Emerging contaminants: an overview of recent trends for their treatment and management for light driven processes

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Supplementary S1 An illustrated example of similar chemical structure of CECs with similar photodegradation performance

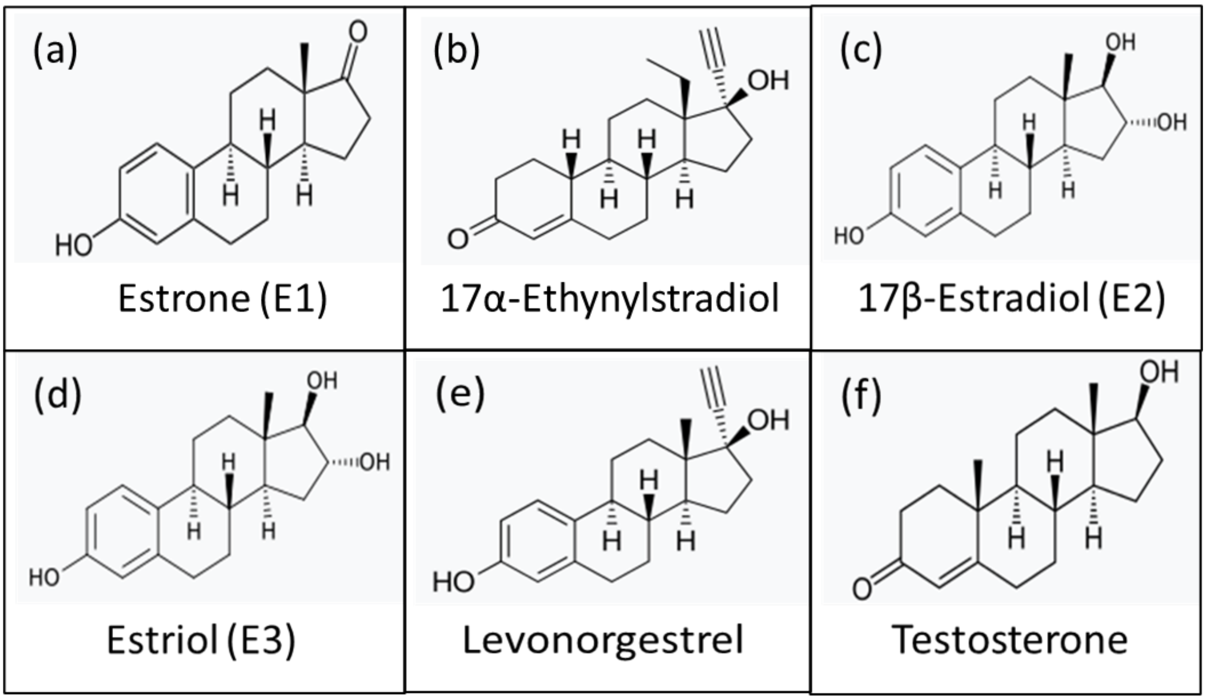

Figure S1. CECs with a similar chemical structure Estrone (a), 17α-Ethynylstradiol (b), 17β-Estradiol (c), Estriol (d), Levonorgestrel (e), Testosterone (f).

These CECs have similar chemical structure and hence likely to have similar degradation performance. X. Ma. et al. reported that Estrone (E1), 17β-estradiol (E2) and 17α-ethinyl estradiol had similar degradation performance using UVC/ H_2O_2 system [1]. The $k_{OH\cdot}$ ($L.mol^{-1}.s^{-1}$) of 17β-Estradiol, Estrone, 17α-Ethynylestradiol and 17α-Estradiol were also reported to be similar ~ 6.0×10^9 [2], indicating that the photodegradation performance by OH· system should be similar. It is however noted that 17α-ethinyl estradiol has a minute higher photodegradation performance than Estrone (E1), 17β-estradiol (E2) and Estriol (E3), due to presence of the ethynyl group, which absorbs UV light easily[3]. Nonetheless, the chemical structure of CECs can be used as a screening tool to access the suitability of different UV processes for its degradation.

Supplementary S2 Bond dissociative energy and their corresponding threshold wavelength

Table S1. Bond dissociative energies and corresponding light 'threshold' wavelength.

Bond	$\Delta E_{298k}(kJ\ mol^{-1})$	λ_D (nm)	Reference
n-C_3H_7-H	407	294	[4]
C_6H_7-H	428	279	[4]
C_6H_7-Cl	393.2 (94Kcal mol^{-1})	315*	[5]
C_6H_7-OH	428 (110Kcal mol^{-1})	279	[4]
H_3C- CH_3	349	343	[4]
H_3C-Cl	340	352	[4]
H_3C-C(O)CH_3	328	365	[4]
HO-OH	211	568	[4]
$HOCH_2$–H	402.1	298*	[5]
1,4-dioxyl-H	383.8	324*	[5]

*estimated values

Supplementary S3 Standard Reduction Potentials in Aqueous Medium for degradation of organic compounds

Table S2: Standard reduction potentials of various oxidizing agents in aqueous medium for degradation of organic compounds, adapted from Bard et al. (1985) [6].

Oxidizing agent	Reduction Reaction	Standard Potential (E^o) (V vs SHE)
Hydroxyl radical (•OH)	$\bullet OH + H^+ + e^- \rightarrow H_2O$	2.80
Sulphate radical ($SO_4^{-\bullet}$)	$SO_4^{-\bullet} + e^- \rightarrow SO_4^{2-}$	2.60
Ozone (O_3)	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.075
Persulphate	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{-\bullet}$	2.01
Hydrogen peroxide (H_2O_2)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.763
Hydroperoxyl radical ($HO_2^\bullet$)	$HO_2^\bullet + 3H^+ + 3e^- \rightarrow 2H_2O$	1.65
	$HO_2^\bullet + H^+ + e^- \rightarrow H_2O_2$	1.44
Chlorine (Cl_2)	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.358

Supplementary S4 Cost Comparison of various light driven AOPs discussed in this review

$$EE/O = \frac{P \times t \times 1000}{V \times 60 \times log\frac{C_O}{C_t}}$$

Where:
P = the power input of the UV-lamp, magnetic stirrer, pump, ozone generator (kW)
t = treatment time (min)
V = the volume of the effluent (L)
C_O = initial concentration of contaminant
C_t = concentration of pollutant at time t

Using E_{EO} allows comparison between systems using different wavelengths and polychromatic spectra. For oxidants (Cl_2, H_2O_2 etc. and catalysts (TiO_2, ZnO etc.), E_{EO} can also be applied as the stored electric energy for the treatment processes [7]. Factors that affect E_{EO} values include oxidant dose, treatment capacity and the recalcitrant nature of the contaminant.

Table S3: Cost analysis of various light driven AOPs.

S/N	Process	Pollutant	[CEC] (mg/L)	Reacting Volume (L)	Treatment time (h)	EEO (kWh m^{-3})	Degradation rate (%)	References
1	UV/TiO_2	Tris-(2-chloroisopropyl) phosphate in synthetic wastewater	1	0.15	0.667	0.000038		[8]
2	UV/PS	Brilliant Green in synthetic wastewater	24.13	0.15	2.48	5.4	99.99	[9]
	UV/PMS				3.16	6.8	99.99	
	UV/H_2O_2				3.6	7.8	99.99	
3	UV/TiO_2 (Pilot)	Real pharmaceutical effluent	COD = 3680	5	2	6.12	80% COD	[10]
4	UV/Cl_2		7.708	0.2	0.0833	0.4595	100	[11]

	UV/NH_2Cl	Iopamidol in synthetic wastewater			0.0833	0.4272	100	
	UV/ClO_2				0.0833	1.1789	100	
	UV/H_2O_2				0.0833	0.3965	100	
5	UV/TiO_2	Saccharin in synthetic wastewater	5	0.15	0.75	134.4	54	[12]
	UV/TiO_2 (LED)				0.5	8.2	100	
6	UV (LP)	Various trace organic compounds in synthetic wastewater	0.1	0.03	varied	0.09 - 15.90	90	[13]
	UV (MP)					0.09 - 12.22	90	
7	UV/Cl_2	28 PPCPs in real/synthetic wastewater	0.001 each	0.75	varied	0.017 - 2.26 (synthetic wastewater) 0.048 - 4.53 (real wastewater)	90	[14]
	UV/H_2O_2					0.17 - 2.38 (synthetic wastewater) 0.22 - 8.09 (real wastewater)	90	
8	UV	Synthetic wastewater with 4 micropollutants	1.00 each	1.2	0.333	65.5 - 499	90	[15]
	UV/H_2O_2					49.5 - 322	90	
	UV/O_3					4.75 - 65.3	90	
	UV/O_3/H_2O_2					5.28 - 44.1	90	
9	UV/O_3/TiO_2	Synthetic wastewater with various VOCs	COD: 2100 - 2300 mg/L	15	2	280	66	[16]
	O_3				1.667	150	29	
	UV/O_3				0.25	35	43	
	UV/O_3/H_2O_2/TiO_2				1	247	43	
	O_3/H_2O_2				1	106	32	
	UV/O_3/H_2O_2				1	156	46	

10	O_3	Groundwater/surface water/sec effluent with micropollutants	0.001 each	9.4	0.333	0.3	33 - 99	[17]
	Electro-Peroxone					0.21	68 - ~100	
	UV/O_3					2.13	76 - ~100	
11	O_3	Synthetic drinking water with PPCPs	10.00 each	1.6	0.167	7.79 - 13.10	66 - 82	[18]
	UV/O_3					8.99 - 14.02	80 - 100	
	$UV/O_3/TiO_2$					4.40 - 7.01	100	
12	UV/H_2O_2	Tertiary wastewater effluent	Varied (0.021 - 1.813)	21	0.0084	0.3741 - 0.8259	Not discussed	[19]
	UV/Cl_2					0.1157 - 7.3390		
	UV/O_3					0.2145 - 0.3521		
	$UV/O_3/H_2O_2$					0.2854 - 0.3625		
	$UV/O_3/Cl_2$					0.2443 - 0.5371		
13	UV/Fenton (UVA)	Synthetic water with valproic acid	50.00	2	2	26.5	100	[20]
	UV/Fenton (UVC)					17	100x`	
	UV/Fenton (Solarbox)					*	89.7	
14	Solar/Fenton	Synthetic water with 5 PPCPs	< 0.1 each	22	Not discussed	0.85	90	[21]
	Solar/Fenton					0.82	90	
	UV/H_2O_2			15.63		1.37	90	
	UV/PDS					1.3	90	
15	UV-Fenton	Synthetic water with carbamazepine	78.2	33	2	19.18	76.2	[22]
	Solar/Fenton				0.432	4.39	82.5	
	UV/Fenton				6	19.73	79.7	
16	Fenton		TOC =	0.5	1	-	55.61	[23]

	UV/Fenton	Synthetic water with pesticides	50 – 250 mg/L			4	63.76	
	Solar/Fenton					-	58.32	
	UV/TiO_2/H_2O_2				5	233	21.54	
17	Fenton	Textile wastewater	COD = 1130 mg/L	0.5	1	0.89	90	[24]
	UV/Fenton				2.33	52.75	90	
	Solar/Fenton				72	0.45	90	

* The solar box with simulated sunlight was excluded from the cost computation, since solar boxes are energy intensive and does not fully represent the cost potential of natural sunlight.

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