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

### This is the author's manuscript

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1789036> since 2021-07-26T10:40:21Z

*Published version:*

DOI:10.1016/j.chemosphere.2021.130668

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

	River water	Tap water	WW
Cl <sup>-</sup> (mg L <sup>-1</sup> )	13	150	13
N-NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	0.54	5.97	0.53
SO <sub>4</sub> <sup>-2</sup> (mg L <sup>-1</sup> )	12.4	105.3	1.1
P-PO <sub>4</sub> <sup>-3</sup> (mg L <sup>-1</sup> )	0.02	1.68	0.02
HCO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	103.4	144.6	103.8
N-NH <sub>3</sub> (mg L <sup>-1</sup> )	0.10	0.24	0.06
N-NO <sub>2</sub> <sup>-</sup> (mg L <sup>-1</sup> )	0.004	0.320	<0,002
F <sup>-</sup> (mg L <sup>-1</sup> )	0.24	0.53	0.12
CaCO <sub>3</sub> (mg L <sup>-1</sup> )	84.4	118.1	84.7
IC (mg <sup>C</sup> L <sup>-1</sup> )	22.5	33.1	21.4
TN (mg <sup>N</sup> L <sup>-1</sup> )	0.98	11.50	0.64
EC (μS cm <sup>-1</sup> )	274.00	932.00	253.00
pH	7.32	7.14	7.68

**Table A.2.** *k* and *R*<sub>0</sub> 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.

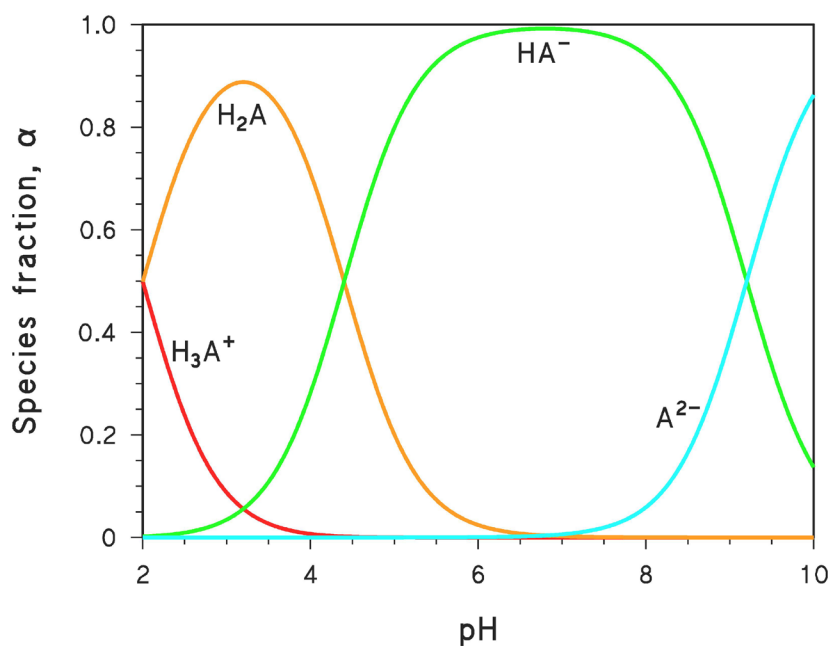
Description of the UV-irradiated water solution	<i>k</i> , (min <sup>-1</sup> )	<i>R</i> <sub>0</sub> , (× 10 <sup>-7</sup> mol L <sup>-1</sup> s <sup>-1</sup> )
Effect of concentration		
2.5 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.20 ± 0.02	0.22 ± 0.02
25 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.11 ± 0.01	1.18 ± 0.10
50 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.09 ± 0.00	1.89 ± 0.05
100 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.06 ± 0.00	2.43 ± 0.06
Effect of pH		
pH=3; 100 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.16 ± 0.00	6.79 ± 0.12
pH=5; 100 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution,	0.07 ± 0.01	3.09 ± 0.40
pH=7; 100 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.05 ± 0.01	2.29 ± 0.27
pH=9; 100 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.04 ± 0.00	1.71 ± 0.20
Effect of additives		
<i>t</i> -butanol; 100 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.05 ± 0.00	1.97 ± 0.10
2.5 mg L <sup>-1</sup> HA; 2.5 mg L <sup>-1</sup> CIL H <sub>2</sub> O solution	0.10 ± 0.01	0.11 ± 0.01
Natural and treated water samples		
Tap water spiked at 2.5 mg L <sup>-1</sup> with CIL	0.19 ± 0.04	0.22 ± 0.04
WW effluent spiked at 2.5 mg L <sup>-1</sup> with CIL	0.07 ± 0.00	0.07 ± 0.00
River water spiked at 2.5 mg L <sup>-1</sup> 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.

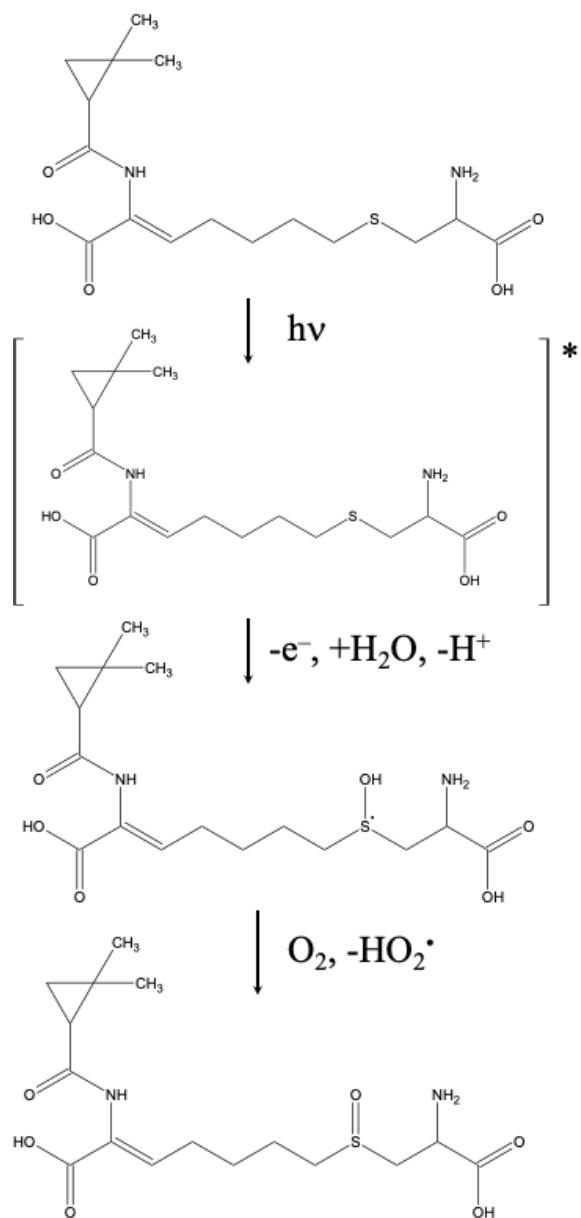
Product	Retention time (min)	Identification Ions (m/z)	Tentative identification
CIL	4.491	359	
P374	1.648	375/359/315	CIL oxidized to a sulfoxide group

**Table A.4.** Molar absorption coefficients at 254 nm ( $\epsilon_x$ ) and direct photolysis quantum yields for 254-nm irradiation ( $\Phi_x$ ) of the different CIL species. Note that  $x = \text{H}_3\text{A}^+$ ,  $\text{H}_2\text{A}$ ,  $\text{HA}^-$  or  $\text{A}^{2-}$ .

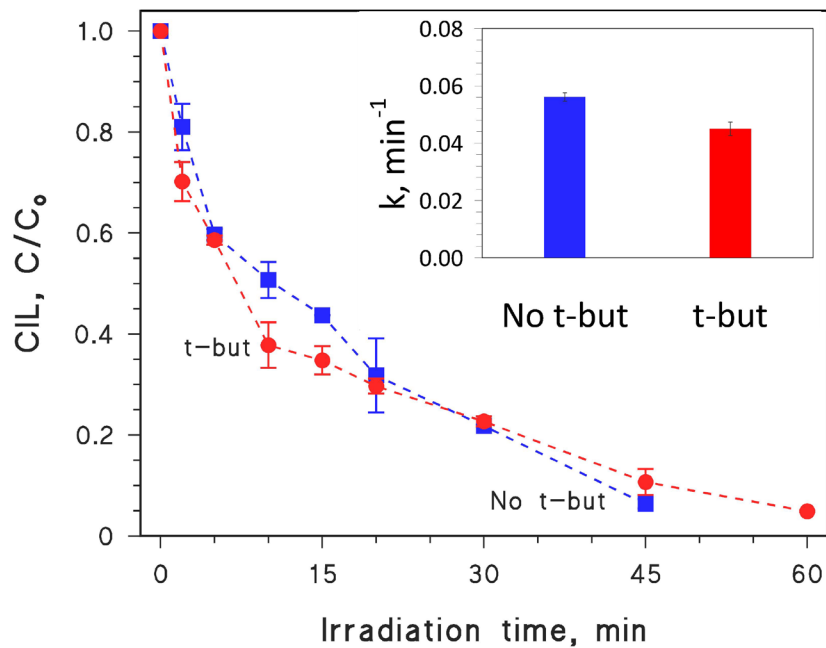
Species $x$	$\epsilon_x, \text{L mol}^{-1} \text{cm}^{-1}$	$\Phi_x, \text{mol E}^{-1}$
$\text{H}_3\text{A}^+$	$2243 \pm 30$	$0.59 \pm 0.03$
$\text{H}_2\text{A}$	$2692 \pm 25$	$(9.3 \pm 0.4) \times 10^{-2}$
$\text{HA}^-$	$1646 \pm 17$	$(4.6 \pm 0.2) \times 10^{-2}$
$\text{A}^{2-}$	$1268 \pm 62$	$(1.3 \pm 0.1) \times 10^{-2}$



**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  $[\text{H}^+] = 10^{-\text{pH}}$ .



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



**Fig. A.3.** Time trends of  $100 \text{ mg L}^{-1}$  CIL upon 254-nm irradiation at near-neutral pH, alone and upon addition of  $100 \text{ mg L}^{-1}$  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.