Supporting Information for

Radical Chemistry and Structural Relationships of PPCP Degradation by UV/Chlorine Treatment in Simulated Drinking Water

Kaiheng Guo[†], Zihao Wu[†], Chii Shang[‡], Bo Yao[‖], Shaodong Hou[†], Xin Yang[†], Weihua Song[*,‖], Jingyun Fang[*,†]

[†] Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China

[‡] Department of Civil and Environmental Engineering, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

[‖] Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, P. R. China

Submitted to

Environmental Science & Technology

Number of pages (including this page): 34

Number of texts: 3

Number of tables: 4

Number of figures: 7

Content lists

Text S1. Analysis of nitrobenzene by GC-MS

The nitrobenzene (NB) samples (10 mL) were pretreated with liquid-liquid extraction procedure by hexane (1 mL). Analysis of NB was carried out on a gas chromatography (GC) system coupled with a mass spectrometer (MS) using electron ionization (Shimadzu, QP2010 Ultra). The column used was an SH-Rxi-5Sil MS capillary column (30 m × 0.25 mm × 0.25 μm, Shimadzu). The sample injection volume was 1.0 μL. The carrier gas was Helium at a flow rate of 1.2 mL min^{-1}, and the injector temperature was 250 °C. The GC temperature program consisted of an initial temperature of 45 °C for 0.5 min, followed by ramping to 150 °C at 20 °C min^{-1}, then ramping to 300 °C at 40 °C min^{-1} and holding for 1 min. The ion source temperature of 230 °C and a GC-MS transfer line temperature of 280 °C were used. The MS detector voltage was set at 0.9 kV. Ions at 77, 123 and 51 a.m.u. were monitored in the SIM mode, and 77 a.m.u was used to quantify NB.

Text S2. Determination of the second-order rate constants between $HO^{\bullet}$ and PPCPs

The second-order rate constants for the reaction of $HO^{\bullet}$ with PPCPs were determined by competition kinetics using ibuprofen as a reference compound (R), which reacts with $HO^{\bullet}$ at a second-order rate constant of 7.2×10^{9} M^{-1} s^{-1}. The UV/H_2O_2 process was used to produce $HO^{\bullet}$ at the H_2O_2 dosage of 10 μM and pH 7. The reaction solution was spiked with the mixture of 1 μg L^{-1} PPCPs. The second-order rate constants of the PPCPs with $HO^{\bullet}$ were calculated from eq S1.

$$\ln\frac{[\mathrm{PPCP}]}{[\mathrm{PPCP}]_0} = \frac{k_{HO\bullet,PPCP}}{k_{HO\bullet,\mathrm{Ibuprofen}}} \times \ln\frac{[\mathrm{Ibuprofen}]}{[\mathrm{Ibuprofen}]_0} \quad \text{(S1)}$$

Text S3. Degradation of caffeine, carbamazepine and gemfibrozil in a $CO_3^{\bullet-}$ system

The degradation of caffeine, carbamazepine and gemfibrozil by $CO_3^{\bullet-}$ was evaluated. To generate $CO_3^{\bullet-}$, the UV/H_2O_2 process was carried out at 50 μM H_2O_2 dosage and pH 8.4. The reaction solution was spiked with 100 mM sodium bicarbonate to scavenge the $HO^{\bullet}$, and yield $CO_3^{\bullet-}$. The reference compounds (R) of $ClO^{\bullet}$ and selected PPCPs were simultaneously spiked into the system at concentrations of 5 μM. The irradiation time was 10 min. All samples were collected at regular intervals, and then HPLC was used for the analysis of PPCPs and reference compounds.

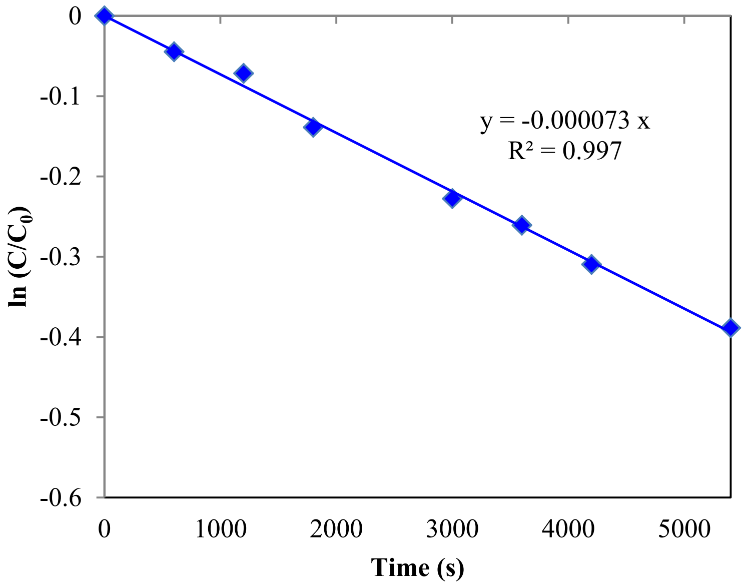


Figure S1. Photolysis of dilute H_2O_2 under UV irradiation at 254 nm. Conditions: average UV fluence rate = 0.78 mW cm^{-2}, $[H_2O_2]_0$ = 200 μM, 25 °C.

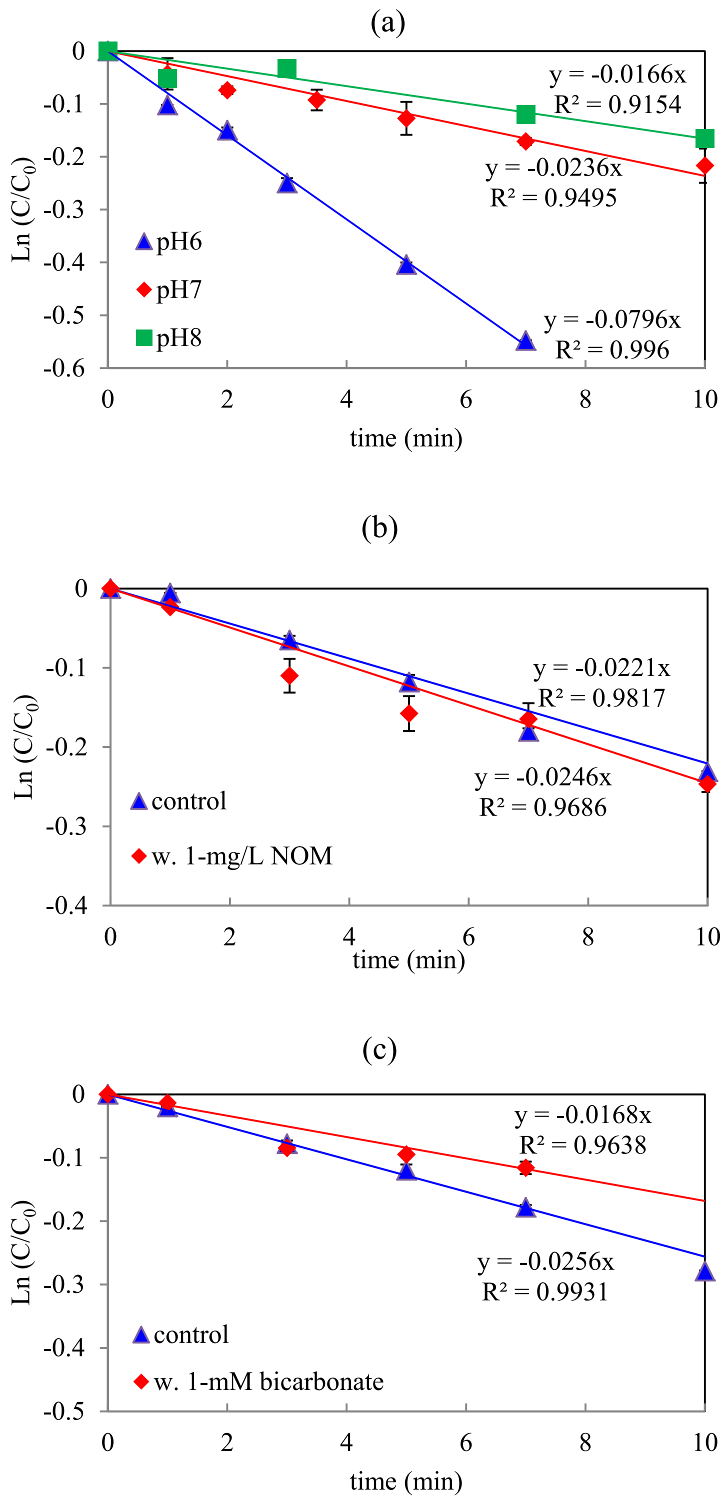
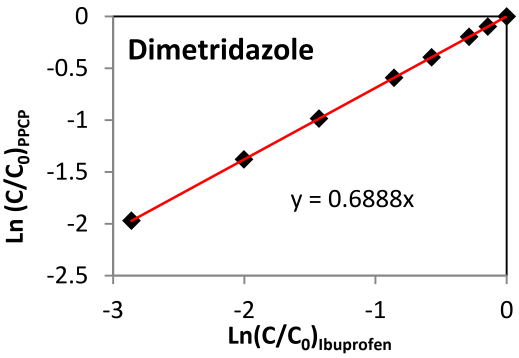
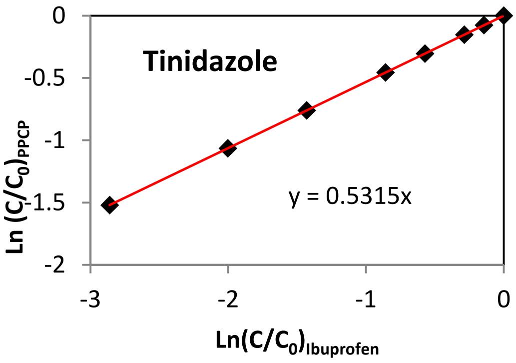
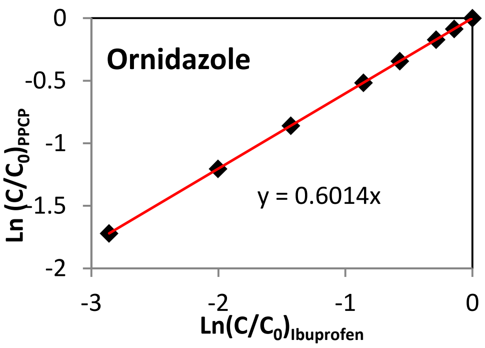
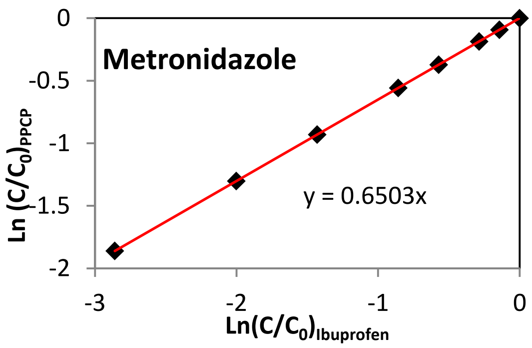


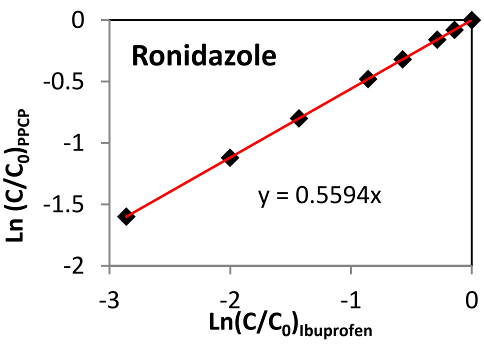
Figure S2. The degradation kinetics of NB in the UV/chlorine process (a) at pH 6, 7, 8; (b) with or without the presence of 1 mg/L NOM at pH 7; (c) with or without the presence of 1 mM bicarbonate at pH 7. Conditions: $[PPCP]_0$ = 1 μg L^{-1}, $[NB]_0$ = 20 nM, $[chlorine]_0$ = 10 μM, $[NOM]_0$ = 1 mg L^{-1}, average UV fluence rate = 0.78 mW cm^{-2}.

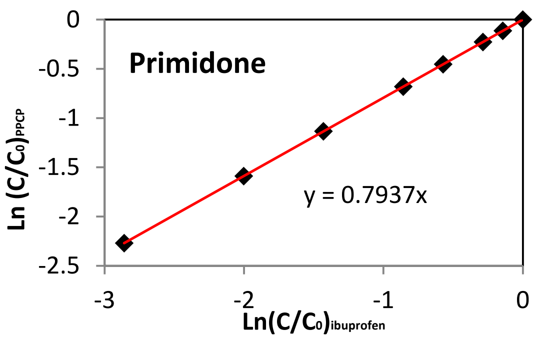

Dimetridazole
y = 0.6888x
Ln (C/C0)PPCP
Ln(C/C0)Ibuprofen

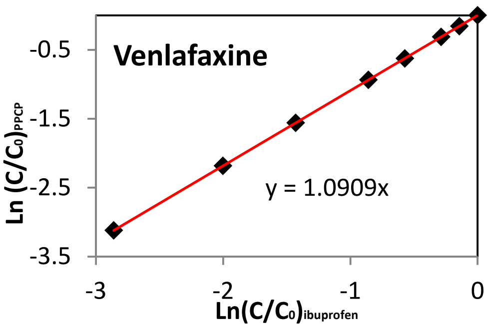

Tinidazole
y = 0.5315x
Ln (C/C0)PPCP
Ln(C/C0)Ibuprofen

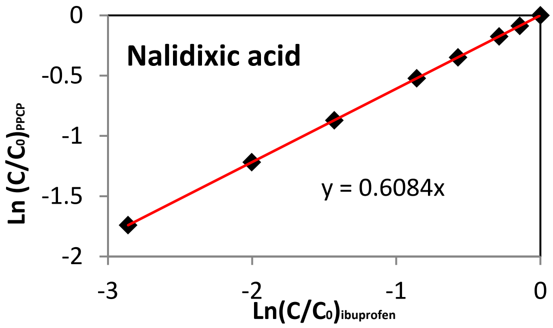

Ornidazole
y = 0.6014x
Ln (C/C0)PPCP
Ln(C/C0)Ibuprofen

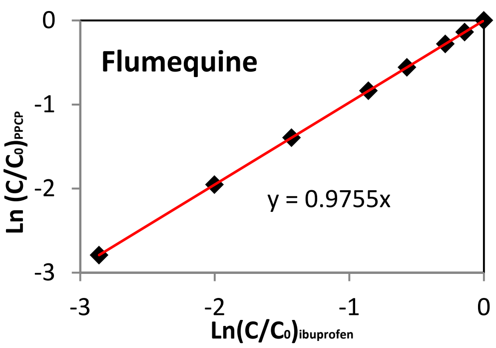

Metronidazole
y = 0.6503x
Ln (C/C0)PPCP
Ln(C/C0)Ibuprofen

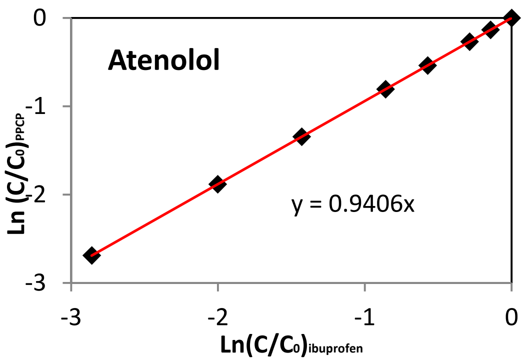

Ronidazole
y = 0.5594x
Ln (C/C0)PPCP
Ln(C/C0)Ibuprofen

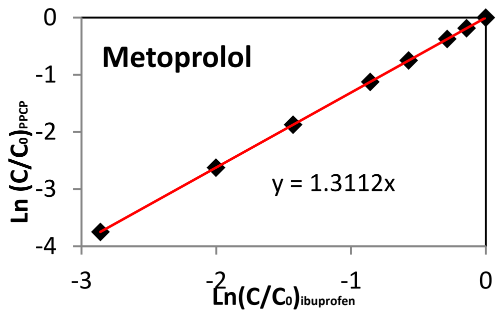

Primidone
y = 0.7937x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

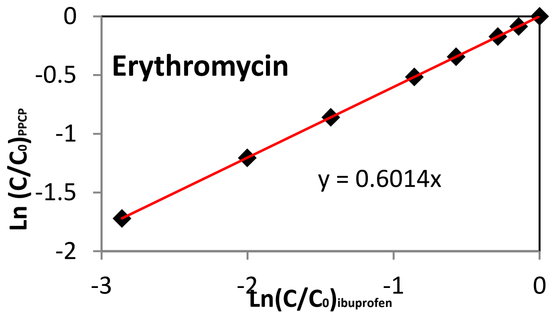

Venlafaxine
y = 1.0909x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

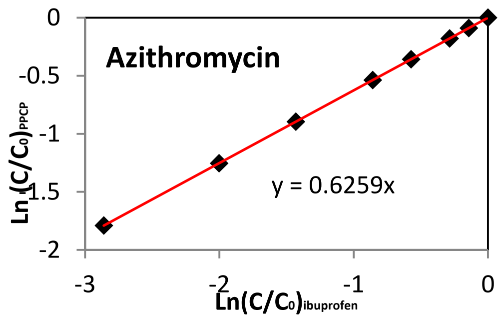

Nalidixic acid
y = 0.6084x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

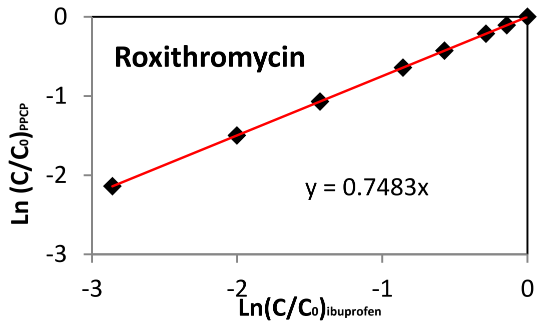

Flumequine
y = 0.9755x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

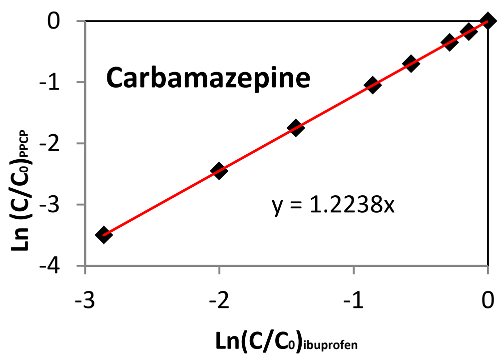

Atenolol
y = 0.9406x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

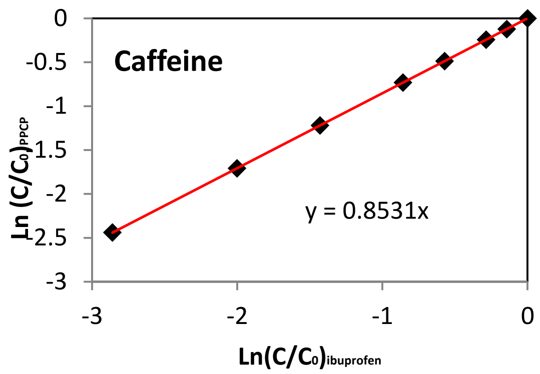

Metoprolol
y = 1.3112x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

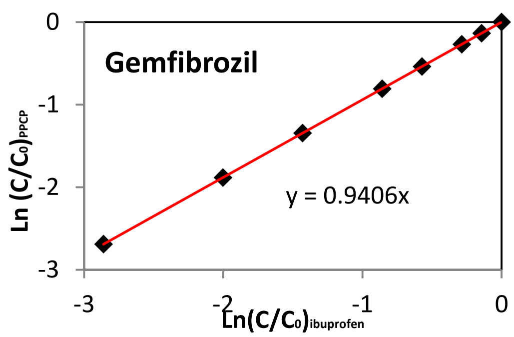

Erythromycin
y = 0.6014x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

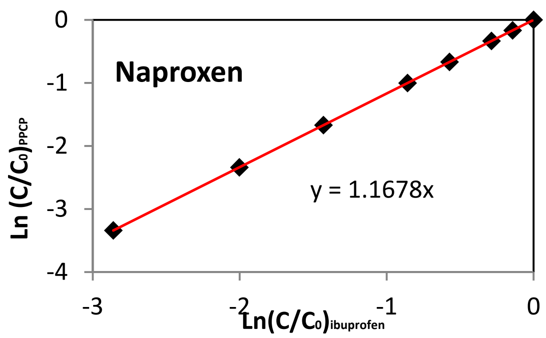

Azithromycin
y = 0.6259x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

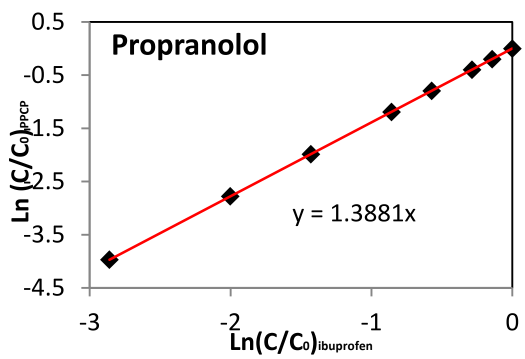

Roxithromycin
y = 0.7483x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

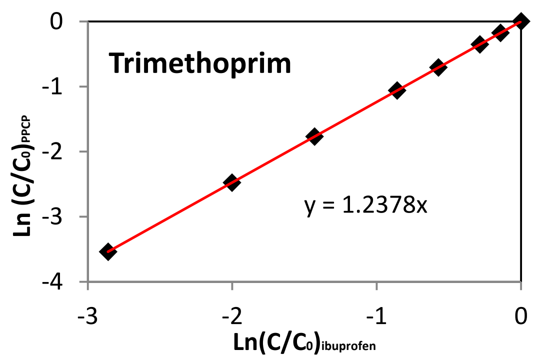

Carbamazepine
y = 1.2238x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen


Caffeine
y = 0.8531x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen


Gemfibrozil
y = 0.9406x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen


Naproxen
y = 1.1678x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen


Propranolol
y = 1.3881x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen


Trimethoprim
y = 1.2378x
Ln (C/C0)PPCP
Ln(C/C0)ibuprofen

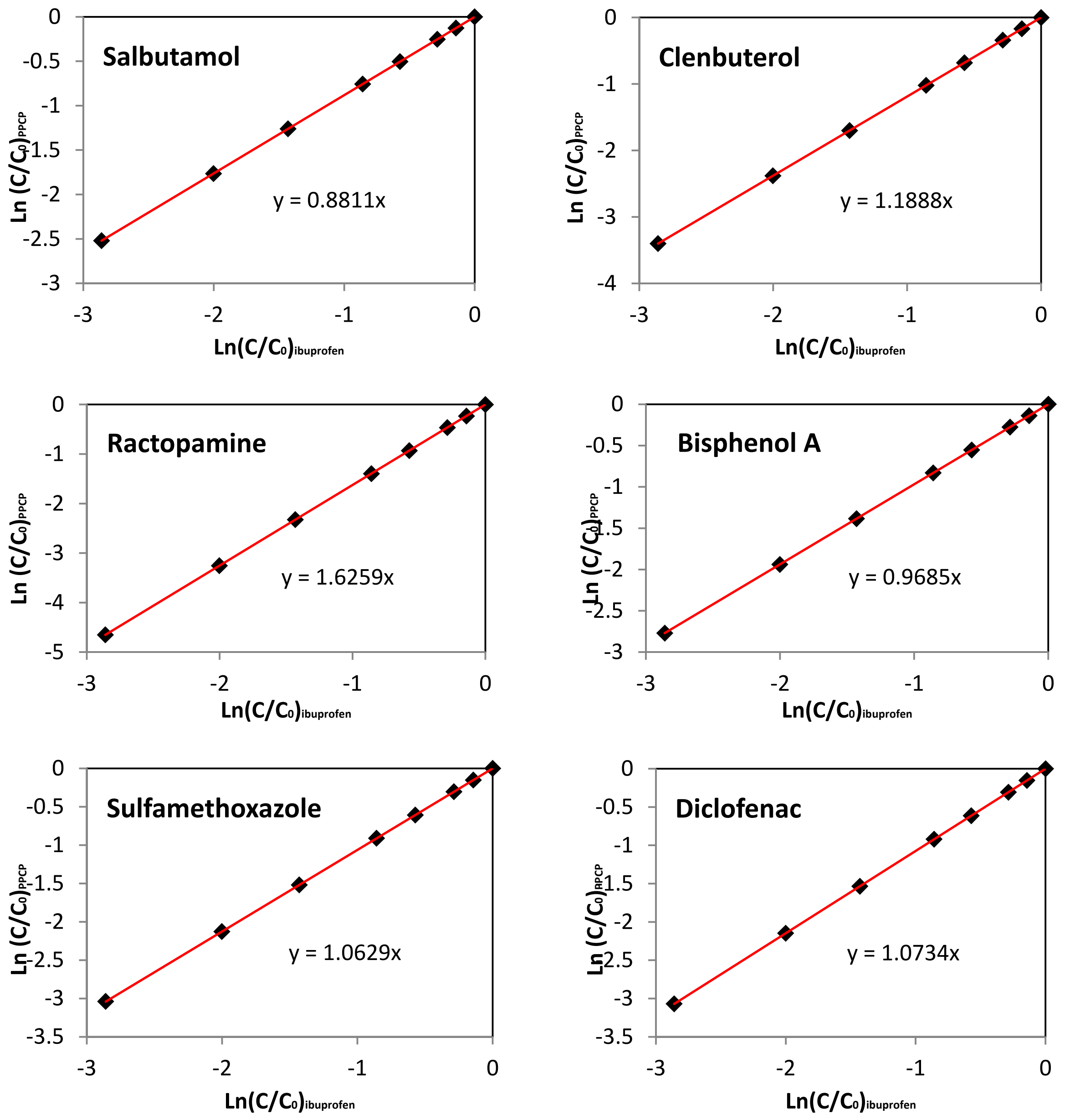


Figure S3. Determination of the second-order rate constants of HO$^{\bullet}$ reacting with PPCPs by competition kinetics using ibuprofen as a reference compound. Conditions: $[PPCP]_0 = 1\ \mu g\ L^{-1}$, $[H_2O_2]_0 = 10\ \mu M$, pH = 7, average UV fluence rate = 0.78 mW cm^{-2}.

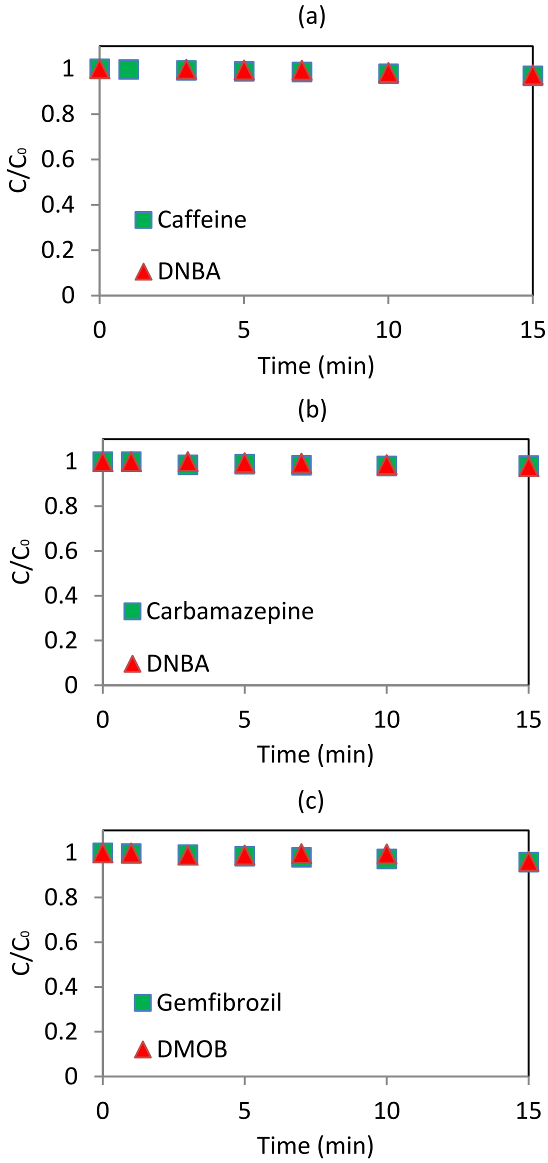


Figure S4. Degradation of (a) caffeine, (b) carbamazepine, (c) gemfibrozil and reference compounds in the $CO_3^{\bullet-}$ system. Conditions: $[PPCP]_0 = 5$ μM, $[R]_0 = 5$ μM, $[H_2O_2]_0 = 50$ μM, $[HCO_3^-]_0 = 100$ mM, average UV fluence rate = 0.78 mW cm^{-2}.

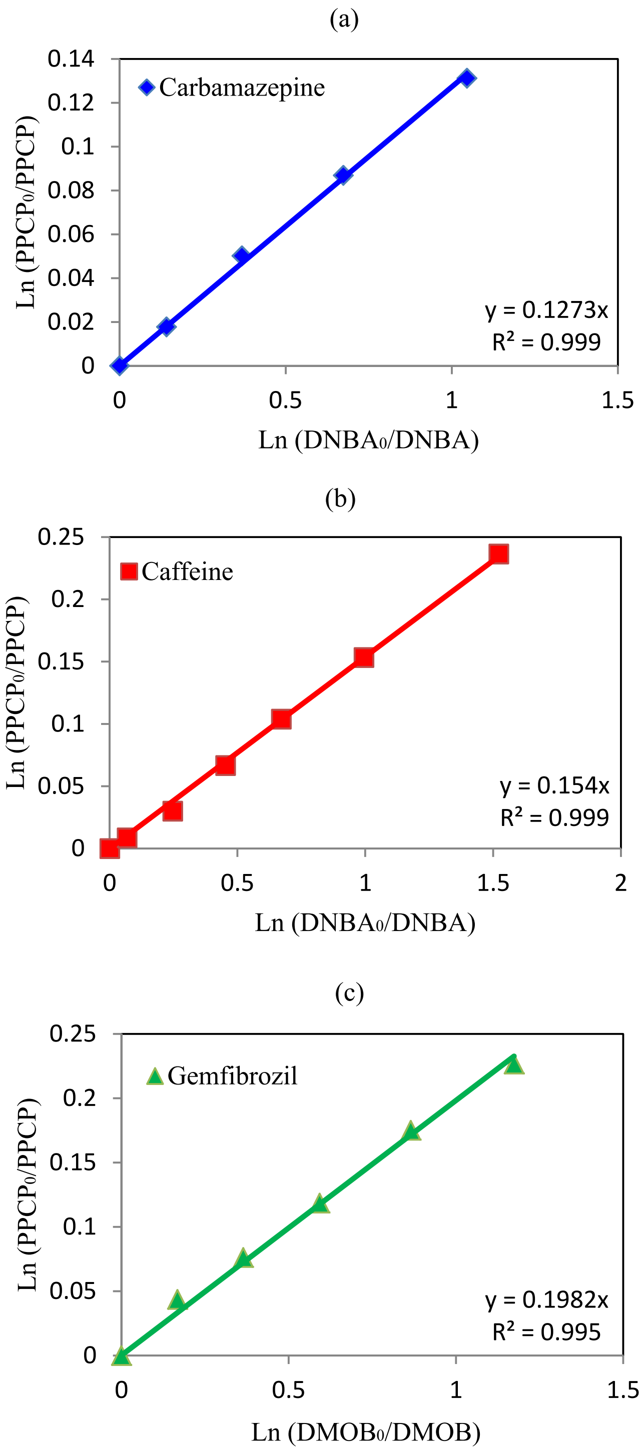


Figure S5. Determination of the second-order rate constants of $ClO^{\bullet}$ reacting with (a) carbamazepine, (b) caffine and (c) gerfibrozil by competition kinetics using 1,4-dimethoxybenzonic acid (DMOB) or 2,5-dimethoxybenzoate ion (DNBA) as reference compounds. Conditions: $[PPCP]_0$ = 5 µM, $[R]_0$ = 5 µM, $[chlorine]_0$ = 50 µM, $[HCO_3^-]_0$ = 100 mM, average UV fluence rate = 0.78 mW cm^{-2}.

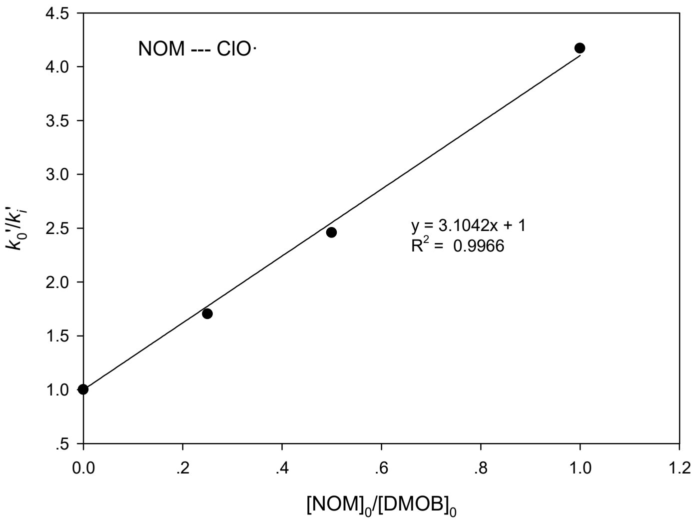


Figure S6. Determination of the second-order rate constant of $ClO^{\bullet}$ reacting with NOM by competition kinetics using DMOB as a reference compound.

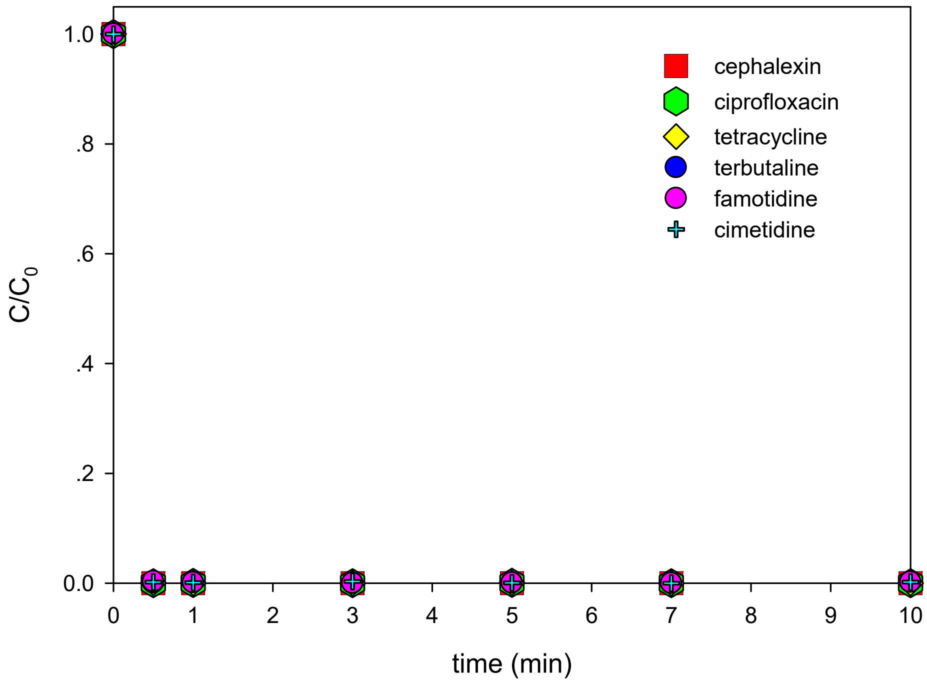


Figure S7. Chlorination of cephalexin, ciprofloxacin, tetracycline, tebutaline, famotidine and cimetidine in group V at pH 7. Conditions: $[PPCP]_0 = 1\ \mu g\ L^{-1}$, $[chlorine]_0 = 10\ \mu M$.

Table S1. MS details for the PPCPs detected by Agilent 6430 triple quadrupole MS

Compound Name	Precursor Ion	Product Ion	Fragmentor	Collision Energy	Ret Time	MS mode
Azithromycin	749.5	158/591.4	130	35/30	5.7	+
Caffeine	195	110/138	110	20/16	4.61	+
Carbamazepine	237.1	179/194	120	36/16	5.64	+
Carbamazepine-D10	247	204	120	15	5.64	+
Celphalexin	348.1	158/174.1	100	8	4.47	+
Celphalexin-D5	353.4	158	100	4	4.47	+
Cimetidine	253.13	95.1/159.1	90	20/8	4.19	+
Ciprofloxacin	332.1	288.2/314.1	135	12/16	4.9	+
Clenbuterol	277.09	203/259	95	8/4	4.9	+
Dimetridazole	142.1	81/96.1	100	28/12	4.82	+
Dimetridazole-D3	145.1	99	100	16	4.82	+
Erthymycin	734.47	158.1/576.4	170	24/12	5.9	+
Famotidine	338.1	155.1/189.1	85	28/12	4.17	+
Flumequine	262.09	202/244.1	100	32/12	5.81	+
Flumequine-C3	265.1	247.1	105	16	5.81	+
Metoprolol	268.2	56/116	135	28/12	4.88	+
Metoprolol-D7	275.3	123	125	16	4.88	+
Metronidazole	172.07	82.1/128.1	90	24/12	4.52	+
Metronidazole-D4	176.1	128	90	12	4.52	+
Nalidiixic acid	233.09	187.1/215.1	95	24/8	5.77	+

Ornidazole	220.05	82.1/128.1	110	28/8	5.05	+
Primidone	219.12	91.1/162.1	90	28/8	4.91	+
Primidone-D5	224.2	167.2	100	8	4.91	+
Propranolol	260.2	56/116	120	32/12	5.3	+
Ractopamine	302.2	164/284.2	105	8/4	4.71	+
Ronidazole	201	140	80	5	4.63	+
Roxithromycin	837.53	158.1/679.5	135	28/12	5.7	+
Roxithromycin-D7	844.6	158	185	36	5.7	+
Salbutamol hemi	240.2	148.1	80	12	4.13	+
Atenolol	267.2	190	120	12	4.18	+
Atenolol-D7	274	145	130	15	4.18	+
Sulfamethoxazole	254	92/156	80	20/8	5.29	+
Terbutaline	226.15	107/152.1	100	28/8	4.13	+
Tetracycline	445.2	410.1/427.2	120	16/8	4.7	+
Tinidazole	248.1	82.1/121	110	32/8	4.9	+
Trimethoprim	291	230/261	145	20/24	4.6	+
Trimethoprim-C3	294.2	231	145	20	4.6	+
Venlafaxine	278.21	58.1/260.2	105	16/4	5.5	+
Venlafaxine-D6	284.3	58.1	110	16	5.5	+
Salbutamol	240.2	222.1	80	4	4.13	+
Chloramphenicol	320.9	257/176/152.1	145	4/5/16	5.35	-
Dicofenac	294	250/214	90	4/16	6.57	-

Gemfibrozil	249.32	121.1	100	8	6.89	-
Ibuprofen	205.12	161.2	80	4	6.62	-
Ibuprofen-D3	208.3	164.1	75	0	6.62	-
Naproxen	229	185/169	70	4/28	6.12	-
Triclocarban	313	160/126	145	8/20	7.03	-
Bisphenol A	227	133	130	28	5.94	-

Table S2. Principle reactions in the UV/chlorine process

NO.	Reactions	Rate constants	References
1*	$HOCl \rightarrow HO^{\bullet} + Cl^{\bullet}$	$r_{HOCl} = \Phi_{HOCl} f_{HOCl} \frac{I_0}{V} L(1 - 10^{-A})$ [a] $f_{HOCl} = \varepsilon_{HOCl} C_{HOCl} L/A$	1
2*	$OCl^{-} \rightarrow O^{\bullet -} + Cl^{\bullet}$	$r_{OCl^-} = \Phi_{OCl^-} f_{OCl^-} \frac{I_0}{V} L(1 - 10^{-A})$ $f_{OCl^-} = \varepsilon_{OCl^-} C_{OCl^-} L/A$	1
3	$H^{+} + OCl^{-} \rightarrow HOCl$	$5.00 \times 10^{10}\ M^{-1}s^{-1}$	2
4	$HOCl \rightarrow H^{+} + OCl^{-}$	$1.60 \times 10^{3}\ s^{-1}$	2
5	$H^{+} + HO_2^{-} \rightarrow H_2O_2$	$5.00 \times 10^{10}\ M^{-1}s^{-1}$	2
6	$H_2O_2 \rightarrow H^{+} + HO_2^{-}$	$1.30 \times 10^{-1}\ s^{-1}$	2
7	$H^{+} + OH^{-} \rightarrow H_2O$	$1.00 \times 10^{11}\ M^{-1}s^{-1}$	2
8	$H_2O \rightarrow H^{+} + OH^{-}$	$1.00 \times 10^{-3}\ s^{-1}$	2
9	$H^{+} + O_2^{\bullet -} \rightarrow HO_2^{\bullet}$	$5.00 \times 10^{10}\ M^{-1}s^{-1}$	2
10	$HO_2^{\bullet} \rightarrow H^{+} + O_2^{\bullet -}$	$7.00 \times 10^{5}\ s^{-1}$	2
11	$H_2PO_4^{-} + H^{+} \rightarrow H_3PO_4$	$5.00 \times 10^{10}\ M^{-1}s^{-1}$	2
12	$H_3PO_4 \rightarrow H_2PO_4^{-} + H^{+}$	$3.87 \times 10^{8}\ s^{-1}$	2
13	$HPO4^{2-} + H^{+} \rightarrow H_2PO_4^{-}$	$5.00 \times 10^{10}\ M^{-1}s^{-1}$	2
14	$H_2PO_4^{-} \rightarrow HPO_4^{2-} + H^{+}$	$3.15 \times 10^{3}\ s^{-1}$	2
15	$PO4^{3-} + H^{+} \rightarrow HPO4^{2-}$	$5.00 \times 10^{10}\ M^{-1}s^{-1}$	2
16	$HPO4^{2-} \rightarrow PO4^{3-} + H^{+}$	$2.50 \times 10^{-2}\ s^{-1}$	2
17	$HO^{\bullet} + HPO4^{2-} \rightarrow HPO4^{\bullet -} + OH^{-}$	$1.50 \times 10^{5}\ M^{-1}s^{-1}$	2
18	$HO^{\bullet} + H_2PO_4^{-} \rightarrow HPO_4^{\bullet -} + H_2O$	$2.00 \times 10^{4}\ M^{-1}s^{-1}$	2

19	$H_2O_2 + HPO_4^{\bullet -} \rightarrow H_2PO_4^{-} + HO_2^{\bullet}$	2.70×10^{7} $M^{-1}s^{-1}$	2
20	$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2$	5.50×10^{9} $M^{-1}s^{-1}$	2
21	$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$	2.70×10^{7} $M^{-1}s^{-1}$	2
22	$HO^{\bullet} + HO_2^{-} \rightarrow HO_2^{\bullet} + OH^{-}$	7.50×10^{9} $M^{-1}s^{-1}$	2
23	$HO^{\bullet} + HO_2^{\bullet} \rightarrow O_2 + H_2O$	7.10×10^{9} $M^{-1}s^{-1}$	3
24	$HO^{\bullet} + O_2^{\bullet -} \rightarrow O_2 + OH^{-}$	1.00×10^{10} $M^{-1}s^{-1}$	2
25	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	8.30×10^{9} $M^{-1}s^{-1}$	2
26	$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^{-} + O_2$	9.70×10^{7} $M^{-1}s^{-1}$	2
27	$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + HO^{\bullet} + H_2O$	3.00 $M^{-1}s^{-1}$	3
28	$O_2^{\bullet -} + H_2O_2 \rightarrow O_2 + HO^{\bullet} + OH^{-}$	1.30×10^{-1} $M^{-1}s^{-1}$	3
29	$O^{\bullet -} + H_2O \rightarrow HO^{\bullet} + OH^{-}$	1.80×10^{6} $M^{-1}s^{-1}$	3
30	$HCO_3^{-} + H^{+} \rightarrow H_2CO_3$	5.00×10^{10} $M^{-1}s^{-1}$	2
31	$H_2CO_3 \rightarrow HCO_3^{-} + H^{+}$	5.00×10^{5} s^{-1}	2
32	$CO_3^{2-} + H^{+} \rightarrow HCO_3^{-}$	5.00×10^{10} $M^{-1}s^{-1}$	2
33	$HCO_3^{-} \rightarrow CO_3^{2-} + H^{+}$	2.50 s^{-1}	2
34	$HO^{\bullet} + CO_3^{2-} \rightarrow CO_3^{\bullet -} + OH^{-}$	3.90×10^{8} $M^{-1}s^{-1}$	2
35	$HO^{\bullet} + HCO_3^{-} \rightarrow CO_3^{\bullet -} + H2O$	8.50×10^{6} $M^{-1}s^{-1}$	3
36	$HO^{\bullet} + H_2CO_3 \rightarrow CO_3^{\bullet -} + H_2O + H^{+}$	1.00×10^{6} $M^{-1}s^{-1}$	2
37	$H_2O_2 + CO_3^{\bullet -} \rightarrow HCO_3^{-} + HO_2^{\bullet}$	4.30×10^{5} $M^{-1}s^{-1}$	2
38	$HO_2^{-} + CO_3^{\bullet -} \rightarrow HCO_3 - + O_2$	3.00×10^{7} $M^{-1}s^{-1}$	2
39	$HO^{\bullet} + CO_3^{\bullet -} \rightarrow X$	3.00×10^{9} $M^{-1}s^{-1}$	2
40	$O_2^{\bullet -} + CO_3^{\bullet -} \rightarrow CO_3^{2-} + O_2$	6.00×10^{8} $M^{-1}s^{-1}$	3

41	$CO_3^{\bullet -} + CO_3^{\bullet -} \rightarrow X$	3.00×10^{7} $M^{-1}s^{-1}$	2
42	$H^{+} + Cl^{-} \rightarrow HCl$	5.00×10^{10} $M^{-1}s^{-1}$	2
43	$HCl \rightarrow H^{+} + Cl^{-}$	8.60×10^{16} s^{-1}	2
44	$HO^{\bullet} + Cl^{-} \rightarrow ClOH^{\bullet -}$	4.30×10^{9} $M^{-1}s^{-1}$	2
45	$ClOH^{\bullet -} \rightarrow HO^{\bullet} + Cl^{-}$	6.10×10^{9} s^{-1}	2
46	$ClOH^{\bullet -} + H^{+} \rightarrow Cl^{\bullet} + OH^{-}$	2.10×10^{10} $M^{-1}s^{-1}$	2
47	$ClOH^{\bullet -} + Cl^{-} \rightarrow Cl_2^{\bullet -} + OH^{-}$	1.00×10^{5} $M^{-1}s^{-1}$	2
48	$Cl^{\bullet} + H_2O \rightarrow ClOH^{\bullet -} + H^{+}$	4.50×10^{3} $M^{-1}s^{-1}$	3
49	$Cl^{\bullet} + OH^{-} \rightarrow ClOH^{\bullet -}$	1.80×10^{10} $M^{-1}s^{-1}$	2
50	$Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^{-} + H^{+}$	2.00×10^{9} $M^{-1}s^{-1}$	2
51	$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet -}$	8.50×10^{9} $M^{-1}s^{-1}$	2
52	$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$	8.80×10^{7} $M^{-1}s^{-1}$	2
53	$Cl^{\bullet} + HOCl \rightarrow ClO^{\bullet} + H^{+} + Cl^{-}$	3.00×10^{9} $M^{-1}s^{-1}$	1
54	$Cl^{\bullet} + OCl^{-} \rightarrow ClO^{\bullet} + Cl^{-}$	8.30×10^{9} $M^{-1}s^{-1}$	1
55	$Cl_2^{\bullet -} \rightarrow Cl^{\bullet} + Cl^{-}$	6.00×10^{4} s^{-1}	2
56	$Cl_2 + OH^{-} \rightarrow HOCl + Cl^{-}$	1.00×10^{9} $M^{-1}s^{-1}$	3
57	$Cl_2^{\bullet -} + Cl_2^{\bullet -} \rightarrow Cl_2 + 2Cl^{-}$	8.30×10^{8} $M^{-1}s^{-1}$	2
58	$Cl_2^{\bullet -} + Cl^{\bullet} \rightarrow Cl_2 + Cl^{-}$	2.10×10^{9} $M^{-1}s^{-1}$	3
59	$Cl_2^{\bullet -} + H_2O_2 \rightarrow HO_2^{\bullet} + 2Cl^{-} + H^{+}$	1.40×10^{5} $M^{-1}s^{-1}$	2
60	$Cl_2^{\bullet -} + HO_2^{\bullet} \rightarrow O_2 + 2Cl^{-} + H^{+}$	3.00×10^{9} $M^{-1}s^{-1}$	2
61	$Cl_2^{\bullet -} + O_2^{\bullet -} \rightarrow O_2 + 2Cl^{-}$	1.00×10^{9} $M^{-1}s^{-1}$	2
62	$Cl_2^{\bullet -} + H_2O \rightarrow Cl^{-} + HClOH$	2.34×10 $M^{-1}s^{-1}$	2

63	$Cl_2^{\bullet-} + OH^- \rightarrow Cl^- + ClOH^{\bullet-}$	$4.50 \times 10^7\ M^{-1}s^{-1}$	[2]
64	$HClOH \rightarrow ClOH^{\bullet-} + H^+$	$1.00 \times 10^8\ s^{-1}$	[2]
65	$HClOH \rightarrow Cl^{\bullet} + H_2O$	$1.00 \times 10^2\ s^{-1}$	[2]
66	$HClOH + Cl^- \rightarrow Cl_2^{\bullet-} + H_2O$	$5.00 \times 10^9\ M^{-1}s^{-1}$	[2]
67	$Cl_2 + Cl^- \rightarrow Cl_3^-$	$2.00 \times 10^4\ M^{-1}s^{-1}$	[2]
68	$Cl_3^- \rightarrow Cl_2 + Cl^-$	$1.10 \times 10^5\ s^{-1}$	[2]
69	$Cl_3^- + HO_2^{\bullet} \rightarrow Cl_2^{\bullet-} + HCl + O_2$	$1.00 \times 10^9\ M^{-1}s^{-1}$	[2]
70	$Cl_3^- + O_2^{\bullet-} \rightarrow Cl_2^{\bullet-} + Cl^- + O_2$	$3.80 \times 10^9\ M^{-1}s^{-1}$	[2]
71	$Cl_2 + H_2O \rightarrow Cl^- + HOCl + H^+$	$2.7 \times 10^{-1}\ M^{-1}s^{-1}$	[2]
72	$Cl^- + HOCl + H^+ \rightarrow Cl_2 + H_2O$	$1.82 \times 10^{-1}\ M^{-2}s^{-1}$	[3]
73	$Cl_2 + H_2O_2 \rightarrow O_2 + 2HCl$	$1.30 \times 10^4\ M^{-1}s^{-1}$	[2]
74	$Cl_2 + O_2^{\bullet-} \rightarrow O_2 + Cl_2^{\bullet-}$	$1.00 \times 10^9\ M^{-1}s^{-1}$	[2]
75	$Cl_2 + HO_2^{\bullet} \rightarrow H^+ + O_2 + Cl_2^{\bullet-}$	$1.00 \times 10^9\ M^{-1}s^{-1}$	[2]
76	$HOCl + H_2O_2 \rightarrow HCl + H_2O + O_2$	$1.10 \times 10^4\ M^{-1}s^{-1}$	[2]
77	$OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$	$1.70 \times 10^5\ M^{-1}s^{-1}$	[2]
78	$HOCl + HO^{\bullet} \rightarrow ClO^{\bullet} + H_2O$	$2.00 \times 10^9\ M^{-1}s^{-1}$	[2]
79	$HOCl + O_2^{\bullet-} \rightarrow Cl^{\bullet} + OH^- + O_2$	$7.50 \times 10^6\ M^{-1}s^{-1}$	[2]
80	$HOCl + HO_2^{\bullet} \rightarrow Cl^{\bullet} + H_2O + O_2$	$7.50 \times 10^6\ M^{-1}s^{-1}$	[2]
81	$OCl^- + HO^{\bullet} \rightarrow ClO^{\bullet} + OH^-$	$8.80 \times 10^9\ M^{-1}s^{-1}$	[2]
82	$OCl^- + O_2^{\bullet-} + H_2O \rightarrow Cl^{\bullet} + 2OH^- + O_2$	$2.00 \times 10^8\ M^{-2}s^{-1}$	[2]
83	$OCl^- + CO3^{\bullet-} \rightarrow ClO^{\bullet} + CO_3^{2-}$	$5.70 \times 10^5\ M^{-1}s^{-1}$	[2]
84	$Cl^{\bullet} + CO_3^{2-} \rightarrow Cl^- + CO_3^{\bullet-}$	$5.00 \times 10^8\ M^{-1}s^{-1}$	[2]

85	$Cl^{\bullet} + HCO_3^- \rightarrow Cl^- + CO_3^{\bullet -} + H^+$	2.20×10^8 $M^{-1}s^{-1}$	2
86	$Cl_2^{\bullet -} + CO_3^{2-} \rightarrow 2Cl^- + CO_3^{\bullet -}$	1.60×10^8 $M^{-1}s^{-1}$	2
87	$ClO^{\bullet} + CO_3^{2-} \rightarrow OCl^- + CO_3^{\bullet -}$	6.00×10^2 $M^{-1}s^{-1}$	4
88	$Cl_2^{\bullet -} + HCO_3^- \rightarrow 2Cl^- + CO_3^{\bullet -} + H^+$	8.00×10^7 $M^{-1}s^{-1}$	2
89	$ClO^{\bullet} + ClO^{\bullet} \rightarrow Cl_2O_2$	2.50×10^9 $M^{-1}s^{-1}$	5
90	$2ClO^{\bullet} + H_2O \rightarrow HOCl + H^+ + ClO_2^-$	2.50×10^9 $M^{-1}s^{-1}$	5
91	$2ClO^{\bullet} + OH^- \rightarrow OCl^- + H^+ + ClO_2^-$	2.50×10^9 $M^{-1}s^{-1}$	5
92	$HO^{\bullet} + ClO^{\bullet} \rightarrow ClO_2^- + H^+$	1.00×10^9 $M^{-1}s^{-1}$	4
93	$HO^{\bullet} + ClO_2^- \rightarrow ClO_2^{\bullet} + OH^-$	6.30×10^9 $M^{-1}s^{-1}$	6
94	$HO^{\bullet} + ClO_2^{\bullet} \rightarrow ClO_3^- + H^+$	4.00×10^9 $M^{-1}s^{-1}$	6
95	$Cl_2^{\bullet -} + ClO_2^- \rightarrow ClO_2^{\bullet} + 2Cl^-$	1.30×10^8 $M^{-1}s^{-1}$	6
96	$ClO^{\bullet} + ClO_2^- \rightarrow OCl^- + ClO_2^{\bullet}$	9.40×10^8 $M^{-1}s^{-1}$	7
97	$NOM + Cl^{\bullet} \rightarrow X$	1.30×10^4 $(mg\ L^{-1})^{-1}s^{-1}$	1
98	$NOM + HO^{\bullet} \rightarrow X$	2.50×10^4 $(mg\ L^{-1})^{-1}s^{-1}$	1
99	$NOM + ClO^{\bullet} \rightarrow X$	4.50×10^4 $(mg\ L^{-1})^{-1}s^{-1}$	This study
100	$NOM + HOCl \rightarrow X$	1.50 $M^{-1}s^{-1}$	8

Note: * In reactions 1 and 2, $r_{HOCl/OCl-}$ is defined as the rate of HOCl or OCl^- decay by UV photolysis, Φ is the apparent quantum yield of HOCl/OCl^- photolysis (mol E^{-1}), I_0 is the photo flux (E s^{-1}), V is the solution volume (L), L is the effective path length (cm), ε is the molar absorption coefficient of HOCl/OCl^-, C is the initial concentration of HOCl or OCl^-, $A = (\varepsilon_{HOCl}C_{HOCl} + \varepsilon_{OCl-}C_{OCl-} + \sum \varepsilon_{others}C_{others})L$, and $f_{HOCl} = \varepsilon_{HOCl}C_{HOCl}\ L/A$ or $f_{OCl-} = \varepsilon_{OCl-}C_{OCl-}\ L/A$.

Table S3. Structures of PPCPs in *groups I-IV*.

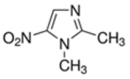
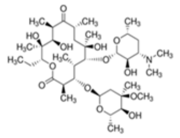
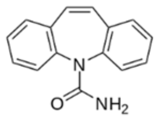
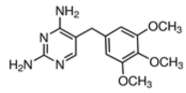
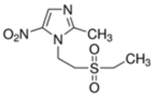
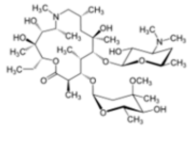
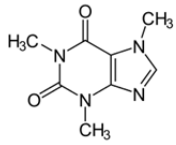
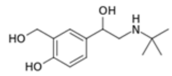
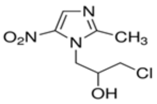
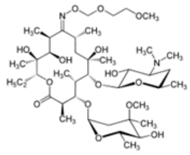
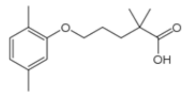
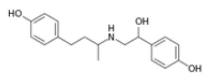
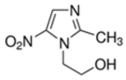
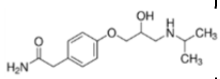
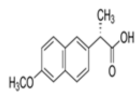
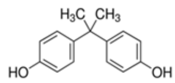
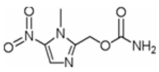
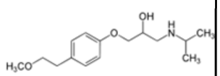
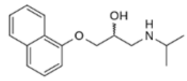
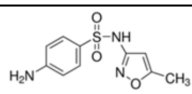
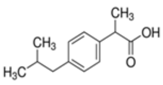
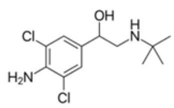
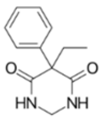
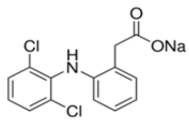
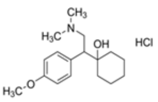
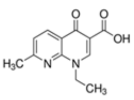
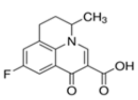
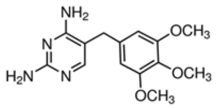
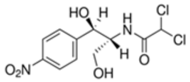
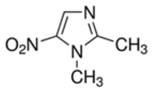
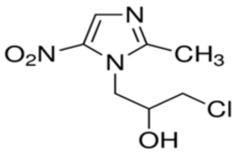
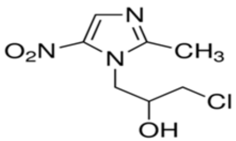
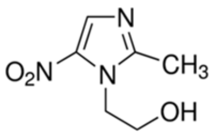
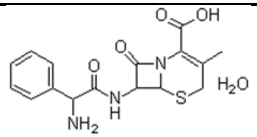
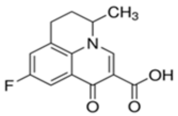
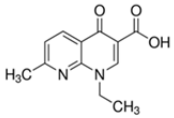
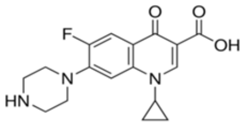
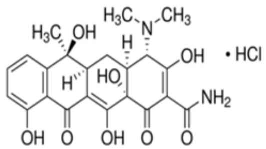
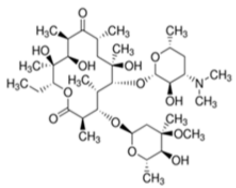
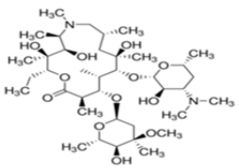
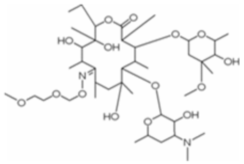
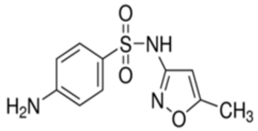
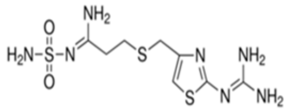
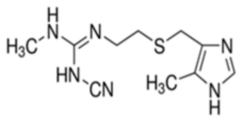
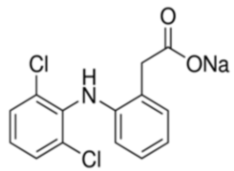
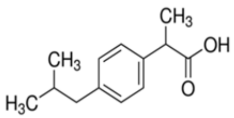
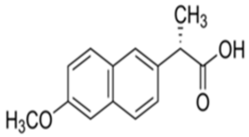
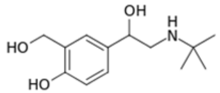
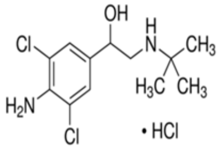
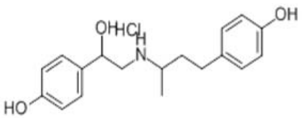
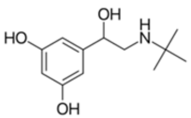
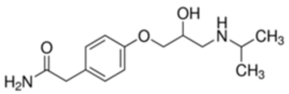
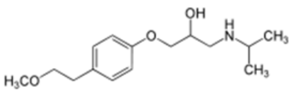
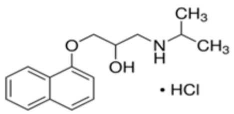
group I		***group II***		***group III***		***group IV***	
Dimetridazole		Erythromycin		Carbamazepine		Trimethoprim	
Tinidazole		Azithromycin		Caffeine		Salbutamol	
Ornidazole		Roxithromycin		Gemfibrozil		Ractopamine	
Metronidazole		Atenolol		Naproxen		Bisphenol A	
Ronidazole		Metoprolol		Propranolol		Sulfamethoxazole	
Ibuprofen				Clenbuterol			
Primidone				Diclofenac			
Venlafaxine							
Nalidixic acid							
Flumequine							

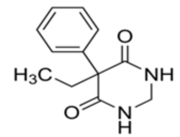
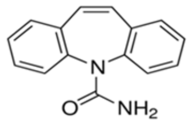
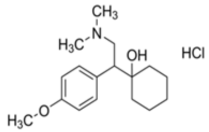
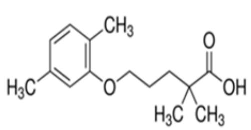
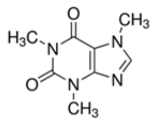
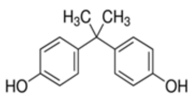
Table S4. List of selected PPCPs and some physical-chemical properties

PPCPs	Structures	pK_a	$Logk_{ow}$	Φ254 (10^{-2}) mol/Einstein	ε254 (10^{3}) L/mol/cm	$k_{HO•}$ ($10^{9}M^{-1}s^{-1}$)	$k_{HO•}$ ($10^{9}M^{-1}s^{-1}$), This study	$k_{CO3•-}$ ($10^{7}M^{-1}s^{-1}$)
Trimethoprim		3.2, 7.1[9-11]	0.91[11]	0.118,[12] 0.09[13]	2.94,[12] 16[13]	6.3±0.85,[11, 14] 7[15]	8.5	1.3[13] 3.45[16]
Chloramphenicol		5.5[17]	1.14[17]	8.40[12]	4.33[12]	5.8[12]	3.575	N.A.
Dimetridazole		2.8[18]	-0.31[19]	0.320[12]	2.24[12]	56[12]	4.95	3.98[20]
Tinidazole		2.3[18]	0.35[19]	0.196[12]	2.34[12]	45[12]	4.248	2.99[20]
Ornidazole		2.72[20].	N.A.	N.A.	N.A.	N.A.	4.39	3.05[20]
Metronidazole		2.58, 14.44[18]	0.02[19]	0.340,[12] 1[13]	2.10,[12] 2.2[13]	44±2,[21] 17.9 (±22)[12]	5.09	3.42[20]

Cephalexin		2.56, 6.88[22]	0.65[22]	N.A.	N.A.	N.A.	N.A.	N.A.
Flumequine		6.5[10, 23]	2.45[24]	N.A.	N.A.	N.A.	6.33	N.A.
Nalidixic acid		N.A.	N.A.	N.A.	N.A.	6.74[25]	5.64	N.A.
Ciprofloxacin		6.2, 8.8 [10, 23]	-0.39[11]	N.A.	N.A.	4.1[11]	N.A.	N.A.
Tetracycline		3.3,[26] 7.68, 9.69[27]	-1.3[11]	0.380[12]	8.82 (±6.66),[12] 4.108[28]	7.7[11]	N.A.	N.A.
Erythromycin		8.9;[22]	3.06, 2.829[22]	N.A.	N.A.	3.8±0.76[11]	3.33	8[13]
Azithromycin		8.59[22]	3.33[22]	N.A.	N.A.	N.A.	3.14	N.A.

Roxithromycin		8.8[29] 9.2[30] 9.17[22]	N.A.	N.A.	N.A.	N.A.	5.53	N.A.
Sulfamethoxazole		1.83, 5.57[22]	0.89[22]	3.79 (±1.15),[12] 8.4[13]	13.2 (±4.5),[12] 13[13]	5.5±0.7,[11] 6[15]	N.A.	26.8[16]
Famotidine		N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Cimetidine		7.1[31]	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Diclofenac		4.15[26]	4.51[11, 26]	29.2 (±8.6),[12] 23[13]	4.77 (±1.16)[12] 6.8[13]	7.5±1.5,[11] 7.5 [32]	N.A.	7.80[13]
Ibuprofen		4.91[11, 33]	3.97[11]	19.2[12]	0.256[12]	7.4±1.2[11]	7.2	0.079[20]

Naproxen		4.15[26, 34, 35]	3.18[11]	2.78 (±2.06),[12] 1.4[13]	4.00 (±0.70)[12] 4.8[13]	8.9±0.65,[14] 9.6 (±0.5)[35]	9.45	5.60[20]
Salbutamol		9.23[20]	N.A.	N.A.	N.A.	2.62[20]	6.18	2.12[20]
Clenbuterol		N.A.	2[26]	2[13]	7.484[28] 3.9[13]	6.6±0.89[14]	9.48	52[13]
Ractopamine		9.62[20]	N.A.	N.A.	N.A.	3.85[20]	10.6	4.99[20]
Terbutaline		N.A.	N.A.	N.A.	N.A.	6.87 ± 0.43[36]	N.A.	N.A.
Atenolol		9.6[33]	0.16[30]	6.5[13]	0.35[13]	7.7±0.55,[14] 8[32]	6.84	0.195[20]
Metoprolol		9.7,[34] 9.6[37]	1.88[37]	3.47 (±4.12)[12] 6.6[13]	0.565 (±0.333),[12] 0.235,[28] 0.33[13]	7.8±0.8[14]	8.2	0.241[20]
Propranolol		9.42[26]	3.48[11]	3.2[13]	0.856[28] 1.3[13]	7.6±4.8,[14] 10±2[38]	9.65	1.42[20]

Primidone		N.A.	0.91[30]	N.A.	N.A.	6.7[11] 7[15]	6.63	N.A.
Carbamazepine		13.9[11]	2.45[11]	0.060[12] 0.33[13]	6.07 [12] 5.8[13]	8.8±1.2,[11] 9[15]	8.8	0.251[20]
Venlafaxine		9.24[39]	N.A.	9.7[13]	0.38[13]	8.8±1.5 [14, 25]	8.83	0.489[20]
Gemfibrozil		4.7[40] 4.42[35]	4.77[40]	9.2[13]	0.37[13]	10[14, 15, 25]	7.68	0.41[20]
Caffeine		10.4,[11, 35] 6.1[40]	-0.07[11]	0.180[12]	3.92[12]	6.9[11, 35]	7.41	N.A.
Bisphenol A		9.6, 10.2[10]	3.32[41]	0.655 (±0.276)[12]	0.750[12]	8.00 (±3.1)[12]	8.77	N.A.

References

(1) Fang, J.; Fu, Y.; Shang, C. The roles of reactive species in micropollutant degradation in the UV/Free chlorine system. Environ. Sci. Technol. **2014,** *48*, 1859-1868.

(2) Grebel, J. E.; Pignatello, J. J.; Mitch, W. A. Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl Radical-Based advanced oxidation processes in saline waters. Environ. Sci. Technol. **2010,** *44*, 6822-6828.

(3) Sun, P.; Tyree, C.; Huang, C. Inactivation of Escherichia coli, Bacteriophage MS2, and Bacillus Spores under UV/H_2O_2 and UV/Peroxydisulfate Advanced Disinfection Conditions. Environ. Sci. Technol. **2016,** *50*, 4448-4458.

(4) NIST, National Institute of Standards and Technology. NDRL/NIST Solution Kinetcis Database on the Web. Http://www3.nd.edu/~ndrlrcdc/index.html (Accessed February 20, 2017). 2017.

(5) Kläning, U. K.; Wolff, T. Laser flash photolysis of HCIO, CIO^-, HBrO and BrO^- in aqueous solution. Reactions of cl- and Br-Atoms. *Ber. Bunsen-Ges. Phys. Chem*. **2010,** *89*, 243-245.

(6) Zuo, Z.; Katsumura, Y.; Ueda, K.; Ishigure, K. Reactions between some inorganic radicals and oxychloridesstudied by pulse radiolysis and laser photolysis. *J. Chem. Soc., Faraday Trans*. **1997,** *93*, 1885-1891.

(7) Alfassi, Z. B.; Huie, R. E.; Mosseri, S.; Neta, P. Kinetics of one-electron oxidation by the ClO radical. *J.phys.chem*. **1987,** *91*, 85 – 88.

(8) Westerhoff, P.; Chao, P.; Mash, H. Reactivity of natural organic matter with aqueous chlorine and bromine. Water Res. **2004,** *38*, 1502-1513.

(9) Adams, C.; Wang, Y.; Loftin, K.; Meyer, M. Removal of antibiotics from surface and distilled water in conventional water treatment processes. J. Environ. Eng. **2002,** *128*, 253-260.

(10) Deborde, M.; von Gunten, U. Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review. Water Res. **2008,** *42*, 13-51.

(11) Yang, X.; Flowers, R. C.; Weinberg, H. S.; Singer, P. C. Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. Water Res. **2011,** *45*, 5218-5228.

(12) Wols, B. A.; Hofman-Caris, C. H. M. Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water. Water Res. **2012,** *46*, 2815-2827.

(13) Wols, B. A.; Harmsen, D. J. H.; Wanders-Dijk, J.; Beerendonk, E. F.; Hofman-Caris, C. H. M. Degradation of pharmaceuticals in UV (LP)/H_2O_2 reactors simulated by means of kinetic modeling and computational fluid dynamics (CFD). Water Res. **2015,** *75*, 11-24.

(14) Wols, B. A.; Hofman-Caris, C. H. M.; Harmsen, D. J. H.; Beerendonk, E. F. Degradation of 40 selected pharmaceuticals by UV/H_2O_2. Water Res. **2013,** *47*, 5876-5888.

(15) Merel, S.; Anumol, T.; Park, M.; Snyder, S. A. Application of surrogates, indicators, and high-resolution mass spectrometry to evaluate the efficacy of UV processes for attenuation of emerging contaminants in water. J. Hazard. Mater. **2015,** *282*, 75-85.

(16) Zhang, R.; Sun, P.; Boyer, T. H.; Zhao, L.; Huang, C. Degradation of pharmaceuticals and metabolite in synthetic human urine by UV, UV/H_2O_2, and UV/PDS. Environ. Sci. Technol. **2015,** *49*, 3056-3066.

(17) Wu, D.; Chen, Y.; Zhang, Y.; Feng, Y.; Shih, K. Ferric iron enhanced chloramphenicol oxidation in pyrite (FeS_2) induced Fenton-like reactions. Sep. Purif. Technol. **2015,** *154*, 60-67.

(18) Prados-Joya, G.; Sánchez-Polo, M.; Rivera-Utrilla, J.; Ferro-garcía, M. Photodegradation of the antibiotics nitroimidazoles in aqueous solution by ultraviolet radiation. Water Res. **2011,** *45*, 393-403.

(19) Méndez-Díaz, J. D.; Prados-Joya, G.; Rivera-Utrilla, J.; Leyva-Ramos, R.; Sánchez-Polo, M.;

Ferro-García, M. A.; Medellín-Castillo, N. A. Kinetic study of the adsorption of nitroimidazole antibiotics on activated carbons in aqueous phase. J. Colloid Interf. Sci. **2010,** *345*, 481-490.

(20) Lian, L.; Yao, B.; Hou, S.; Fang, J.; Yan, S.; Song, W. Kinetic study of hydroxyl and sulfate radical-mediated oxidation of pharmaceuticals in wastewater effluents. Environ. Sci. Technol. **2017,**.

(21) Sánchez-Polo, M.; Rivera-Utrilla, J.; Prados-Joya, G.; Ferro-García, M. A.; Bautista-Toledo, I. Removal of pharmaceutical compounds, nitroimidazoles, from waters by using the ozone/carbon system. Water Res. **2008,** *42*, 4163-4171.

(22) Le-Minh, N.; Khan, S. J.; Drewes, J. E.; Stuetz, R. M. Fate of antibiotics during municipal water recycling treatment processes. Water Res. **2010,** *44*, 4295-4323.

(23) Dodd, M. C.; Shah, A. D.; von Gunten, U.; Huang, C. Interactions of fluoroquinolone antibacterial agents with aqueous chlorine: reaction kinetics, mechanisms, and transformation pathways. Environ. Sci. Technol. **2005,** *39*, 7065-7076.

(24) Miralles-Cuevas, S.; Arqués, A.; Maldonado, M. I.; Sánchez-Pérez, J. A.; Malato Rodríguez, S. Combined nanofiltration and photo-Fenton treatment of water containing micropollutants. Chem. Eng. J. **2013,** *224*, 89-95.

(25) Abdelmelek, S. B.; Greaves, J.; Ishida, K. P.; Cooper, W. J.; Song, W. Removal of pharmaceutical and personal care products from reverse osmosis retentate using advanced oxidation processes. Environ. Sci. Technol. **2011,** *45*, 3665-3671.

(26) Kim, I.; Yamashita, N.; Tanaka, H. Photodegradation of pharmaceuticals and personal care products during UV and UV/H2O2 treatments. *Chemosphere*. **2009,** *77*, 518-525.

(27) Reactions of tetracycline antibiotics with chlorine dioxide and free chlorine..

(28) Sahoo, M. K.; Sinha, B.; Marbaniang, M.; Naik, D. B. Degradation and mineralization of Calcon using

UV365/H2O2 technique: Influence of pH. *Desalination*. **2011,** *280*, 266-272.

(29) Huber, M. M.; GÖbel, A.; Joss, A.; Hermann, N.; LÖffler, D.; McArdell, C. S.; Ried, A.; Siegrist, H.; Ternes, T. A.; von Gunten, U. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. Environ. Sci. Technol. **2005,** *39*, 4290-4299.

(30) Trenholm, R. A.; Vanderford, B. J.; Snyder, S. A. On-line solid phase extraction LC-MS/MS analysis of pharmaceutical indicators in water: A green alternative to conventional methods. *Talanta*. **2009,** *79*, 1425-1432.

(31) Buth, J. M.; Arnold, W. A.; McNeill, K. Unexpected products and reaction mechanisms of the aqueous chlorination of cimetidine. Environ. Sci. Technol. **2007,** *41*, 6228-6233.

(32) Wert, E. C.; Rosario-Ortiz, F. L.; Snyder, S. A. Effect of ozone exposure on the oxidation of trace organic contaminants in wastewater. Water Res. **2009,** *43*, 1005-1014.

(33) Lee, Y.; von Gunten, U. Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). Water Res. **2010,** *44*, 555-566.

(34) Acero, J. L.; Benitez, F. J.; Real, F. J.; Roldan, G. Kinetics of aqueous chlorination of some pharmaceuticals and their elimination from water matrices. Water Res. **2010,** *44*, 4158-4170.

(35) Broséus, R.; Vincent, S.; Aboulfadl, K.; Daneshvar, A.; Sauvé, S.; Barbeau, B.; Prévost, M. Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. Water Res. **2009,** *43*, 4707-4717.

(36) Yang, W.; Ben Abdelmelek, S.; Zheng, Z.; An, T.; Zhang, D.; Song, W. Photochemical transformation of terbutaline (pharmaceutical) in simulated natural waters: Degradation kinetics and mechanisms. Water Res. **2013,** *47*, 6558-6565.

(37) Nam, S.; Yoon, Y.; Choi, D.; Zoh, K. Degradation characteristics of metoprolol during UV/chlorination reaction and a factorial design optimization. J. Hazard. Mater. **2015,** *285*, 453-463.

(38) Benner, J.; Salhi, E.; Ternes, T.; von Gunten, U. Ozonation of reverse osmosis concentrate: Kinetics and efficiency of beta blocker oxidation. Water Res. **2008,** *42*, 3003-3012.

(39) Li, X.; Wang, Y.; Zhao, J.; Wang, H.; Wang, B.; Huang, J.; Deng, S.; Yu, G. Electro-peroxone treatment of the antidepressant venlafaxine: Operational parameters and mechanism. J. Hazard. Mater. **2015,** *300*, 298-306.

(40) Westerhoff, P.; Yoon, Y.; Snyder, S.; Wert, E. Fate of Endocrine-Disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. Environ. Sci. Technol. **2005,** *39*, 6649-6663.

(41) Stackelberg, P. E.; Gibs, J.; Furlong, E. T.; Meyer, M. T.; Zaugg, S. D.; Lippincott, R. L. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Sci. Total Environ. **2007,** *377*, 255-272.