Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

On the role of Graphene oxide/titania catalyst to remove mixtures of pharmaceutical contaminants from water and wastewater

Supplementary Material

M. Checa[1], F.J. Beltrán[1,*], F. J. Rivas[1], E. Cordero[2]

[1] Departamento de Ingeniería Química y Química Física. Instituto Universitario de Investigación del Agua, Cambio Climático y Sostenibilidad. Universidad de Extremadura. 06006 Badajoz. Spain.
[2] Departamento de Ingeniería Eléctrica, Electrónica y Automática. Escuela de Ingenierías Industriales. Universidad de Extremadura. 06006 Badajoz. Spain

*Corresponding address (Email: fbeltran@unex.es, Telephone: 0034924289387)

1. Relevant CECs information

Table S1. Relevant properties of selected CECs[a].

CEC name		Molecular weight g mol^{-1}	k_D[b] $M^{-1}s^{-1}$	Ref. k_D	z[c] mol O_3 / mol CEC	Ref. z	k_{HO}[d]. $M^{-1}s^{-1}$ x10^{-9}	Ref. k_{OH}	D_i [1] $m^2 s^{-1}$ x10^{10}
Acetaminophen (Paracetamol)	AAP	151.16	4.11 x 10^6	2	2	2	7.10	3	7.94
Antipyrine (Phenazone)	ANT	188.23	6.15 10^5	4	1	5	5.20	3	6.81
Caffeine	CAF	194.19	650	6	1	7	5.90	6	6.86
Ketorolac	KET	255.27	3.4 10^5	4	1	-	5.00	4	5.78
Metoprolol	MET	534.73	2000	8	2	8	7.30	8	5.19
Diclofenac	DCF	296.33	10^6	9	2	10	7.50	3	5.50
Hydrochlorothiazide	HCT	297.83	3.0 x 10^5	11	2	11	5.07	12	6.22
Sulfamethoxazole	SMX	253.28	4.15 x 10^5	13	2	14	5.50	3	6.17

[a]For super index numbers see literature section 5 below. [b]Rate constant of ozone-CEC direct reaction. [c]Stoichiometric ratio of ozone-CEC reaction. [d]Rate constant of hydroxyl radical-CEC reaction.

2. Characterization properties of GO-TiO_2

Table S2. Main properties of the studied catalyst

	SBET m^2g^{-1}	Particle size nm	RAMAN DB/GB[a]	Band Gap eV
0.5GO/TiO_2	157	8.2	1.25	1.66
1GO/TiO_2	194	8.5	1.32	1.59
1.5GO/TiO_2	226	8.7	1.36	1.55

The low band gap exhibited is associated with the presence of F and B residuals from the catalyst synthesis that benefits Vis-light absorption ranges of the solid. Further information related to catalyst properties influence in photocatalytic ozonation process and catalyst reusability can be found in a previous work[15].

3. Preliminary studies

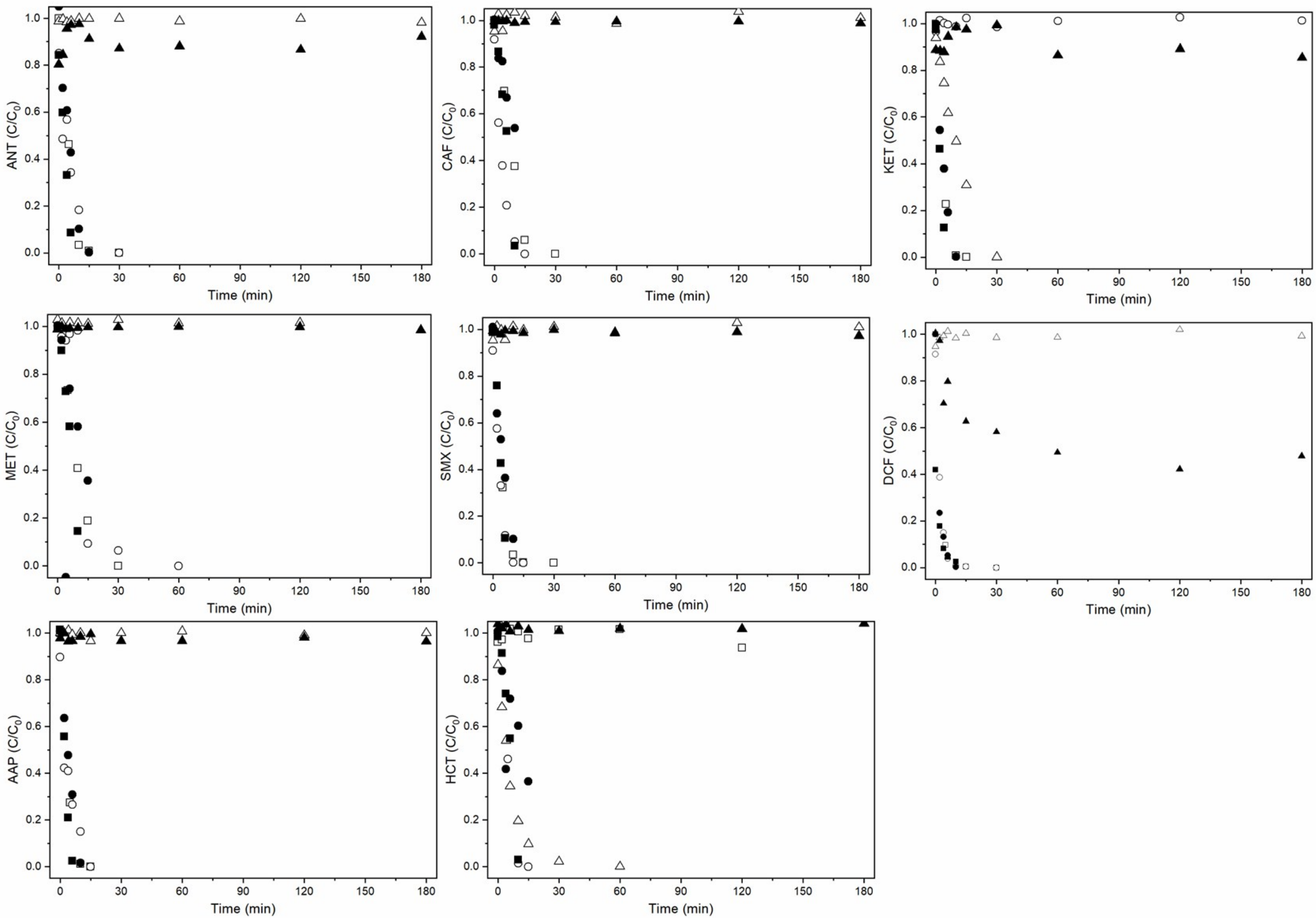

Figure S 1. Individual CECs variation with time under different processes in UPW. CEs concentration: 10 ppm of each one, Catalyst: 1GO/TiO_2–LPD *0.25 g L^{-1}, Fluency: 244 W m^{-2}.* ***PhCatOz(■), PhOz (○), CatOz (●), Oz(△),PhCatOx(▲), PhOx (□).***

4. Kinetic considerations

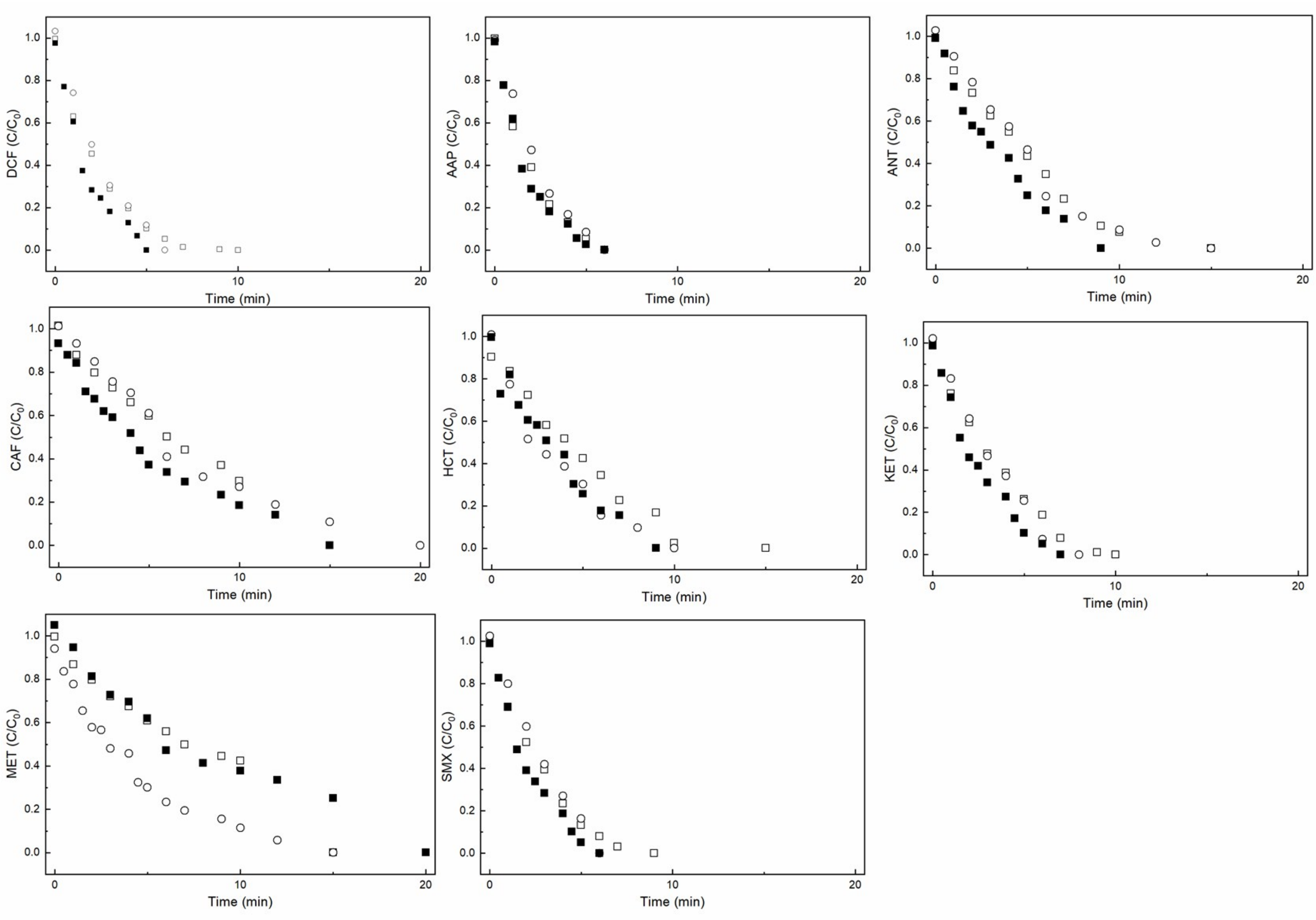

Figure S2. Individual CECs variation with time under different processes in SEMWW. CECs concentration: 10 ppm of each one. Catalyst: 1.5GO/TiO_2 *0.4 g L^{-1}., Fluency: 303 W m^{-2}.* ***PhCatOz(■), PhOz (○), Oz (□).***

Table S3. Concentrations of ozone in the gas exiting the reactor and values of instantaneous reaction factor, F_i, at 1-minute reaction in the three ozone processes studied.

Process	**C_{O3g} x10^5 M**	**F_i**							
		AAP	**ANT**	**CAF**	**SMX**	**KET**	**MET**	**HCT**	**DCF**
Ozonation	3.23	7.59	4.33	3.43	3.60	3.04	2.55	3.62	4.13
Photolytic Ozonation	3.00	9.97	4.88	3.77	3.89	3.40	2.82	2.75	6.73
Photocatalytic Ozonation	1.76	8.36	3.99	4.76	4.30	2.85	2.56	6.46	4.36

F_i calculated from equations (10) to (12) with He=115 atm L mol^{-1} [16]. D_M and z values from table S1. D_{O3}= 1.39 x 10^9 m^2 s^{-1} [17]. C_M from data in Figure S2.

Table S4. Ha numbers of the reactions between ozone and CECs while present in water during ozonation in SEMWW[a].

t. min	AAP	ANT	CAF	SMX	KET	MET	HCT	DCF
0	14.72	5.14	0.14	3.06	3.42	0.16	1.84	6.55
1	11.25	4.72	0.13	2.55	2.99	0.15	1.77	6.02
2	9.21	4.42	0.12	2.22	2.71	0.14	1.65	5.64
3	6.84	4.08	0.12	1.93	2.36	0.14	1.48	5.21
4	5.29	3.82	0.11	1.49	2.13	0.13	1.39	4.88
5	3.37	3.40	0.11	1.12	1.75	0.12	1.26	4.34
6	-	3.05	0.10	0.87	1.48	0.12	1.14	3.89
8	-	2.49	0.09	0.53	0.96	0.11	0.92	3.18
10	-	1.68	0.08	-	0.35	0.11	0.79	-
12	-	1.42	0.08	-	-	0.10	-	-

[a]From equation (9) with k_D values from Table S1, CECs concentration from Figure S2, k_L=3.92x10^5 ms^{-1}. Ha > 0.3 means fast or moderate kinetic regime. Ha<0.3 means slow kinetic regime.

Table S5. Ha numbers of the reactions between ozone and CECs while present in water during photolytic ozonation in SEMWW[a].

t. min	AAP	ANT	CAF	SMX	KET	MET	HCT	DCF
0	14.67	5.24	0.14	3.11	3.46	0.16	1.95	5.89
1	12.65	4.91	0.13	2.74	3.12	0.16	1.70	4.99
2	10.12	4.57	0.13	2.37	2.74	0.14	1.39	4.08
3	7.59	4.17	0.12	1.99	2.34	0.14	1.29	3.20
4	6.04	3.91	0.12	1.60	2.08	0.13	1.20	2.64
5	4.26	3.52	0.11	1.24	1.72	0.13	1.07	1.98
6	-	2.55	0.09	-	0.92	0.11	0.76	-
8	-	2.00	0.08	-	-	0.10	0.60	-
10	-	1.53	0.07	-	-	0.10	-	-
12	-	0.85	0.06	-	-	0.09	-	-
15	-	-	0.05	-	-	0.08	-	-

[a]From equation (9) with k_D values from table S1, CECs concentration from Figure S2, k_L=3.92x10^5 ms^{-1}. Ha > 0.3 means fast or moderate kinetic regime. Ha<0.3 means slow kinetic regime.

Table S6. Ha numbers of the reactions between ozone and CECs while present in water during photocatalytic ozonation in SEMWW[a].

t. min	AAP	ANT	CAF	SMX	KET	MET	HCT	DCF
0	13.97	4.86	0.17	3.28	3.18	0.17	2.87	5.60
1	11.09	4.26	0.17	2.74	2.76	0.15	2.60	4.41
2	7.55	3.71	0.15	2.06	2.17	0.13	2.23	3.02
3	6.00	3.41	0.14	1.75	1.87	0.12	2.05	2.42
4	4.94	3.18	0.13	1.42	1.67	0.12	1.91	2.03
5	2.27	2.44	0.11	0.75	1.02	0.09	1.46	-
6	-	2.06	0.11	-	0.73	0.08	1.21	-
7	-	1.82	0.10	-	-	0.08	1.13	-
9	-	-	0.07	-	-	0.07	-	-
10	-	-	0.06	-	-	0.06	-	-
12	-	-	0.04	-	-	-	-	-

[a]From equation (9) with k_D values from table S1, CECs concentration from Figure S2, k_L=3.92x10^5 ms^{-1} Ha > 0.3 means fast or moderate kinetic regime. Ha<0.3 means slow kinetic regime

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