	0.26731	0.26707	0.2952	0.27536	0.27511	0.30802
C33	-0.29849	-0.2994	-0.21623	-0.31025	-0.31098	-0.21904
H34	0.26353	0.26324	0.29273	0.27066	0.27042	0.3048
H35	0.26783	0.26754	0.29547	0.2746	0.27433	0.30705
O36	-0.53346	-0.53364	-0.38853	-0.5473	-0.54746	-0.38454
C37	0.27721	0.2774	0.24378	0.28313	0.2833	0.2439
C38	-0.27387	-0.27392	-0.26051	-0.28292	-0.28296	-0.26819
C39	-0.27448	-0.27449	-0.25217	-0.28494	-0.28493	-0.2693
C40	-0.23766	-0.23774	-0.21564	-0.24231	-0.24238	-0.22945
H41	0.2653	0.26528	0.27647	0.27227	0.27225	0.28394
C42	-0.23781	-0.23786	-0.22533	-0.2427	-0.24274	-0.2339
H43	0.26522	0.26525	0.27644	0.27172	0.27175	0.28316
C44	-0.25454	-0.25467	-0.23276	-0.2625	-0.26262	-0.23645
H48	0.25951	0.25945	0.26946	0.26607	0.26601	0.27603
H46	0.25949	0.25945	0.26957	0.26622	0.26618	0.27649
H47	0.25817	0.25809	0.26633	0.26447	0.2644	0.27272

Table S2. Fukui function table of deltamethrin molecules

	B3LYP	M06		B3LYP	M06
C1	-0.00353	-0.005895	N25	0.01651	0.017585
C2	0.007045	0.005215	C26	0.00998	0.00355
C3	0.009365	0.00664	C27	0.091545	0.11633
H4	0.006775	0.00518	C28	0.04571	0.053875
H5	0.005915	0.004755	C29	0.010995	0.007095
C6	-0.00163	-0.001355	H30	0.013025	0.014835
H7	0.004215	0.003035	C31	0.04916	0.06112
H8	0.00296	0.00237	H32	0.014065	0.016455
H9	0.002035	0.00148	C33	0.041585	0.04597
C10	-0.00197	-0.001675	H34	0.014745	0.01719
H11	0.003395	0.002795	H35	0.013965	0.01636
H12	0.004185	0.003265	O36	0.072555	0.08146
H13	0.00026	-0.000145	C37	-0.01681	-0.0197
C14	0.064385	0.059455	C38	0.006705	0.007385
H15	0.01028	0.008755	C39	0.01116	0.007815
C16	0.001835	0.001455	C40	0.01105	0.006465
C17	0.050985	0.04104	H41	0.005595	0.005845
Br18	0.1804	0.16995	C42	0.006265	0.00442
Br19	0.19632	0.19274	H43	0.005595	0.005705
O20	0.007865	0.005615	C44	0.010955	0.013085
O21	0.00339	0.001575	H48	0.005005	0.00501
C22	-0.00231	-0.00265	H46	0.00506	0.005155
H23	0.005875	0.0071	H47	0.00412	0.00416
C24	-0.00658	-0.00784			

Table S3. Degradation products detected by GC-MS

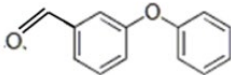
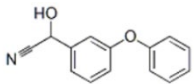
Peak Time	m/z	Name	Structural formula
19.868 min	198	P3	
19.868 min	281	P1 (2R) -2-hydroxy-2- (3- phenoxyphenyl) acetonitrile	

Table S4. The characteristics of the secondary effluent used in this experiment

	COD (mg/L)	pH	NH3-N (mg/L)	TP (mg/L)	Turbidity
Value	62	6.56	3.0	0.3	0.67