SUPPLEMENTARY MATERIAL

Continuous UV-C/H_2O_2 and UV-C/Chlorine applied to municipal secondary effluent and nanofiltration retentate: removal of contaminants of emerging concern, ecotoxicity, and reuse potential

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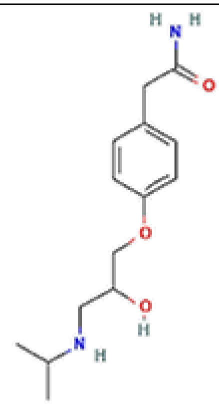
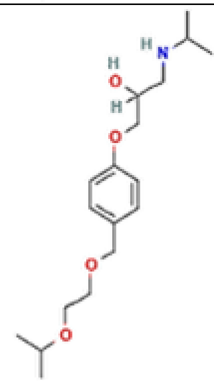
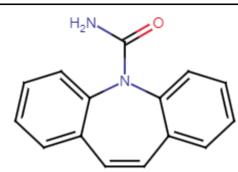
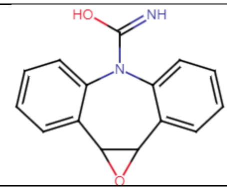
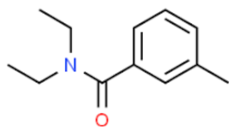
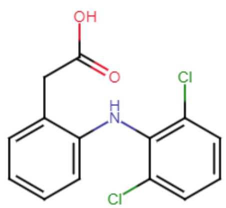
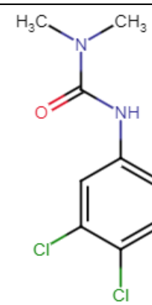
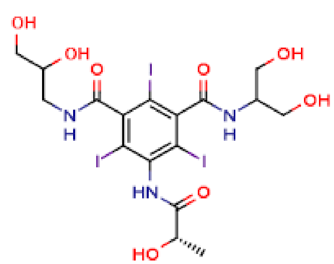
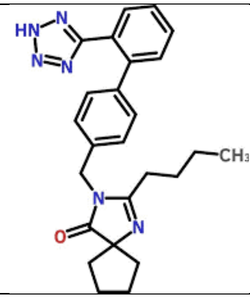
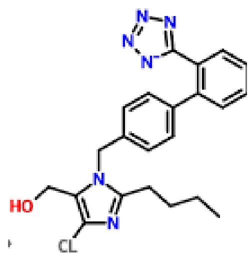
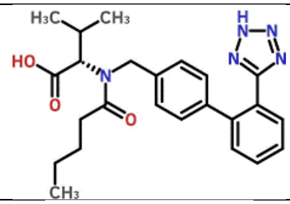
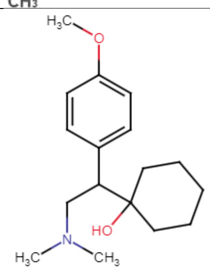
MATERIAL AND METHODS

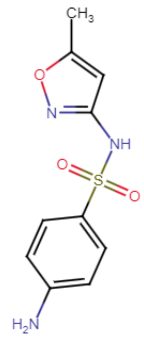
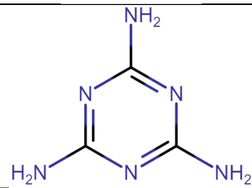
Chemicals

Table SM-1. List of the target CECs selected for testing and respective abbreviations and chemical composition.

CAS no.	Contaminant Acronym	Molecule structure	Organic functional group*	Chemical composition	MW (g mol^{-1})	pKa	Log K_{OW}	PNEC (µg L^{-1})
29122-68-7	Atenolol ATNL			$C_{14}H_{22}N_2O_3$	266.336	9.6	0.43	150.0
66722-44-9	Bisoprolol BSPL		**Aromatics:** arene, benzene ring; **CHN-containing:** amine, amine secondary; **CHO-containing:** alkanol, ether;	$C_{18}H_{31}NO_4$	325.443	9.5	2.20	92.0
298-46-4	Carbamazepine CBZ		**Aromatics:** arene, benzene ring; **CH only:** alkene; **CHNO-containing:** urea **CHO-containing:** carbonyl	$C_{15}H_{12}N_2O$	236.269	13.94	2.77	2.00

36507-30-9	Carbamazepine 10,11-epoxide CBZ-EPX		**Aromatics:** arene, benzene ring; **CHN-containing:** iminyl; **CHO-containing:** epoxide, ether	$C_{15}H_{12}N_2O_2$	252.268	-	1.97	2.57
134-62-3	N.N-diethyl-meta-toluamide DEET			$C_{12}H_{17}NO$	191.274	-	2.50	88.0
15307-86-5	Diclofenac DCF		**Aromatics:** aniline, arene, benzene ring; **CHN-containing:** amine, amine secondary; **CHO-containing:** carbonyl, carboxilic acid; **Halogen-containing:** aryl chloride, aryl halide, leaving group	$C_{14}H_{11}Cl_2NO_2$	296.148	4.15	4.26	0.05
330-54-1	Diuron DRN		**Aromatics:** arene, benzene ring; **CHNO-containing:** urea; **CHO-containing:** carbonyl; **Halogen-containing:** aryl chloride, aryl halide, leaving group	$C_9H_{10}Cl_2N_2O$	233.1	13.55	2.53	0.07
73334-07-3	Iopromide IOP		**Aromatics:** arene, benzene ring; **CHNO-containing:** carbomaxamide, carboxamide secundary, carboxamide tertiary **CHO-containing:** alkanol, carbonyl, 1,2-diol, ether; **Halogen-containing:** aryl halide, aryl iodide, leaving	$C_{18}H_{24}I_3N_3O_8$	791.112	9.9	-0.44	0.14

			group					
138402-11-6	Irbesartan ISTN		**Aromatics:** arene, azarene, benzene ring, heteroarene **CHN-containing:** amidine, amine, aminyl; **CHNO-containing:** carboxamide, carboxmide tertiary; **CHO-containing:** carbonyl;	$C_{25}H_{28}N_6O$	428.53	4.12	5.39	700
124750-99-8	Losartan LSTN		**Aromatics:** arene, azarene, benzene ring, heteroarene; **CHN-containing:** amine, amine tertiary; **CHO-containing:** alkanol; **Halogen-containing:** aryl chloride, aryl halide, leaving group	$C_{22}H_{23}ClN_6O$	422.91	4.9	5.00	0.0019
137862-53-4	Valsartan VSTN			$C_{24}H_{29}N_5O_3$	435.519	4.73	5.27	560.0
93413-69-5	Venlafaxine VLX		**Aromatics:** arene, benzene ring; **CH only:** alkene; **CHN-containing:** amine, amine tertiary; **CHO-containing:** alkanol, ether;	$C_{17}H_{27}NO_2$	277.402	9.4	2.74	0.88

723-46-6	Sulfamethoxazole SMX		**Aromatics:** aniline, arene, azarena, arene, benzene ring, heteroarene; **CHN-containing:** amine, amine primary; **S-containing:** sulfonamide;	$C_{10}H_{11}N_3O_3S$	253.279	3.92	0.79	0.60
108-78-1	Melamine MLN		**Aromatics:** aniline, arene, azaarene, heteroarene **CHN-containing:** amine, amine primary;	$C_3H_6N_6$	126.12	5.00	-0.59	3.54

*Organic functional group was determined by an open online tool – ACE functional group finder [https://epoch.uky.edu/ace/public/fnalGroups.jsp].

CECs Quantification by Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)

Analysis was performed by direct injection of 45 µL of the sample into the chromatographic system Acquity UPLC® H class interfaced to a Xevo TQD triple quadrupole mass spectrometer (Waters, Milford, MA, USA). Separation took place in a Luna C18 100A column (50 mm × 2 mm, 3 µm particle size) supplied by Phenomenex (Torrance, CA, USA), with constant temperature of 30 °C and 0.2 mL min^{-1} flow rate. The mobile phases consisted of (A) 1 mM ammonium fluoride in ultrapure water and (B) 1 mM ammonium fluoride in MeOH. The gradient was as follows: 0-1 min, 0% B; 1-8 min, linear gradient to 100% B; 7-13 min, 100% B and finally 13-20 min, 0% B. Nitrogen was used as nebulising and drying gas and Argon was used as collision gas. The analyses were determined in the ESI positive and negative polarities, and the acquisition mode was multiple-reaction monitoring (MRM). Two MRM transitions were used as a quantifier (Q) and qualifier (q) for each compound (Table SM-2). The quantification of CECs was performed by the standard addition method spiking each real matrix with the target CECs at 5 different concentration levels (LOQ-50 µg/L). Linearity, in terms of R^2 was higher than 0.990 for all analytes in both matrices and repeatability, in terms of RSD (%) was lower than 15 % (5 consecutive injections of the 10 µg/L spiked level in each matrix). The method limits of quantification (LQ) are shown in Table SM-3 and were estimated by extrapolating the signal to noise (S/N) obtained from the chromatographic peaks at the specific native concentration in real samples (or the lowest addition level if the CECs were not present) to a S/N of 10.

Table SM-2. Instrumental LC-MS/MS parameters.

CECs	Retention time (min)	Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (V)	Cone voltage (V)	ESI mode
ATNL	5.7	267	145 (Q) 190 (q)	30 16	38	+
BSPL	7.5	326	116 (Q) 204 (q)	20 18	45	+
CBZ	7.9	237	194 (Q) 179 (q)	20 38	40	+
CBZ-EPX	7.1	253	180 (Q) 210 (q)	25 12	39	+
DCF	8.7	294 296	250 (Q) 252 (q)	10 10	33	-
DEET	8.2	192	119(Q) 91(q)	15 25	25	+
DRN	8.4	233	72 (Q) 160 (q)	20 20	30	+
IOP	5.2	792	559 (Q) 573 (q)	25 15	50	+
ISTN	8.6	434	179 (Q) 350 (q)	65 28	50	-
LSTN	8.3	421	127 (Q) 157 (q)	30 25	30	-
VSTN	8.4	434	179 (Q) 350 (q)	25 20	35	+
MLN	1.5	127	85 (Q) 69 (q)	15 20	45	+
SMX	6.2	254	92 (Q) 156 (q)	25 15	35	+
VLX	7.9	278	58 (Q) 260 (q)	20 10	25	+

Note: Capillary voltages: 3.5 and 1.5 kV in positive and negative polarities, respectively. Source temperature: 350 ºC. Desolvation gas (N_2) flow: 650 L h^{-1}. Cone gas (N_2) flow: 5 L h^{-1}. Collision energy (CE) and cone voltage (CV) were adjusted for every transition. (Q) quantifier transition; (q) qualifier transition.

Table SM-3. LC-MS/MS method LQs in municipal secondary effluent and nanofiltration retentate

CECs	Municipal Secondary Effluent LQ (μg L^{-1})	Nanofiltration Retentate LQ (μg L^{-1})
ATNL	0.15	0.18
BSPL	0.15	0.22
CBZ	0.03	0.05
CBZ-EPX	0.02	0.10
DCF	0.25	0.40
DEET	0.03	0.05
DRN	0.08	0.08
IOP	0.80	1.0
ISTN	0.20	0.30
LSTN	0.80	1.0
VSTN	0.44	0.17
MLN	0.75	1.0
SMX	0.10	0.10
VLX	0.15	0.20

RESULTS AND DISCUSSION

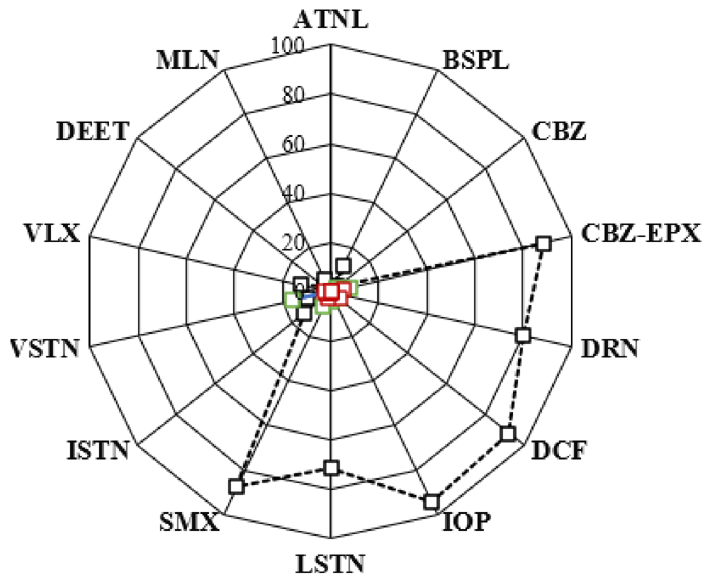


Figure SM-1. Removal percentage for the 14 target CECs spiked in MSE (10 μg L^{-1} for each) under UV-C irradiation (3.3 kJ L^{-1}) without oxidant dosage (─□─) and under dark conditions with H_2O_2 (─□─) or NaClO (─□─) dosage.

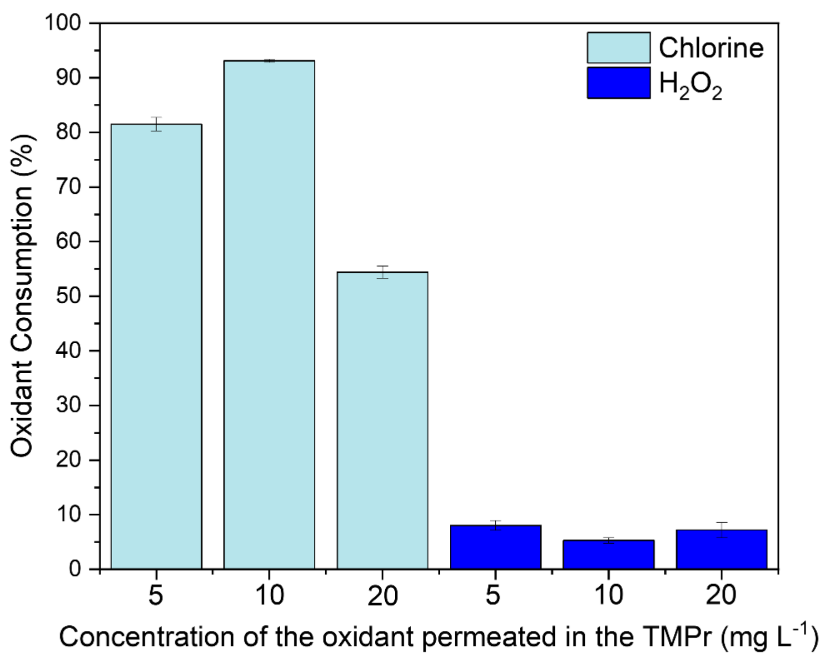


Figure SM-2. Consumption of the oxidants for the photo-treatment tests performed with MSE. Conditions: treatment time 3.4 min, UV-C dose of 3.3 kJ L^{-1}.

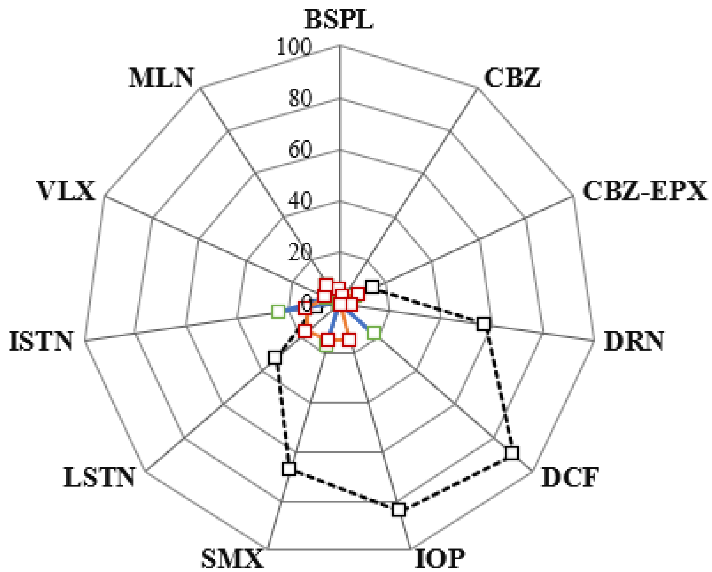


Figure SM-3. Removal percentage for the 11 target CECs present in NF_R under UV-C irradiation (3.3 kJ L^{-1}) without oxidant dosage (─□─) and under dark conditions with H_2O_2 (─□─) or NaClO (─□─) dosage.

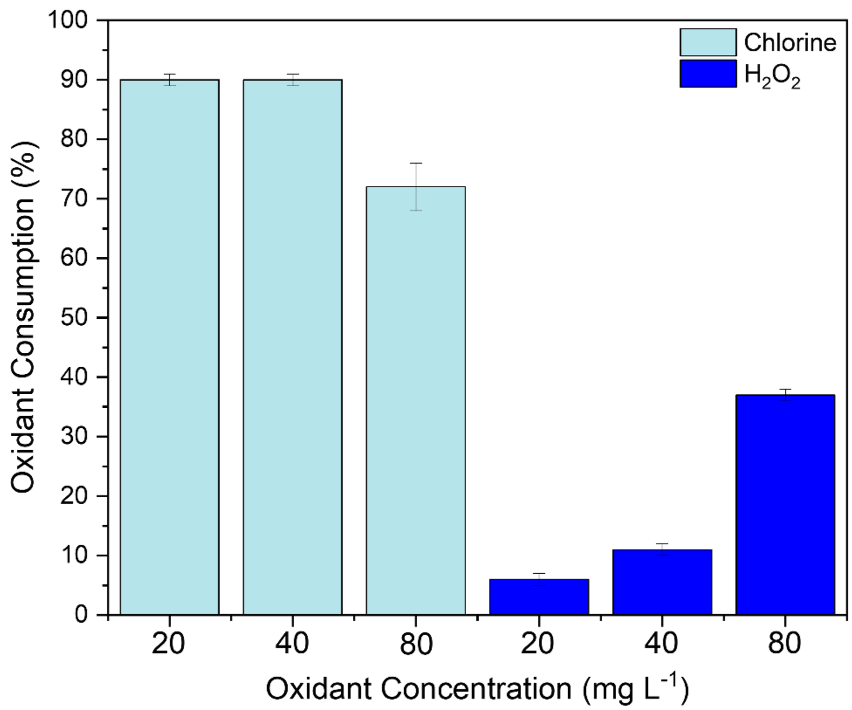


Figure SM-4. Consumption of the oxidants for the photo-treatment tests performed with NF_R. Conditions: treatment time 3.4 min, UV-C dose of 3.3 kJ L^{-1}.

Table SM-4. Physicochemical characterization of MSE before and after standalone UV-C (test #1); standalone H_2O_2 at 20 mg L^{-1} (test #2) and Chlorine at 20 mg L^{-1} (test #3); UV-C/H_2O_2 with H_2O_2 permeation at 5 mg L^{-1} (test #4), 10 mg L^{-1} (test #5), and 20 mg L^{-1} (test #6); UV-C/Chlorine with free chlorine permeation at 5 mg L^{-1} (test #7), 10 mg L^{-1} (test #8), and 20 mg L^{-1} (test #9).

Sample	COD	DIC	DOC	Abs.$_{254}$	SUVA$_{254}$	Turb.	pH	Conduc.	TSS	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{2-}	Na^{2+}	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Unit	mg L^{-1}			-	$Lmg^{-1}m^{-1}$	NTU	-	µS cm^{-1}	mg L^{-1}										
MSE	74	39	23	0.231	0.984	3.1	7.70	846	14	130	2	13	43	5	112	14	18	8	31
Test #1	79	38	24	0.208	0.870	3.1	7.68	864	7	136	3	15	44	6	117	15	18	9	34
Test #2	68	38	23	0.226	0.995	3.7	7.65	864	10	128	3	12	42	6	113	15	17	9	33
Test #3	74	36	24	0.243	0.999	3.1	7.98	910	12	151	3	19	44	6	127	15	18	9	34
Test #4	77	36	24	0.170	0.708	1.1	7.85	857	4	132	3	19	46	6	114	13	18	9	34
Test #5	76	36	23	0.164	0.701	1.1	7.61	867	5	133	3	19	43	6	112	13	18	9	34
Test #6	70	35	23	0.171	0.735	1.4	7.54	837	6	132	3	21	42	6	113	12	18	9	33
Test #7	67	37	24	0.196	0.829	1.4	7.87	879	2	142	3	15	43	5	118	14	17	9	33
Test #8	69	36	24	0.190	0.793	1.8	7.93	936	3	151	3	16	43	5	125	14	18	9	33
Test #9	72	36	24	0.191	0.810	1.2	8.02	920	4	154	3	18	46	6	129	13	18	9	34

Note: MSE – Municipal secondary effluent; COD = chemical oxygen demand; DIC = dissolved inorganic carbon; DOC = dissolved organic carbon; Turb. = turbidity; Conduc. = electrical conductivity; TSS = total suspended solids.

Table SM-5. Physicochemical characterization of NF_R before and after standalone UV-C (test #10); standalone H_2O_2 at 80 mg L^{-1} (test #11) and Chlorine at 80 mg L^{-1} (test #12); UV-C/H_2O_2 with H_2O_2 permeation at 20 mg L^{-1} (test #13), 40 mg L^{-1} (test #14), and 80 mg L^{-1} (test #15); UV-C/Chlorine with free chlorine permeation at 20 mg L^{-1} (test #16), 40 mg L^{-1} (test #17), and 80 mg L^{-1} (test #18).

Sample	COD	DIC	DOC	$Abs._{254}$	$SUVA_{254}$	Turb.	pH	Conduc.	TSS	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{2-}	Na^{2+}	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Unit	mg L^{-1}			-	$Lmg^{-1}m^{-1}$	NTU	-	µS cm^{-1}	mg L^{-1}										
NF_R	206	65	51	1.168	2.28	1.7	8.08	2204	9	561	27	135	636	79	751	57	111	44	224
Test #10	164	58	53	1.133	2.13	2.7	8.06	2092	5	625	31	165	639	86	543	52	115	46	234
Test #11	151	61	53	1.179	2.22	3.4	8.04	2031	7	478	32	172	627	85	541	56	117	46	237
Test #12	144	57	53	1.134	2.16	3.0	8.11	2297	13	481	38	152	630	87	651	47	114	47	239
Test #13	161	61	54	1.063	1.98	2.9	8.07	2117	30	480	38	155	641	84	541	55	117	46	234
Test #14	122	60	52	1.034	2.00	2.5	7.92	2106	11	482	38	161	639	85	543	55	115	46	233
Test #15	151	60	51	1.028	2.00	3.1	7.87	2090	8	481	37	157	637	86	544	54	115	47	237
Test #16	165	67	52	1.104	2.12	2.6	7.98	2002	8	549	32	136	649	82	793	58	110	43	225
Test #17	135	66	51	1.103	2.22	3.2	8.21	2135	16	611	33	140	633	82	597	61	113	45	232
Test #18	140	67	51	1.058	2.07	3.4	8.26	2290	18	483	40	157	629	82	637	59	117	46	233

Note: NF_R = nanofiltration retentate from urban wastewater; COD = chemical oxygen demand; DIC = dissolved inorganic carbon; DOC = dissolved organic carbon; Turb. = turbidity; Conduc. = electric conductivity; TSS = total suspended solids.