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APPENDIX

UVC-induced direct photolysis as an efficient process for the degradation of cilastatin in natural and waste water

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	River water	Tap water	ww
CI ⁻ (mg L ⁻¹)	13	150	13
N-NO ₃ ⁻ (mg L ⁻¹)	0.54	5.97	0.53
SO ₄ -2 (mg L ⁻¹)	12.4	105.3	1.1
P-PO4 ⁻³ (mg L ⁻¹)	0.02	1.68	0.02
HCO ₃ ⁻ (mg L ⁻¹)	103.4	144.6	103.8
N-NH ₃ (mg L ⁻¹)	0.10	0.24	0.06
N-NO ₂ ⁻ (mg L ⁻¹)	0.004	0.320	<0,002
F ⁻ (mg L ⁻¹)	0.24	0.53	0.12
CaCO₃ (mg L ⁻¹)	84.4	118.1	84.7
IC (mg ^c L ⁻¹)	22.5	33.1	21.4
TN (mg ^N L ⁻¹)	0.98	11.50	0.64
EC (µS cm⁻¹)	274.00	932.00	253.00
рН	7.32	7.14	7.68

Table A.1. Composition of the water samples used in this work.

Table A.2. k and R_0 values for the different UV-irradiated aqueous solutions of cilastatin (CIL). The error values correspond to the standard deviation of replicate experiments rounded to significant digits.

Description of the UV-irradiated water solution	<i>k,</i> (min ⁻¹)	<i>R</i> o, (× 10 ⁻⁷ mol L ⁻¹ s ⁻¹)
Effect of concentration		
2.5 mg L^{-1} CIL H ₂ O solution	0.20 ± 0.02	0.22 ± 0.02
25 mg L^{-1} CIL H ₂ O solution	0.11 ± 0.01	1.18 ± 0.10
50 mg L^{-1} CIL H ₂ O solution	0.09 ± 0.00	1.89 ± 0.05
100 mg L^{-1} CIL H ₂ O solution	0.06 ± 0.00	2.43 ± 0.06
Effect of pH		
pH=3; 100 mg L ^{-1} CIL H ₂ O solution	0.16 ± 0.00	6.79 ± 0.12
pH=5; 100 mg L ^{-1} CIL H ₂ O solution,	0.07 ± 0.01	3.09 ± 0.40
pH=7; 100 mg L ^{-1} CIL H ₂ O solution	0.05 ± 0.01	2.29 ± 0.27
pH=9; 100 mg L ^{-1} CIL H ₂ O solution	0.04 ± 0.00	1.71 ± 0.20
Effect of additives		
<i>t</i> -butanol; 100 mg L ^{-1} CIL H ₂ O solution	0.05 ± 0.00	1.97 ± 0.10
2.5 mg L ⁻¹ HA; 2.5 mg L ⁻¹ CIL H ₂ O solution	0.10 ± 0.01	0.11 ± 0.01
Natural and treated water samples		
Tap water spiked at 2.5 mg L^{-1} with CIL	0.19 ± 0.04	0.22 ± 0.04
WW effluent spiked at 2.5 mg L^{-1} with CIL	0.07 ± 0.00	0.07 ± 0.00
River water spiked at 2.5 mg L ^{−1} with CIL	0.11 ± 0.01	0.12 ± 0.01

Table A.3.	Analytical	characteristics	of CIL	and of the	identified	degradation	product	eluting	during th	۱e
photolysis (of CIL.									

Product	Retention time (min)	Identification Ions (m/z)	Tentative identification
CIL	4.491	359	
P374	1.648	375/359/315	CIL oxidized to a sulfoxide group

Table A.4. Molar absorption coefficients at 254 nm (ε_x) and direct photolysis quantum yields for 254nm irradiation (Φ_x) of the different CIL species. Note that $x = H_3A^+$, H_2A , HA^- or A^{2-} .

Species x	ε _x , L mol ^{−1} cm ^{−1}	Φ_x , mol E ⁻¹
H ₃ A ⁺	2243±30	0.59±0.03
H_2A	2692±25	(9.3±0.4)×10 ⁻²
HA⁻	1646±17	(4.6±0.2)×10 ⁻²
A ²⁻	1268±62	(1.3±0.1)×10 ⁻²



Fig. A.1. Relative abundances of the different CIL species, as a function of pH. The species fractions were derived from **Eqs. (1-4)**, using $[H^+] = 10^{-pH}$.



Fig. A.2. Tentative mechanism for the oxidation of the sulfide moiety of CIL to a sulfoxide group.



Fig. A.3. Time trends of 100 mg L⁻¹ CIL upon 254-nm irradiation at near-neutral pH, alone and upon addition of 100 mg L⁻¹ t-butanol. Data points are linked with dashed lines to visualize trends. **Inset:** respective pseudo-first order photodegradation rate constants, together with their sigma-level error bounds. Some error bars are too small to be visible.