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Efficient degradation of cytotoxic contaminants of emerging concern by UV-C/H_2O_2

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Legend

Text S1 HPLC methods.

For measuring diclofenac, the mobile phase was 50:50 (v: v) 1% acetic acid in water: acetonitrile at a flow rate of 0.3 mL min^{-1}. For analyzing triclosan, the mobile phase was 25:75 (v: v) water: acetonitrile at a flow rate of 0.2 mL min^{-1}. For the analysis of atrazine, the mobile phase was 50:50 (v: v) water: methanol at a flow rate of 0.4 mL min^{-1}. The detection wavelength was set at 276 nm for diclofenac, 234 nm for triclosan, and 222 nm for atrazine. The injection volume was 50 μL, and the column temperature was 25 ℃.

Table S1 Water quality parameters of field water samples *,**.

	pH	Total alkalinity (mg L^{-1} CaCO3)	TOC (mg L^{-1})	UV-vis absorbance at 254 nm	$SUVA_{254}$ (L mg^{-1} m^{-1})
RAW	7.5	58	3.0	0.0790	2.67
FLIN	7.6	49	1.9	0.0434	2.35
GACI	7.8	49	1.6	0.0339	2.09
CUVI	7.6	50	1.3	0.0161	1.27
LH	7.2	140	7.8	0.263	3.39

*Abbreviation: RAW, FLIN, GACI, and CUVI were collected from the local water works, Mar. 31, 2015, representing water samples of raw water from Ohio River, sand filtration influent, granular activated carbon (GAC) influent, and GAC effluent. LH represented the water samples from Lake Harsha, Ohio, Mar.27, 2015.

** Data were previously reported by Liu et al[1].

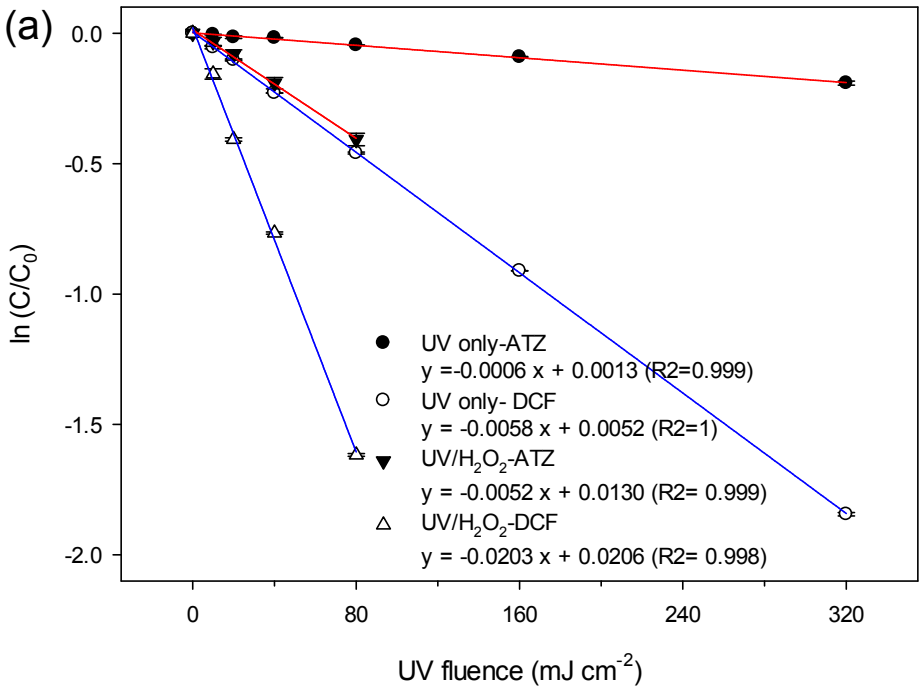
Table S2 One-way ANOVA analysis results of the cytotoxicity of diclofenac during the treatment of UV-C/H_2O_2. (Reaction conditions: $[Diclofenac]_0$ = 1 μM, $[H_2O_2]_0$ = 1 mM, pH = 7.4 (adjusted by 10 mM of phosphate buffer).)

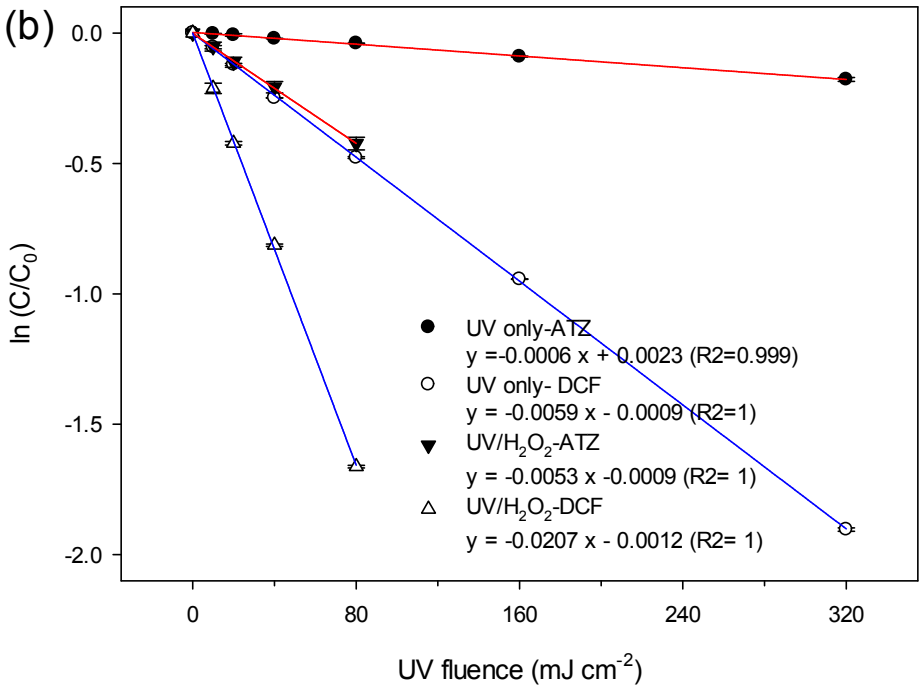
Parameter					
Table Analyzed			Diclofenac		
One-way analysis of variance					
P value			0.0145		
P value summary			*		
Are means signif. different? (P < 0.05)			Yes		
Number of groups			6		
F			4.567		
R squared			0.6555		
ANOVA Table			SS	df	MS
Treatment (between columns)			0.3064	5	0.06128
Residual (within columns)			0.161	12	0.01342
Total			0.4674	17	
Tukey's Multiple Comparison Test	**Mean Diff.**	**q**	**Significant? P < 0.05?**	**Summary**	**95% CI of diff**
A0 vs A40	-0.1012	1.514	No	ns	-0.4190 to 0.2165
A0 vs A80	0.0267	0.3992	No	ns	-0.2910 to 0.3444
A0 vs A160	0.2574	3.849	No	ns	-0.06030 to 0.5752
A0 vs A320	0.1997	2.986	No	ns	-0.1180 to 0.5174
A0 vs A640	0.2075	3.102	No	ns	-0.1103 to 0.5252

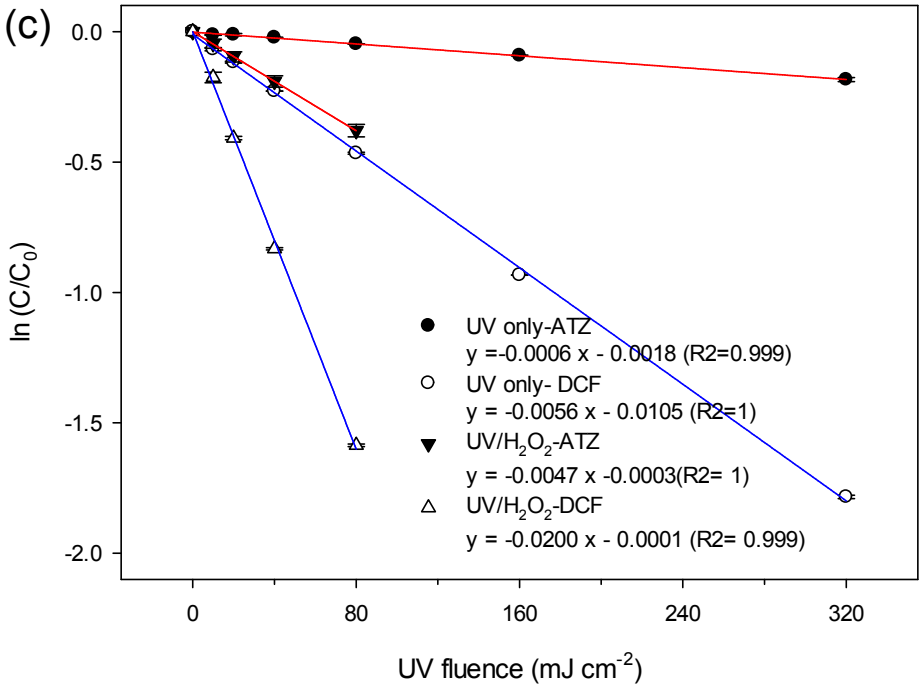
A40 vs A80	0.1279	1.913	No	ns	-0.1898 to 0.4457
A40 vs A160	0.3587	5.363	Yes	*	0.04093 to 0.6764
A40 vs A320	0.3009	4.5	No	ns	-0.01680 to 0.6187
A40 vs A640	0.3087	4.616	No	ns	-0.009034 to 0.6264
A80 vs A160	0.2307	3.45	No	ns	-0.08700 to 0.5485
A80 vs A320	0.173	2.587	No	ns	-0.1447 to 0.4907
A80 vs A640	0.1808	2.703	No	ns	-0.1370 to 0.4985
A160 vs A320	-0.05773	0.8633	No	ns	-0.3755 to 0.2600
A160 vs A640	-0.04997	0.7471	No	ns	-0.3677 to 0.2678
A320 vs A640	0.007767	0.1161	No	ns	-0.3100 to 0.3255

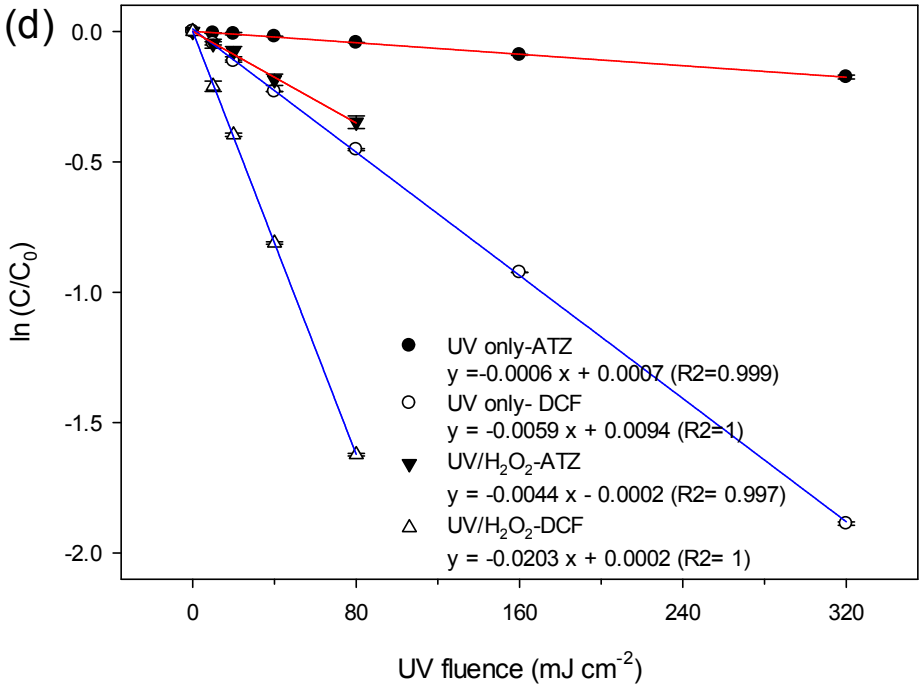
Table S3 One-way ANOVA analysis results of the cytotoxicity of triclosan during the treatment of UV-C/H_2O_2. (Reaction conditions: $[Diclofenac]_0$ = 1 μM, $[H_2O_2]_0$ = 1 mM, pH = 7.4 (adjusted by 10 mM of phosphate buffer).)

Parameter					
Table Analyzed			triclosan		
One-way analysis of variance					
P value			0.8986		
P value summary			ns		
Are means signif. different? (P < 0.05)			No		
Number of groups			6		
F			0.3083		
R squared			0.1138		
ANOVA Table			SS	df	MS
Treatment (between columns)			0.02318	5	0.004636
Residual (within columns)			0.1805	12	0.01504
Total			0.2037	17	
Dunnett's Multiple Comparison Test	**Mean Diff.**	**q**	**Significant? P < 0.05?**	**Summary**	**95% CI of diff**
B0 vs B40	-0.03977	0.3971	No	ns	-0.3303 to 0.2508
B0 vs B80	0.04133	0.4128	No	ns	-0.2492 to 0.3319
B0 vs B160	0.03213	0.3209	No	ns	-0.2584 to 0.3227
B0 vs B320	-0.00677	0.06758	No	ns	-0.2973 to 0.2838
B0 vs B640	0.07023	0.7014	No	ns	-0.2203 to 0.3608


(a)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
80
160
240
320
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0006 x + 0.0013 (R2=0.999)
UV only- DCF
y = -0.0058 x + 0.0052 (R2=1)
UV/H2O2-ATZ
y = -0.0052 x + 0.0130 (R2= 0.999)
UV/H2O2-DCF
y = -0.0203 x + 0.0206 (R2= 0.998)


(b)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
80
160
240
320
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0006 x + 0.0023 (R2=0.999)
UV only- DCF
y = -0.0059 x - 0.0009 (R2=1)
UV/H2O2-ATZ
y = -0.0053 x -0.0009 (R2= 1)
UV/H2O2-DCF
y = -0.0207 x - 0.0012 (R2= 1)


(c)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
80
160
240
320
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0006 x - 0.0018 (R2=0.999)
UV only- DCF
y = -0.0056 x - 0.0105 (R2=1)
UV/H2O2-ATZ
y = -0.0047 x -0.0003(R2= 1)
UV/H2O2-DCF
y = -0.0200 x - 0.0001 (R2= 0.999)


(d)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
80
160
240
320
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0006 x + 0.0007 (R2=0.999)
UV only- DCF
y = -0.0059 x + 0.0094 (R2=1)
UV/H2O2-ATZ
y = -0.0044 x - 0.0002 (R2= 0.997)
UV/H2O2-DCF
y = -0.0203 x + 0.0002 (R2= 1)

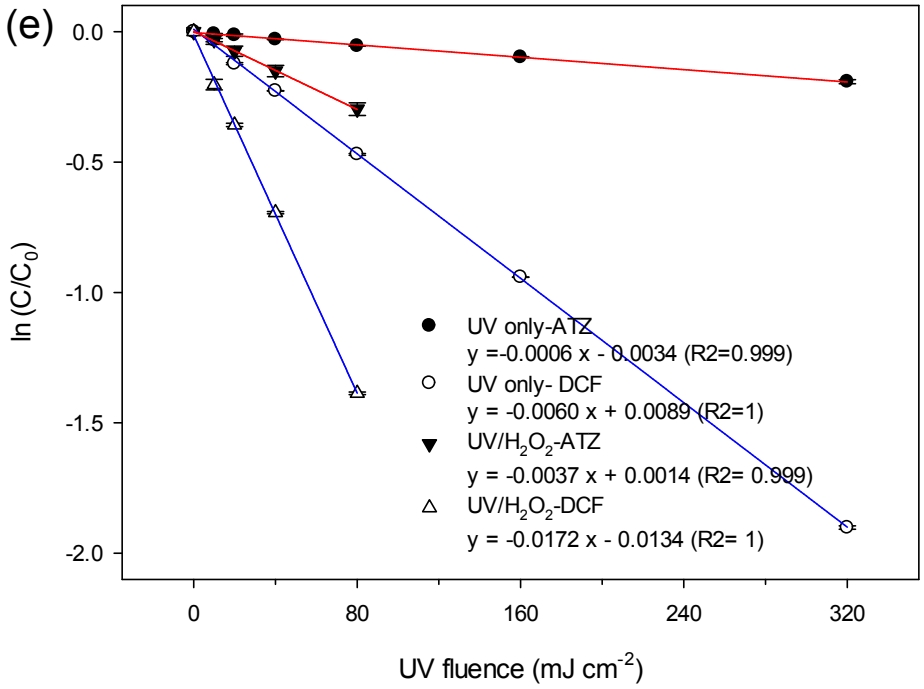
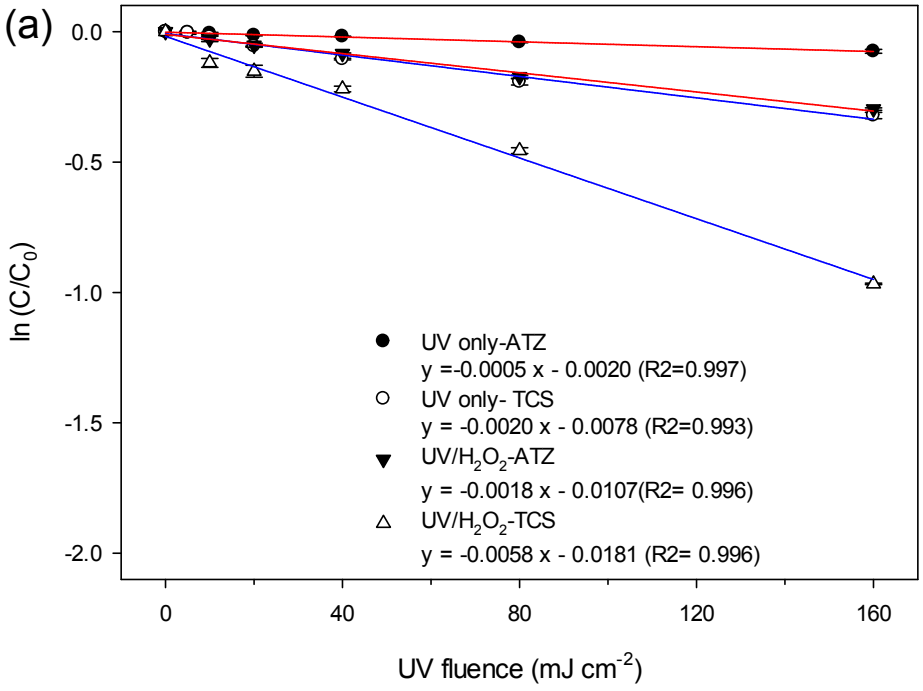
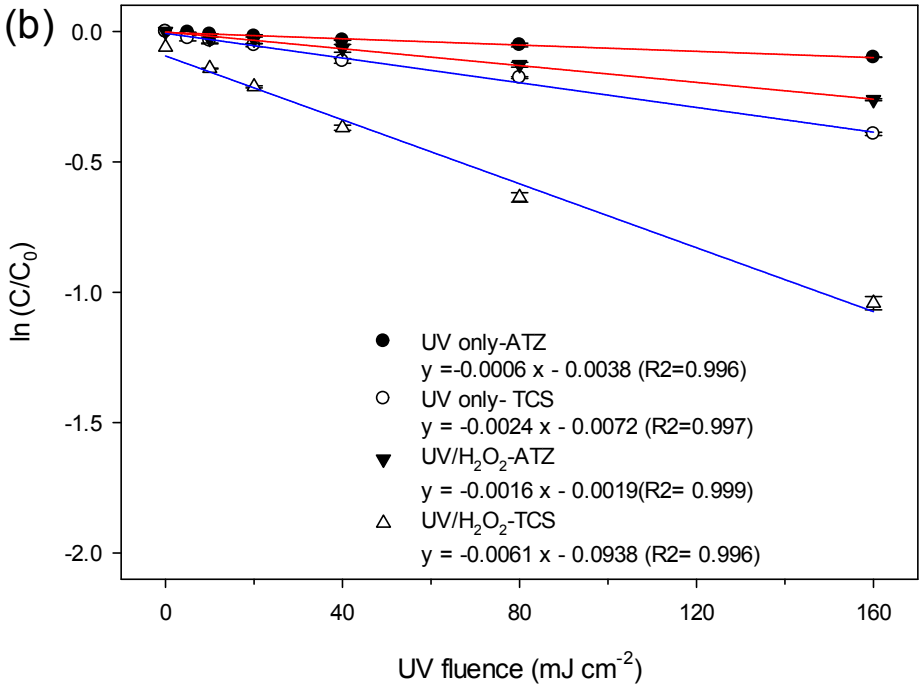
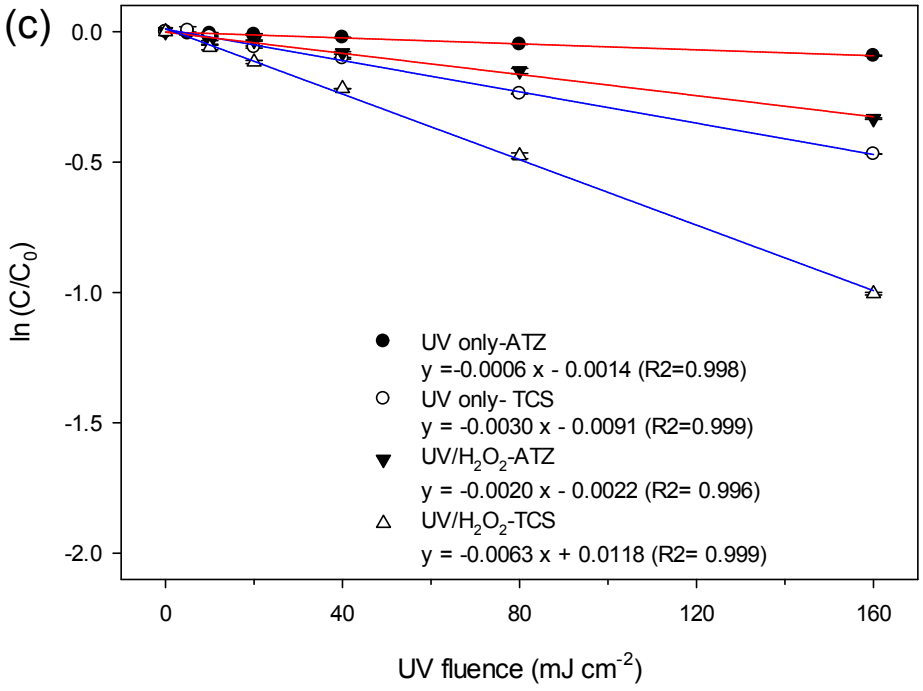
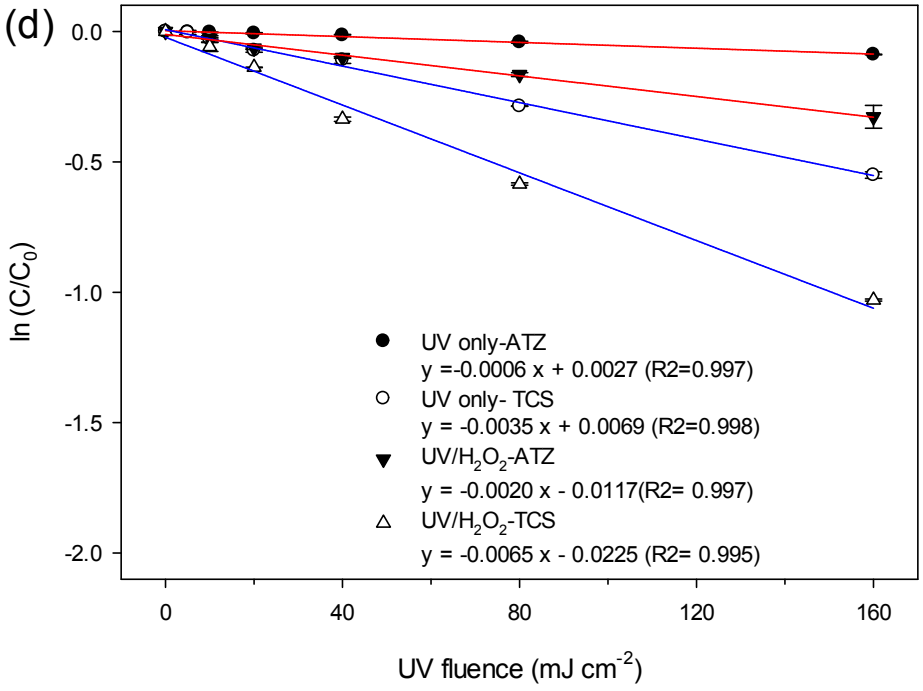


Fig. S1 Determination of second-order rate constants of diclofenac (DCF) with hydroxyl radical using atrazine (ATZ) as a competitor at pH 5.3 (a), 5.9 (b), 6.6 (c), 7.4 (d), and 8.5 (e). $[DCF]_0$ = 1 μM, $[ATZ]_0$ = 1 μM, $[H_2O_2]_0$ = 1 mM, 10 mM phosphate buffer.


(a)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
40
80
120
160
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0005 x - 0.0020 (R2=0.997)
UV only- TCS
y = -0.0020 x - 0.0078 (R2=0.993)
UV/H2O2-ATZ
y = -0.0018 x - 0.0107(R2= 0.996)
UV/H2O2-TCS
y = -0.0058 x - 0.0181 (R2= 0.996)


(b)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
40
80
120
160
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0006 x - 0.0038 (R2=0.996)
UV only- TCS
y = -0.0024 x - 0.0072 (R2=0.997)
UV/H2O2-ATZ
y = -0.0016 x - 0.0019(R2= 0.999)
UV/H2O2-TCS
y = -0.0061 x - 0.0938 (R2= 0.996)


(c)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
40
80
120
160
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0006 x - 0.0014 (R2=0.998)
UV only- TCS
y = -0.0030 x - 0.0091 (R2=0.999)
UV/H2O2-ATZ
y = -0.0020 x - 0.0022 (R2= 0.996)
UV/H2O2-TCS
y = -0.0063 x + 0.0118 (R2= 0.999)


(d)
0.0
-0.5
-1.0
-1.5
-2.0
ln (C/C0)
0
40
80
120
160
UV fluence (mJ cm-2)
UV only-ATZ
y =-0.0006 x + 0.0027 (R2=0.997)
UV only- TCS
y = -0.0035 x + 0.0069 (R2=0.998)
UV/H2O2-ATZ
y = -0.0020 x - 0.0117(R2= 0.997)
UV/H2O2-TCS
y = -0.0065 x - 0.0225 (R2= 0.995)

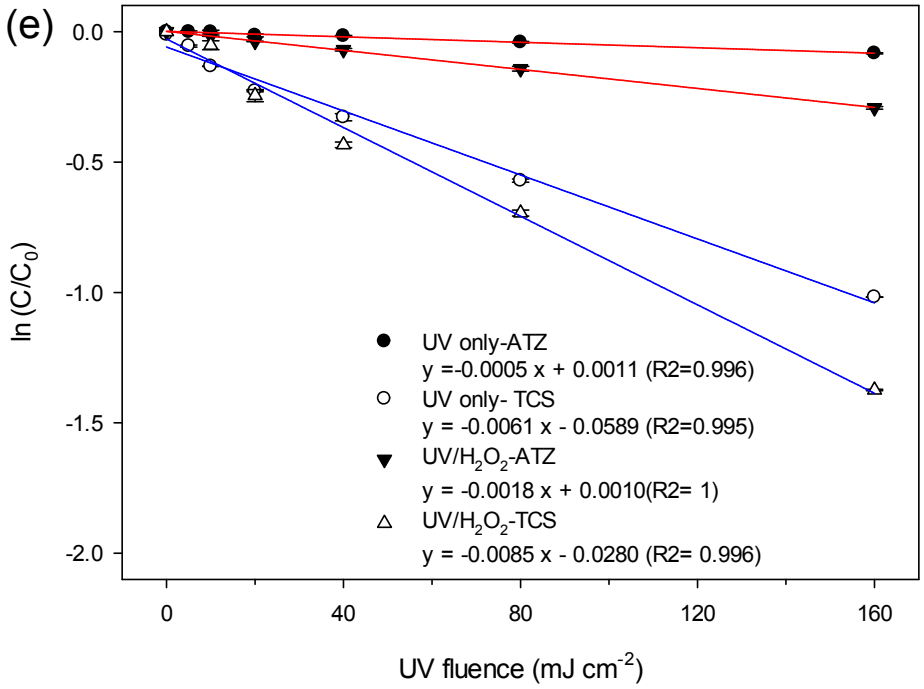


Fig. S2 Determination of second-order rate constants of triclosan (TCS) with hydroxyl radical using atrazine (ATZ) as a competitor at pH 5.3 (a), 5.9 (b), 6.6 (c), 7.4 (d), and 8.5 (e). $[DCF]_0$ = 1 μM, $[ATZ]_0$ = 1 μM, $[H_2O_2]_0$ = 1 mM, 10 mM phosphate buffer.

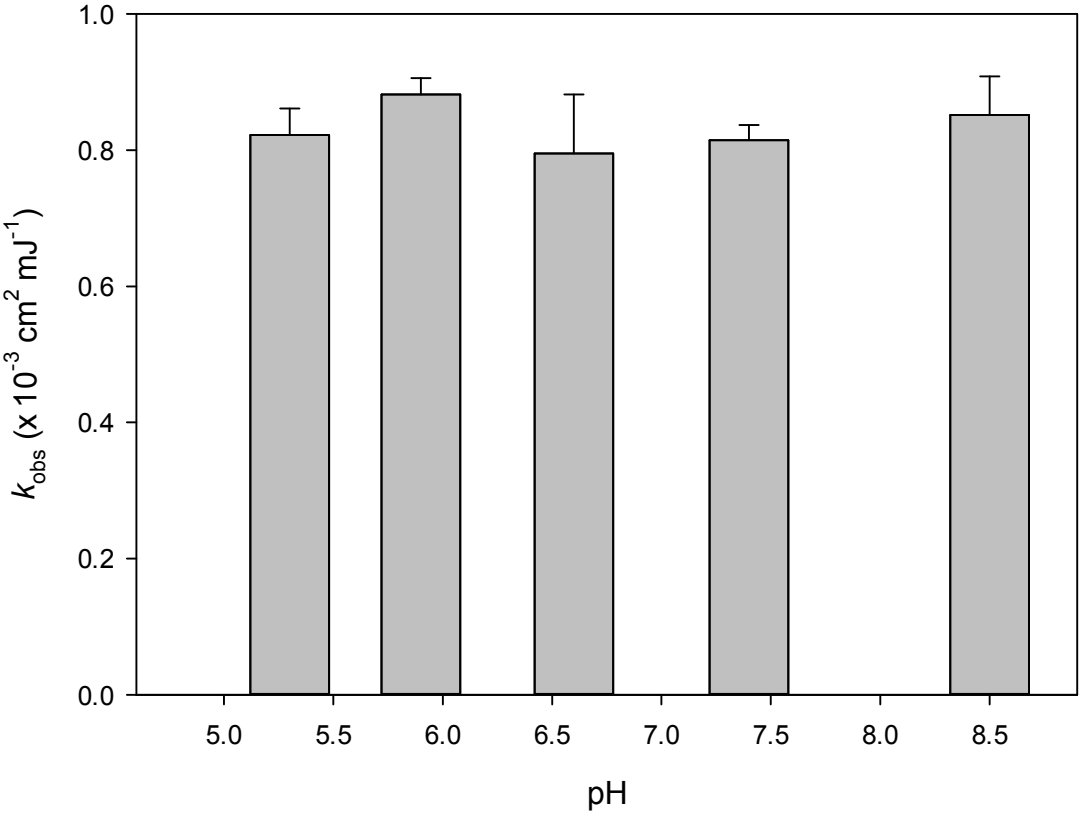


Fig. S3 Effect of pH on the k_{obs} during estrone degradation by UV only. Reaction conditions: $[estrone]_0$ = 1 μM, $[H_2O_2]_0$ = 1 mM, 10 mM phosphate buffer.

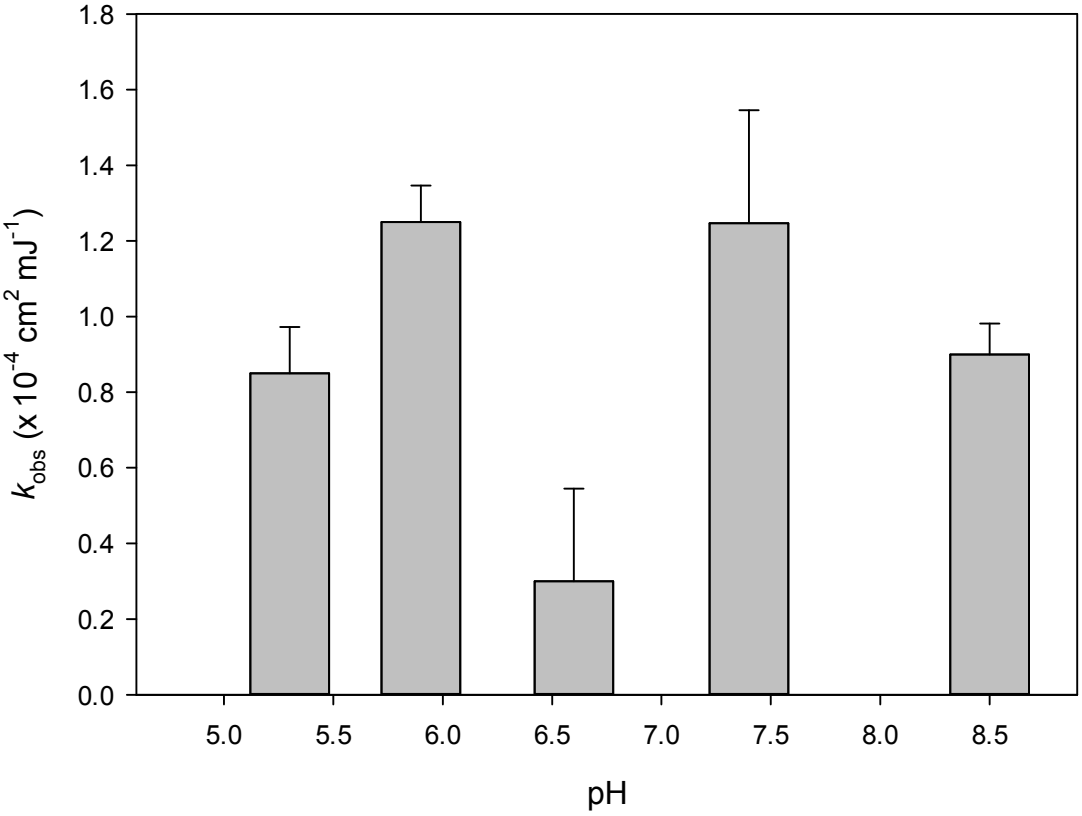
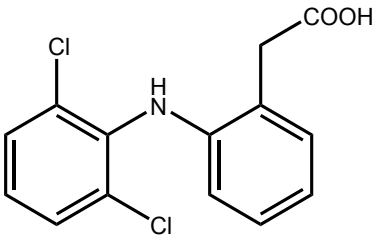
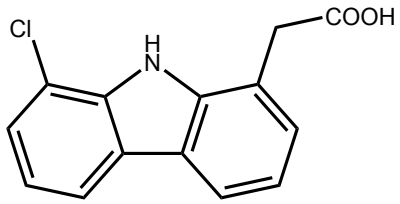


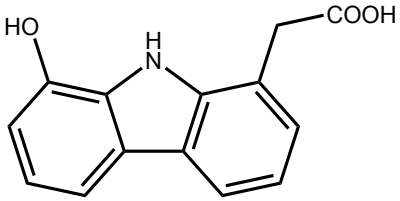
Fig. S4 Effect of pH on the degradation of 17β-estradiol by UV only. Reaction conditions: [17β-estradiol]$_0$ = 1 μM, [H_2O_2]$_0$ = 1 mM, 10 mM phosphate buffer.



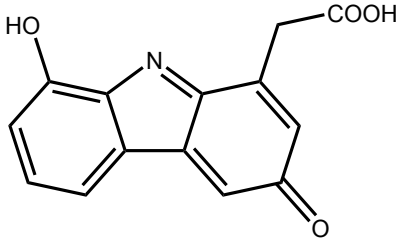
Diclofenac



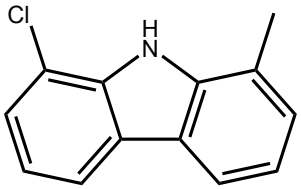
2-(8-chloro-9H-carbazol-1-yl)acetic acid



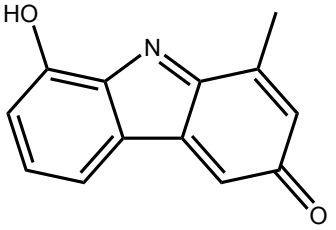
2-(8-hydroxy-9H-carbazol-1-yl)acetic acid



2-(8-hydroxy-3-oxo-3H-carbazol-1-yl)acetic acid



8-methyl-9H-carbazol-1-ol



8-hydroxy-1-methyl-3H-carbazol-3-one

Fig. S5 Possible structure of the transformation products during the degradation of diclofenac in UV/H_2O_2 reported in previous study[2].

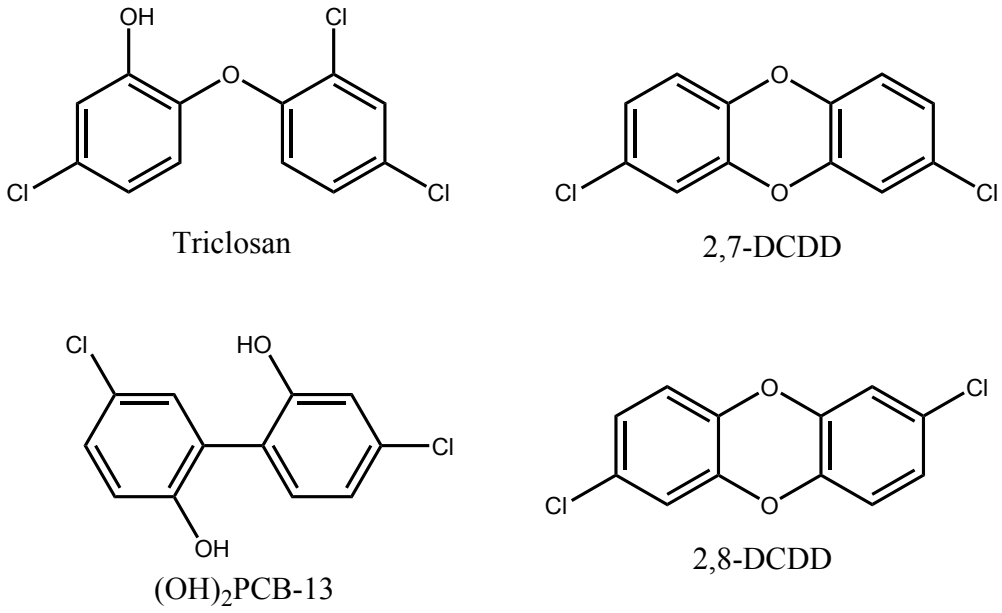


Fig. S6 Possible structure of the transformation products during the degradation of triclosan in •OH-based advanced oxidation processes reported in previous study[3, 4].

1. Y. Liu, X. He, X. Duan, Y. Fu, D. Fatta-Kassinos and D. D. Dionysiou, *Water Research*, 2016, **95**, 195-204.
2. K. Lekkerkerker-Teunissen, M. J. Benotti, S. A. Snyder and H. C. van Dijk, *Separation and Purification Technology*, 2012, **96**, 33-43.
3. Y. Gao, Y. Ji, G. Li and T. An, *Water Research*, 2014, **49**, 360-370.
4. S. Kliegman, S. N. Eustis, W. A. Arnold and K. McNeill, *Environmental Science & Technology*, 2013, **47**, 6756-6763.