Supplementary Information

Efficacy and mechanism of the artificial sweetener saccharin degradation by thermally activated persulfate in aquatic environments

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Text S1 Description of the chemicals/reagents used in this study.

Saccharin (99%), sodium persulfate ($Na_2S_2O_8$, 98%), monopotassium phosphate (KH_2PO_4, 98%), dipotassium phosphate (K_2HPO_4, 99%), sodium hydroxide (NaOH, 97%), sodium chloride (NaCl, 99%), sodium nitrate ($NaNO_3$, 99%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 98%) and ethanol (EtOH, 99.8%) were obtained from Sigma–Aldrich (USA). Sulfuric acid (H_2SO_4, 97%), sodium bicarbonate ($NaHCO_3$, 99.7%) and phosphoric acid (85%) were purchased from Fluka (Switzerland). *tert*-Butanol (t-BuOH, 99%) was obtained from Alfa Aesar (USA). HPLC-grade methanol (99.9%) was acquired from Duksan Pure Chemicals (Korea). The Suwannee River fulvic acid standard material (1S101F) (99%) was purchased from the International Humic Substance Society (USA). All solutions were prepared by using a Milli-Q water purification system (resistivity of 18.2 MΩ-cm; Merck Millipore, USA). All the solutions utilized in this work were stored in amber glass bottles in a 4 °C refrigerator until further use.

Table S1 Degradation of saccharin in different treatment processes.

Treatment process	Saccharin removal rate	Experimental condition	Reference
Electro-Fenton	Complete removal in less than 30 min	– [saccharin] = 0.2 mM (≈36.6 mg/L) – [Fe^{2+}] = 0.2 mM – pH = 3.0 – I = 200 mA	(Lin et al., 2016)
Metal organic framework (MOF) material activated peroxymonosulfate – MOF material: Bio-MOF-11-Co catalyst	60.7% removal after 120 min	– [saccharin] = 50 mg/L – [MOF material] = 1 g/L – [PMS] = 10 g/L	(Ma et al., 2021a)
UV/persulfate	85.39% removal after 60 min	– [saccharin] = 0.11 mM (≈20 mg/L) – [persulfate] = 1.05 mM – pH = 7.0	(Ma et al., 2021b)
UV/H_2O_2	99.61% removal after 60 min	– [saccharin] = 20 mg/L – [H_2O_2] = 1.05 mM – pH = 7.0	(Ye et al., 2022)
Ozonation	>99% removal after 60 min	– [saccharin] = 20 mg/L – pH = 7.0 – ozone flow rate = 7.10 mg/min	(Lin et al., 2023)
Thermal/persulfate	Complete removal after 90 min	– [saccharin] = 5 mg/L – [persulfate] = 100 mg/L – pH = 7.0 – temperature = 70 °C	This study

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Ma, X.Y., Tang, L.J., Deng, J., Liu, Z.H., Li, X.Y., Wang, P. and Li, Q.S. 2021b. Removal of saccharin by UV/persulfate process: Degradation kinetics, mechanism and DBPs formation. J Photoch Photobio A 420.

Table S2 Conditions of the chromatographic analysis of saccharin transformation byproducts.

	Saccharin transformation byproducts
Mode	gradient
Total elution time	11 min
Mobile phases	A: 1 mM ammonium acetate in DI water B: 1 mM ammonium acetate in LCMS-grade methanol
Flow rate	1 mL/min
Injection volume	20 μL
Gradient condition	- 0 min: 90% (A): 10% (B) - 0.5 min: 95% (A): 5% (B) - 3 min: 60% (A): 40% (B) - 6 min: 40% (A): 60% (B) - 7 min: 0% (A): 100% (B) - 9 min: 0% (A): 100% (B) - 9.5 min: 95% (A): 5% (B) - 11 min: 95% (A): 5% (B)

Table S3 Conditions of the mass spectrometric analysis of saccharin transformation byproducts.

Mode	ESI negative
Ion source gas 1	50 L/h
Ion source gas 2	50 L/h
Curtain gas	20 L/h
Temperature	500 °C
Ion spray voltage floating	–4500 V
Mass scan range	50–500 m/z
Declustering potential	–98 V
collision energy	–10 V

Table S4 Summary of thermal/persulfate treatments applied to different contaminants

Contaminant	Initial compound concentration	Persulfate dosage	Operating temperature	Removal rate	Pseudo-first-order rate constant	Reference
carbamazepine	0.04 mM	1 mM	70 ˚C	100% after 80 min	0.0566 min^{-1}	(Deng et al., 2013)
naproxen	0.05 mM	1 mM	60 ˚C	100% after 90 min	0.0269 min^{-1}	(Ghauch et al., 2015)
triclosan	0.031 mM	0.155 mM	70 ˚C	100% after 120 min	0.0097 min^{-1}	(Gao et al., 2016)
valsartan	500 μg/L	100 mg/L	50 ˚C	100% after 30 min	0.1453 min^{-1}	(Arvaniti et al., 2020)
congo red	20 mg/L	1 mM	60 ˚C	–	0.0313 min^{-1}	(Luo et al., 2020)
ofloxacin	0.03 mM	4 mM	70 ˚C	100% after 80 min	0.0611 min^{-1}	(Li et al., 2022)
dexamethasone	500 μg/L	100 mg/L	50 ˚C	98% after 45 min	0.0782 min^{-1}	(Arvaniti et al., 2022)
acyclovir	40 μM	2 mM	70 ˚C	95% after 30 min	0.0326 min^{-1}	(Ding et al., 2023)
saccharin	5 mg/L	100 mg/L	70 ˚C	100% after 90 min	0.0230 min^{-1}	This study

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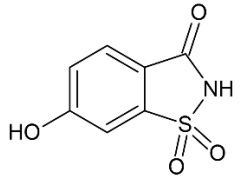
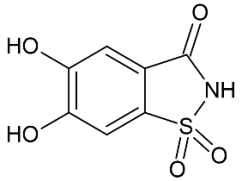
Table S5 Water quality conditions of the sampled water matrices.

Water matrices	Solution pH	TOC (mg/L)	Alkalinity (mM HCO_3^-)	NO_3^- (mM)	Cl^- (mM)
Groundwater	6.35	6.05	0.82	0.24	1.25
WWTP effluent	7.37	10.30	1.09	0.31	0.94
River water	7.6	11.30	1.82	0.05	1.58

Table S6 Mass spectrometry information obtained for the saccharin byproducts TP1 and TP2.

Byproducts	Formula	Retention time (min)	Measured m/z $[M–H]^-$	Theoretical m/z $[M–H]^-$	Mass error (Δppm)	Proposed structure
TP1	$C_7H_5NO_4S$	1.86	197.9870	197.9866	–0.1	
TP2	$C_7H_5NO_5S$	1.92	213.9820	213.9816	0.4	

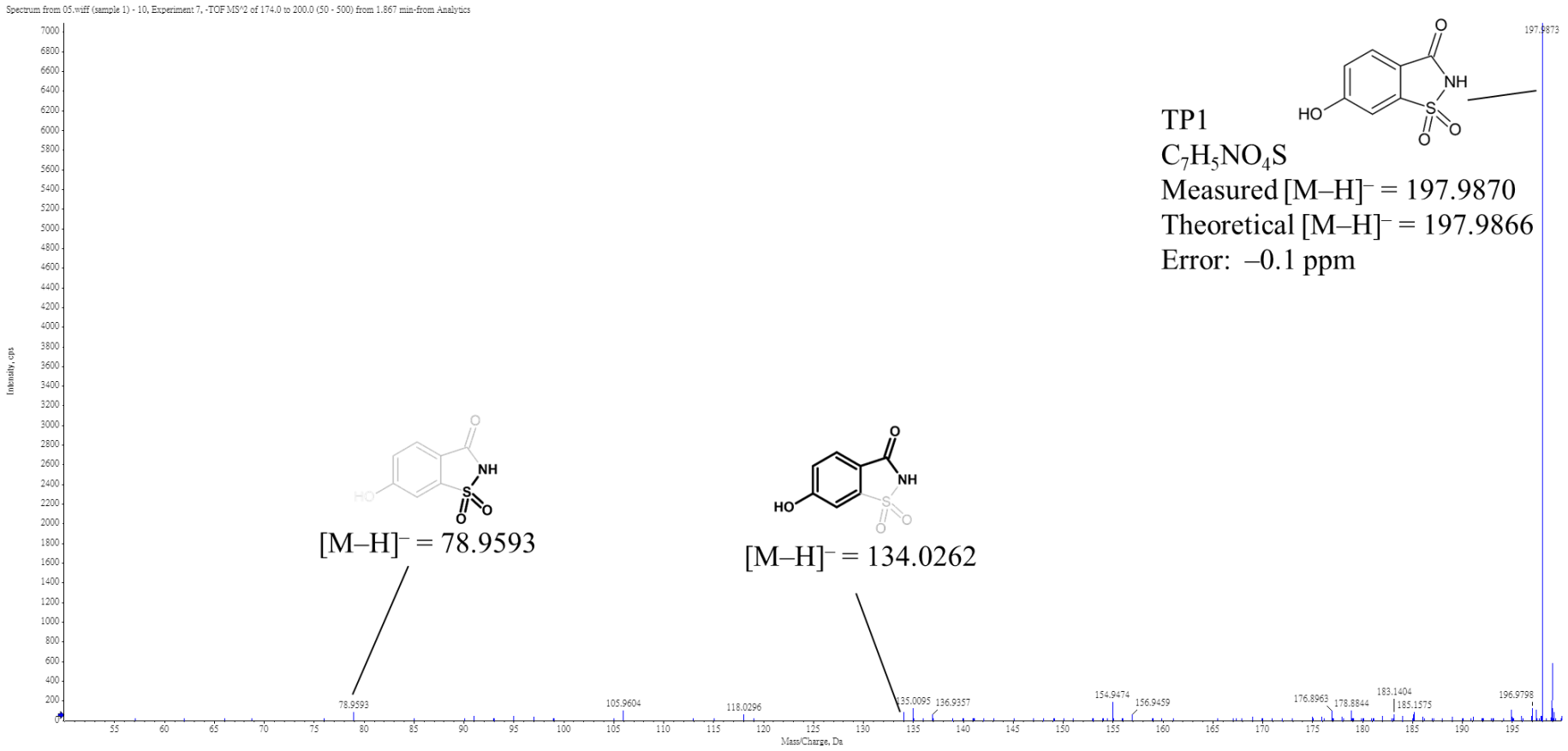


Figure S1(a) MS^2 fragmentation spectrum of TP1

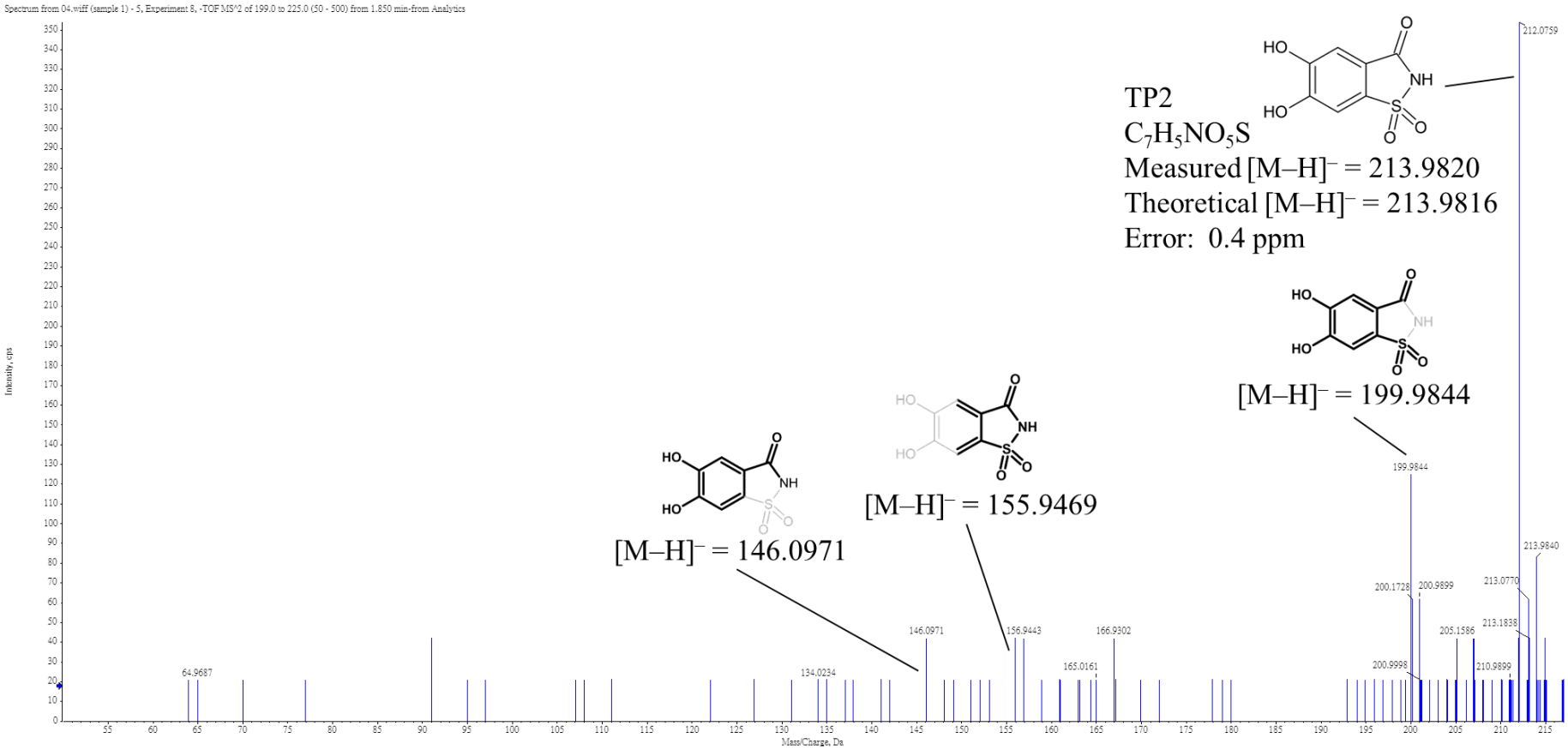


Figure S1(b) MS^2 fragmentation spectrum of TP2

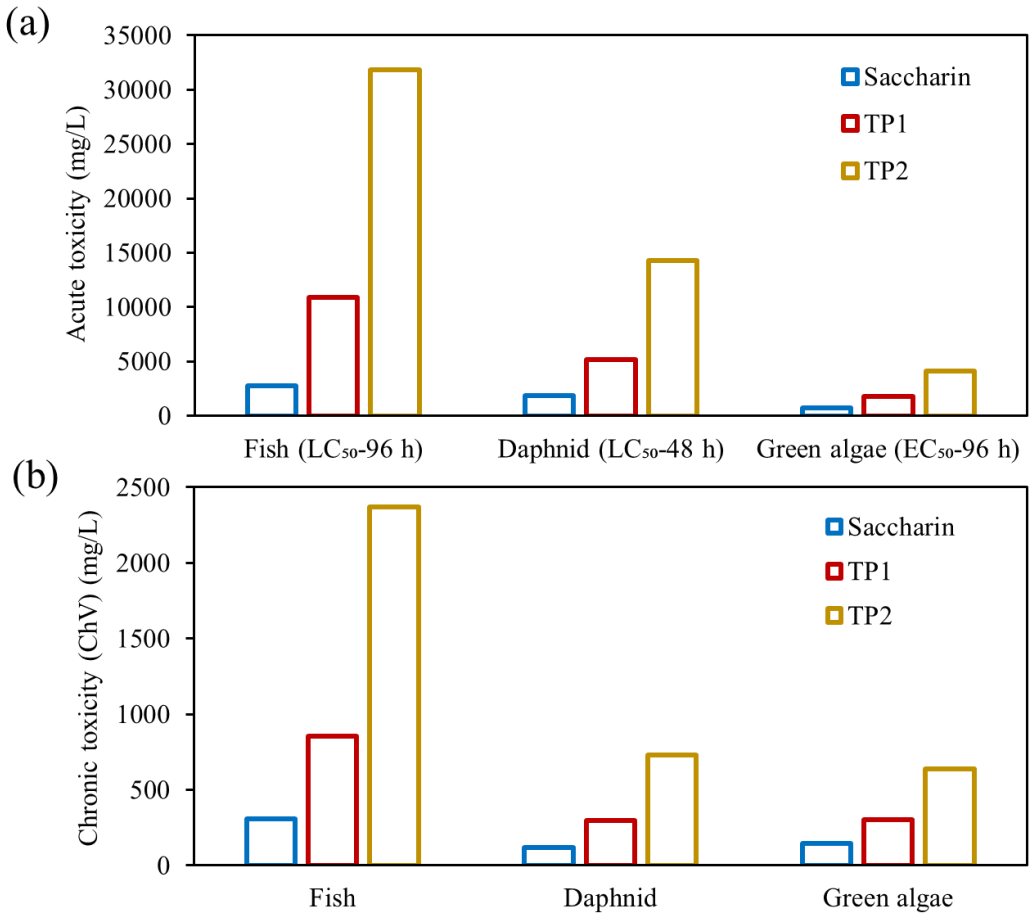


Figure S2 (a) Acute and (b) chronic toxicity of saccharin and the byproducts TP1 and TP2 toward the aquatic organisms fish, daphnids and green algae predicted by ECOSAR.