UVC-induced degradation of cilastatin in natural water and treated wastewater

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22 November 2024

APPENDIX

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

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

	River water	Tap water	WW
Cl^- (mg L^{-1})	13	150	13
$N\text{-}NO_3^-$ (mg L^{-1})	0.54	5.97	0.53
SO_4^{-2} (mg L^{-1})	12.4	105.3	1.1
$P\text{-}PO_4^{-3}$ (mg L^{-1})	0.02	1.68	0.02
HCO_3^- (mg L^{-1})	103.4	144.6	103.8
$N\text{-}NH_3$(mg L^{-1})	0.10	0.24	0.06
$N\text{-}NO_2^-$ (mg L^{-1})	0.004	0.320	<0,002
F^- (mg L^{-1})	0.24	0.53	0.12
$CaCO_3$ (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
pH	7.32	7.14	7.68

Table A.2. k and R_o 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	k, (min^{-1})	R_o, ($\times 10^{-7}$ mol L^{-1} s^{-1})
Effect of concentration		
2.5 mg L^{-1} CIL H_2O solution	0.20 ± 0.02	0.22 ± 0.02
25 mg L^{-1} CIL H_2O solution	0.11 ± 0.01	1.18 ± 0.10
50 mg L^{-1} CIL H_2O solution	0.09 ± 0.00	1.89 ± 0.05
100 mg L^{-1} CIL H_2O solution	0.06 ± 0.00	2.43 ± 0.06
Effect of pH		
pH=3; 100 mg L^{-1} CIL H_2O solution	0.16 ± 0.00	6.79 ± 0.12
pH=5; 100 mg L^{-1} CIL H_2O solution,	0.07 ± 0.01	3.09 ± 0.40
pH=7; 100 mg L^{-1} CIL H_2O solution	0.05 ± 0.01	2.29 ± 0.27
pH=9; 100 mg L^{-1} CIL H_2O solution	0.04 ± 0.00	1.71 ± 0.20
Effect of additives		
t-butanol; 100 mg L^{-1} CIL H_2O solution	0.05 ± 0.00	1.97 ± 0.10
2.5 mg L^{-1} HA; 2.5 mg L^{-1} CIL H_2O 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 the 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 254-nm irradiation (Φ_x) of the different CIL species. Note that $x = H_3A^+$, H_2A, HA^- or A^{2-}.

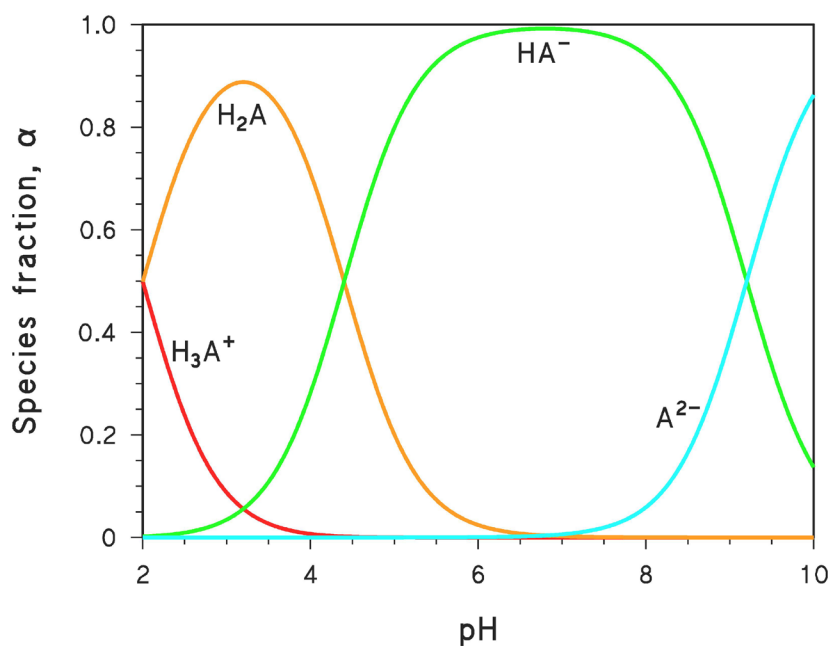| Species x	ε_x, L mol^{-1} cm^{-1}	Φ_x, mol E^{-1}
H_3A^+	2243 ± 30	0.59 ± 0.03
H_2A	2692 ± 25	$(9.3 \pm 0.4) \times 10^{-2}$
HA^-	1646 ± 17	$(4.6 \pm 0.2) \times 10^{-2}$
A^{2-}	1268 ± 62	$(1.3 \pm 0.1) \times 10^{-2}$

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 $[H^+] = 10^{-pH}$.
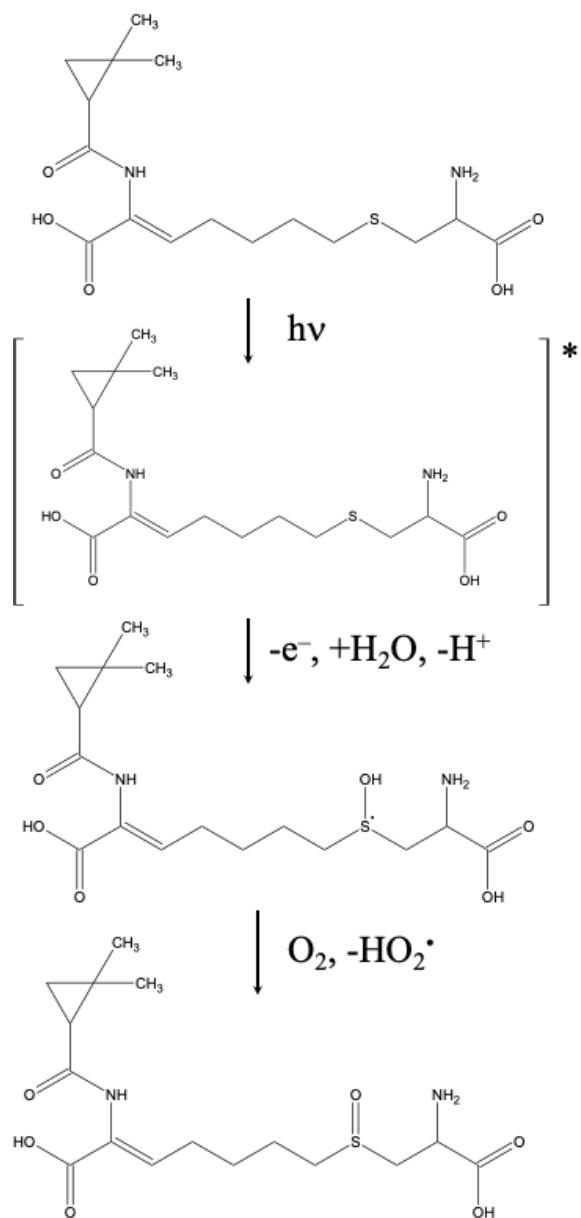
Fig. A.2. Tentative mechanism for the oxidation of the sulfide moiety of CIL to a sulfoxide group.
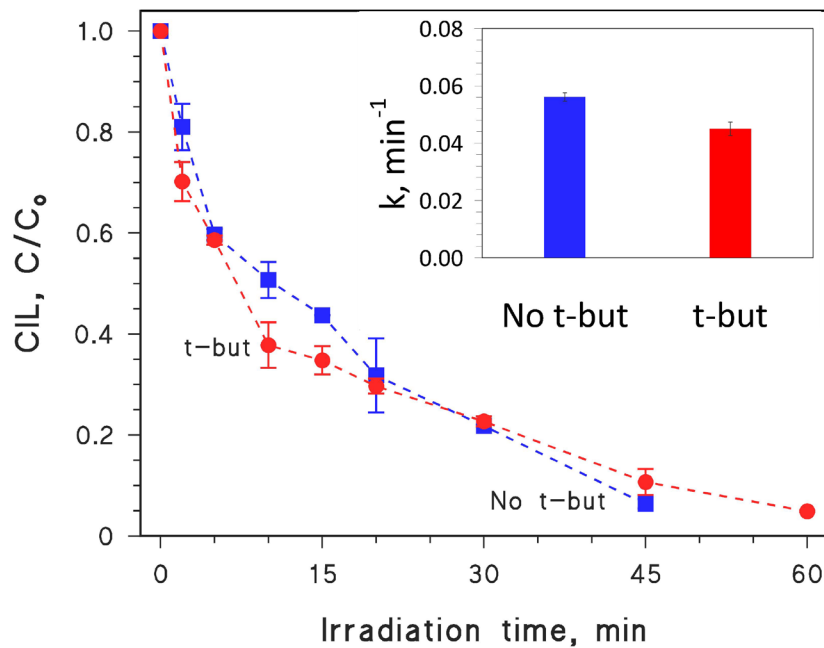
Fig. A.3. Time trends of 100 mg L^{-1} CIL upon 254-nm irradiation at near-neutral pH, alone and upon addition of 100 mg L^{-1} t-butanol. Data points are linked with dashed lines to visualize trends. **Inset:** respective pseudo-first order photodegradation rate constants, together with their sigma-level error bounds. Some error bars are too small to be visible.