Supplementary Information

Improving UV/H_2O_2 performance following tertiary treatment of municipal wastewater

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Coagulation mixing conditions:

Mixing conditions used for coagulation-flocculation experiments are presented in Table S1.

Table S1. Mixing conditions for coagulation-flocculation experiments.

Process	Mixer Speed (rpm)	Time (min)
Rapid mix	290	1
Flocculation 1	55	10
Flocculation 2	20	10
Sedimentation	0	30

·OH and H_2O_2 production during UV photolysis of DOM:

Photolysis of DOC has been observed to result in ·OH and H_2O_2 generation [1,2]. To determine if ·OH and H_2O_2 was being generated during UV experiments, gabapentin, which has been shown as resistant to degradation by UV_{254} photolysis [3] and has a high reaction rate with ·OH ($9.1 \times 10^9\ M^{-1}s^{-1}$) [4] was spiked into each pre-UV water matrix at a concentration of μg/L and measured before and after 600 s of UV exposure. In parallel, H_2O_2 was measured before and after 600 s and 1200 s of exposure. Removal of gabapentin was less than 2.5% and H_2O_2 was not detected using the titanium IV oxysulfate colorimetry method, therefore, it was concluded that ·OH and H_2O_2 were not being produced during the UV exposure times used for this study.

Modeled $[\cdot OH]_{ss}$:

Modeled $[\cdot OH]_{ss}$ values were determined for each pre-UV/H_2O_2 water matrix following methods presented by Wols et al. (2013) (Section 2, equations 1-4)[5]. Literature-obtained second-order rate constants for carbamazepine ($k_{\cdot OH} = 9.5 \times 10^9\ M^{-1}s^{-1}$) and primidone ($k_{\cdot OH} = 6.7 \times 10^9\ M^{-1}s^{-1}$) and ·OH scavengers ($k_{\cdot OH, DOC} = 5.8 \times 10^8\ M^{-1}s^{-1}$, $k_{\cdot OH, NO_2^-} = 1.0 \times 10^{10}\ M^{-1}s^{-1}$, $k_{\cdot OH, CO_3^{2-}} = 3.9 \times 10^8\ M^{-1}s^{-1}$ $k_{\cdot OH, NO_3^-} = 5.0 \times 10^6\ M^{-1}s^{-1}$ and $k_{\cdot OH, HCO_3^-} = 8.5 \times 10^6\ M^{-1}s^{-1}$) were used. Results are presented in Figure S1.

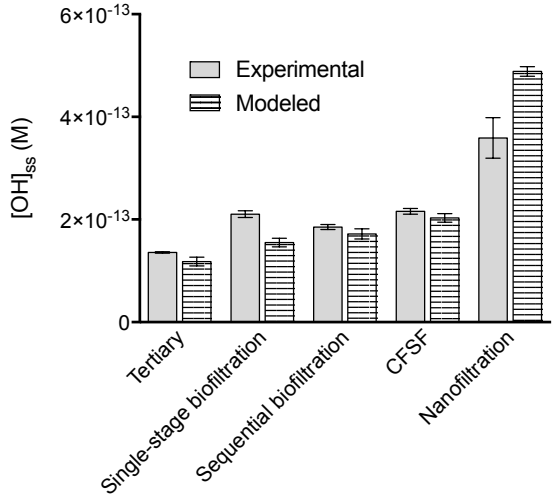

Figure S1. A comparison between modeled and experimentally-determined $[\cdot OH]_{ss}$.

Degradation of TOrCs:

Table S2. Percent degradation of TOrCs after 100 s and 600 s of UV exposure, with and without 10 mg/L H_2O_2.

Water	Experiment	Diclofenac	Iopromide	Sulfamethoxazole	Benzotriazole	Caffeine	Metoprolol	Phenytoin	Venlafaxine	Carbamazepine	Gabapentin	Primidone
Tertiary	100s UV	54%	24%	19%	2%	0%	0%	6%	3%	0%	0%	1%
	100s UV/H_2O_2	44%	25%	24%	15%	9%	13%	19%	13%	15%	8%	10%
	600s UV	100%	84%	76%	15%	0%	5%	40%	9%	5%	0%	2%
	600s UV/H_2O_2	100%	91%	87%	61%	44%	58%	76%	60%	63%	39%	44%
Single-stage biofiltration	100s UV	56%	39%	21%	4%	0%	3%	5%	2%	5%	1%	1%
	100s UV/H_2O_2	73%	48%	32%	21%	18%	23%	26%	22%	27%	13%	19%
	600s UV	100%	89%	77%	13%	0%	6%	43%	8%	6%	2%	6%
	600s UV/H_2O_2	100%	94%	92%	71%	56%	70%	82%	71%	73%	52%	59%
Sequential biofiltration	100s UV	54%	21%	20%	0%	0%	1%	5%	2%	1%	2%	2%
	100s UV/H_2O_2	71%	58%	30%	19%	14%	22%	25%	19%	23%	12%	14%
	600s UV	100%	88%	74%	0%	0%	4%	37%	7%	4%	2%	0%
	600s UV/H_2O_2	100%	95%	91%	67%	52%	67%	79%	68%	69%	49%	54%
CFSF	100s UV	28%	39%	22%	0%	2%	1%	8%	1%	0%	0%	0%
	100s UV/H_2O_2	71%	44%	33%	18%	18%	22%	32%	23%	23%	11%	17%
	600s UV	100%	92%	79%	13%	2%	7%	39%	12%	5%	0%	8%
	600s UV/H_2O_2	100%	94%	92%	71%	56%	69%	85%	70%	70%	49%	58%
Nanofiltration	100s UV	66%	29%	34%	1%	3%	1%	14%	6%	1%	0%	2%
	100s UV/H_2O_2	87%	46%	65%	41%	31%	38%	48%	40%	40%	25%	32%
	600s UV	100%	94%	100%	16%	10%	11%	50%	16%	7%	2%	8%
	600s UV/H_2O_2	100%	100%	100%	99%	88%	99%	100%	99%	98%	80%	90%

Pseudo-first order degradation rates:

Table S3. Pseudo-first order degradation rates in time- and fluence-based units with 10 mg/L H_2O_2 addition. The *k'* plots were developed using seven discrete samples (Table S4) taken at fluence values ranging from 0 to 1200 mJ/cm^2 for each pre-UV treated water matrix.

	Tertiary		Single-stage biofiltration		Sequential biofiltration		CFSF		Nanofiltration	
k' × 10^{-3}	s^{-1}	cm^2/mJ	s^{-1}	cm^2/mJ	s^{-1}	cm^2/mJ	s^{-1}	cm^2/mJ	s^{-1}	cm^2/mJ
Diclofenac	9.8	9.7	11.1	10.7	10.5	10.1	11.6	11.0	14.1	12.6
Iopromide	3.5	3.6	4.4	4.2	4.6	4.4	4.3	4.1	5.3	4.7
Sulfamethoxazole	3.0	3.0	3.6	3.4	3.4	3.3	3.5	3.3	7.3	6.5
Benzotriazole	1.4	1.3	1.9	1.8	1.5	1.4	2.0	1.9	3.5	3.1
Caffeine	0.8	0.8	1.3	1.2	1.1	1.1	1.3	1.3	2.3	2.1
Metoprolol	1.2	1.2	1.8	1.8	1.7	1.6	1.9	1.8	3.4	3.0
Phenytoin	2.1	2.1	2.6	2.5	2.4	2.3	2.8	2.7	4.3	3.8
Venlafaxine	1.3	1.3	1.9	1.9	1.7	1.7	2.0	1.9	3.6	3.2
Carbamazepine	1.4	1.4	2.0	2.0	1.8	1.7	2.0	1.9	3.1	2.8
Gabapentin	0.7	0.7	1.1	1.1	1.0	1.0	1.1	1.1	2.1	1.9
Primidone	0.9	0.9	1.4	1.3	1.2	1.2	1.5	1.4	2.6	2.3

Table S4. TOrC data used to develop *k'* plots. Notes provided below.

Treatment	Fluence (mJ/cm^2)	Exposure Time (s)	Benzotriazole	Caffeine	CBZ	Diclofenac	Gabapentin	Iopromide	Metoprolol	Phenytoin	Primidone	SMX	Venlafaxine
Tertiary UV + H_2O_2*	0	0	10350	1186	1782	2217	2133	836	1310	1250	1100	1096	1758
	100	98	8819	1083	1512	1245	1966	628	1145	1013	996	840	1528
	200	198	7288	981	1242	274	1799	419	980	776	891	585	1298
	400	396	6026	848	1018	41	1632	220	822	566	793	328	1054
	600	594	4136	680	690	ND	1314	93	571	319	625	164	733
	1000	991	2950	583	484	ND	1069	30	406	169	456	61	511
Tertiary UV	100	98	11368	1401	1864	1175	2526	841	1413	1353	1300	1121	1985
	600	586	9832	1423	1750	30	2414	197	1354	870	1286	356	1872
Single-stage BF UV+ H_2O_2	0	0	5968	1344	1816	2075	1276	1154	1273	1377	1302	1260	2022
	100	96	4775	1114	1353	631	1112	624	992	1028	1064	876	1600
	200	193	3976	1006	1134	205	964	480	815	731	939	612	1289
	400	385	2685	785	746	41	784	186	588	465	720	305	900
	600	578	1908	619	535	ND	636	114	419	290	568	162	640
	1000	963	959	407	268	ND	440	16	223	109	357	59	326
	1200	1155	684	330	184	ND	369	ND	157	72	270	42	224
Single-stage BF UV	100	96	5735	1358	1725	964	1264	726	1235	1306	1285	1014	1976
	600	587	5217	1348	1715	4320	1256	169	1206	810	1227	336	1874
Sequential BF UV+ H_2O_2	0	0	5780	1304	1726	2215	1383	1160	1189	1375	1234	1265	1950
	100	96	4699	1126	1351	709	1223	516	942	1039	1068	905	1590
	200	192	4192	1071	1215	277	1178	500	867	885	974	706	1410
	400	385	2715	800	788	46	882	162	566	497	723	314	910
	600	577	2067	648	576	27	735	100	418	333	596	160	670
	1000	962	1652	434	299	ND	509	ND	221	130	364	44	352
	1200	1172	1121	384	249	ND	479	ND	194	92	324	30	292
Sequential BF UV	100	96	10999	1331	1714	1070	1360	922	1173	1306	1213	1018	1907
	600	577	10880	1322	1667	51	1362	178	1140	890	1237	362	1819
CFSF UV+ H_2O_2	0	0	10888	1474	1862	2584	2409	1367	1487	1519	1358	1424	2084
	100	94	9037	1223	1459	844	2158	802	1184	1059	1140	983	1629
	200	189	7331	1113	1194	289	1877	616	971	794	944	700	1329
	400	378	4983	832	759	33	1499	199	659	449	716	339	890
	600	567	3621	693	623	ND	1297	148	523	299	612	191	705

	1000	952	1652	416	281	ND	816	ND	238	106	322	47	309
	1200	1133	1172	332	204	ND	671	ND	172	71	273	30	223
CFSF	100	94	10999	1446	1875	1911	2427	870	1477	1400	1362	1128	2055
UV	600	567	9518	1441	1780	28	2410	179	1392	960	1260	368	1839
	0	0	9594	1390	1310	1588	1307	1181	1244	1549	1232	1239	1691
	100	89	6080	1008	843	376	1011	700	826	899	885	521	1084
	200	178	4537	812	618	112	827	346	604	600	709	271	782
Nanofiltration UV+ H_2O_2	400	356	2292	518	323	33	573	199	313	266	414	88	395
	600	600	1112	306	167	ND	370	75	152	126	245	29	194
	1000	891	571	200	96	ND	248	ND	85	61	153	ND	90
	1200	1069	230	123	57	ND	138	ND	32	38	78	ND	35
Nanofiltration	100	89	9540	1352	1300	669	1326	874	1229	1359	1216	864	1606
UV	600	534	8188	1265	1230	ND	1287	191	1125	863	1144	75	1447

Notes:

(1) ND = not detected; SMX = sulfamethoxazole; CBZ = Carbamazepine; and BF = biofiltration

(2) TOrC measurement was performed using a High Performance Liquid Chromatography (Knauer PLATINBLUE UHPLC) coupled with tandem mass spectrometry (LC-MS/MS) (SCIEX QTRAP 6500) with direct injection as described elsewhere[6].

(3) 10 mg/L H_2O_2 added where indicated.

(4) (*) Measurement error occurred during analysis of tertiary effluent sample, UV dose of 1200 mJ/cm^2. Therefore, data did not get analyzed.

Work Cited for SI:

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