Supporting Information

Degradation of ciprofloxacin by 185/254 nm vacuum ultraviolet: kinetics, mechanism and toxicology

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SI Content

Text S1. Qualitative and quantitative analysis of CIP and its products.

1 HPLC separation

The samples were injected into a LC-30AD liquid chromatograph system (Shimadzu, Japan) with a Waters Symmetry C-18 column (2.1 × 150 mm, 3.5 μm) prior to the MS analysis. The injection volume was 5 μL, and the mobile phase was a gradient elution of 0.1% formic acid water solution (mobile phase A) and acetonitrile (mobile phase B). The gradient elution was programmed as follows: 0-1.0 min, 10% B; 1.0-2.0 min, 10%-90% B; 2.0-4.0 min, 90% B; 4.0-4.1 min, 90%-10% B; 4.1-6.0 min, 10% B (40°C, 0.3 mL min^{-1}).

2 Reaction intermediate analysis

The identification of intermediates was performed using a TripleTOF 5600+ high-resolution tandem mass spectrum (HRMS) (Applied Biosystems SCIEX, USA) equipped with a Turbo V ESI ion source and a triple quadrupole time-of-flight (TOF) device. The instrumentation conditions are listed in Table S1. Nitrogen served both as the turbo and the collision gas. Mass calibrations and resolution adjustments on the quadrupoles and TOF were performed automatically using a 10^{-5} M solution of polypropylene glycol introduced via a model II Harvard infusion pump. The scan range was set at *m/z* 50-500. The data were analyzed using PeakView and MasterView (Applied Biosystems SCIEX, USA). The concentrations of CIP and its degrading intermediates were verified also with the TripleTOF 5600+ HRMS.

Text S2. Toxicology analysis

1 Analysis of intracellular ROS

After treatment, *E. coli* was harvested and suspended in 200 μL of 2',7'-Dichlorofluorescein diacetate to obtain a cell concentration at approximate 10^6 cells per milliliter. Subsequently, samples were placed in the dark at 37

ºC for 20 min, and then analyzed with a FACScan flow cytometer (BD, USA) to measure ROS. Upon cleavage of the acetate groups by intracellular esterases and oxidation, the nonfluorescent 2',7'-Dichlorofluorescein diacetate was converted to the fluorescent 2',7'-dichlorofluorescein, which was monitored using a fluorescence plate reader (Bio-TEK, USA) with an excitation wavelength at 488 nm and an emission wavelength at 530 nm.

2 Analysis of membrane potential and apoptosis

Analysis of MP followed a similar procedure in ref. [1]. Briefly, the lyophilized JC-1 reagent was dissolved with 125 μL DMSO per vial to yield a JC-1 stock solution. The 1-fold assay buffer was prepared by diluting the 10-fold assay buffer in deionized water. Next, the JC-1 dye solution was prepared by diluting the JC-1 stock solution 1:100 with 1-fold assay buffer.

After the collected cells were suspended in 200 μL of JC-1 dye solution, all the samples were incubated at 25 ºC for 15 min in a dark place. Subsequently, the stained cells were pipetted to tubes with BD CaliBRITE™ beads and analyzed by flow cytometer. Ten thousand cells of each sample were analyzed by the laser beam at the excitation wavelength of 488 nm individually. The detector measured emission intensity was set at 605 to 625 nm. For each cell, the scattered light was detected by a photo diode at 2 different positions (forward and side scattered light) and converted into electric signals and fluorescence intensity. The JC-1 monomers emitted green fluorescence, whereas, the aggregates emitted red fluorescence. These two kinds of fluorescence were captured through 527 and 590 nm long-pass filters, respectively.

Quantitative analysis of apoptotic cell death caused by the mixture of 1H-BT intermediate products was analyzed using the Annexin V-FITC Apoptosis Detection Kit (KeyGEN BioTECH, China). The cells were analyzed with a FACScan flow cytometer.

Table S1. Operational parameters of mass spectrum.

Parameter (unit)	TripleTOF 5600+
Ion source mode	Positive
Scan mode	Full scan
ESI needle voltage (V)	4000
Turbo-gas temperature (°C)	350
Curtain gas pressure (psi)	40
Nebulizer gas pressure (psi)	35
Auxiliary gas pressure (psi)	40
Declustering potential (V)	60
CID energy (eV)	20 ± 15

Table S2. Molar absorption coefficients of different solutions.

Contents	Molar absorption coefficient	
	254 nm (M^{-1} cm^{-1})	185 nm (M^{-1} cm^{-1})
CIP	12925 ± 654*	18807 ± 815*
EtOH	0.65 ± 0.07	31.31 ± 5.3
TBA	1.40 ± 0.10	14.72 ± 2.1
ascorbic acid	1924 ± 64	3130 ± 184
OH^-	34 ± 4	3039 ± 206
Cl^-	258 ± 29	3307 ± 164
NO_3^-	144 ± 56	4736 ± 216
SO_4^{2-}	209 ± 38	396 ± 29
$H_2PO_4^-$	224 ± 29	344 ± 38
HCO_3^-	114 ± 38	464 ± 64

*Molar absorption coefficient of CIP differed by pH values [2]. Only the molar absorption coefficient at pH = 7.0 is presented here.

Table S3. Reaction rate constant of different scavengers.

Scavenger type	Reaction formula	$k_{\cdot OH}$ (M^{-1} s^{-1})	Condition	References
EtOH	EtOH + ·OH → products	1.9×10^9	neutral	[3]
TBA	TBA + ·OH → products	6.0×10^8	neutral	[3]
ascorbic acid	·OH + ascorbic acid → H_2O + ·ascorbic acid	1.0×10^{10}	neutral	[3]
Cl^-	$\cdot OH + Cl^- \rightarrow \cdot ClOH^-$	4.3×10^9	pH = 2	[3]
NO_3^-	--	1×10^5	--	[4]
CO_3^{2-}	$\cdot OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\cdot -}$	3.9×10^8	neutral	[3]
SO_4^{2-}	--	--	--	--
$H_2PO_4^-$	$\cdot OH + H_2PO_4^- \rightarrow OH^- + H_2PO_4^{\cdot}$	2.0×10^4	neutral	[3]
HCO_3^-	$\cdot OH + HCO_3^- \rightarrow CO_3^{\cdot -} + H_2O$	8.5×10^8	neutral	[3]

Table S4. EE/O values for VUV system.

System	P (kW)	k_{app} (s^{-1})	t (h)	V (m^3)	EE/O_e	(kWh m^{-3} $order^{-1}$)
pH = 3.0	3.14×10^{-6}	0.0022	0.088	2.0×10^{-5}		0.014
pH = 5.0	3.14×10^{-6}	0.0027	0.073	2.0×10^{-5}		0.011
pH = 7.0 (control)	3.14×10^{-6}	0.0049	0.039	2.0×10^{-5}		0.006
pH = 9.0	3.14×10^{-6}	0.0021	0.093	2.0×10^{-5}		0.015
pH = 11.0	3.14×10^{-6}	0.0014	0.136	2.0×10^{-5}		0.021
Humic acid (100 mg L^{-1})	3.14×10^{-6}	0.0014	0.139	2.0×10^{-5}		0.022
NO_3^- (100 mg L^{-1})	3.14×10^{-6}	0.0039	0.050	2.0×10^{-5}		0.008
Cl^- (100 mg L^{-1})	3.14×10^{-6}	0.0033	0.058	2.0×10^{-5}		0.009
SO_4^{2-} (100 mg L^{-1})	3.14×10^{-6}	0.0050	0.038	2.0×10^{-5}		0.006
$H_2PO_4^-$ (100 mg L^{-1})	3.14×10^{-6}	0.0049	0.040	2.0×10^{-5}		0.006
HCO_3^- (100 mg L^{-1})	3.14×10^{-6}	0.0013	0.144	2.0×10^{-5}		0.023

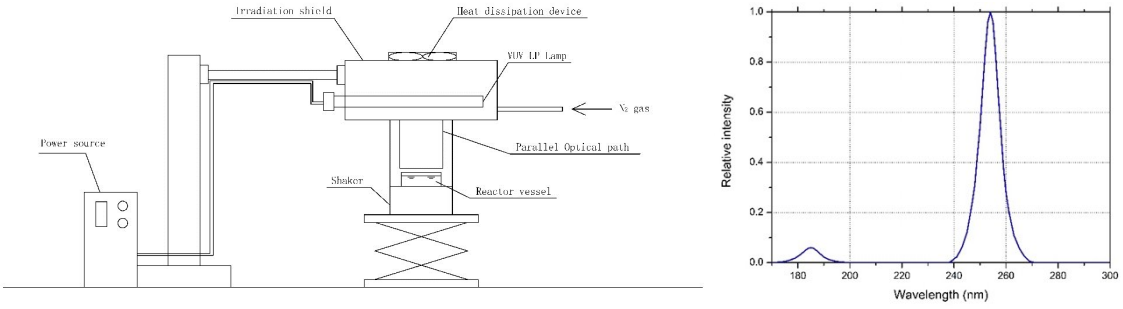

Figure S1. Irradiation module and emission spectra for VUV lamp.

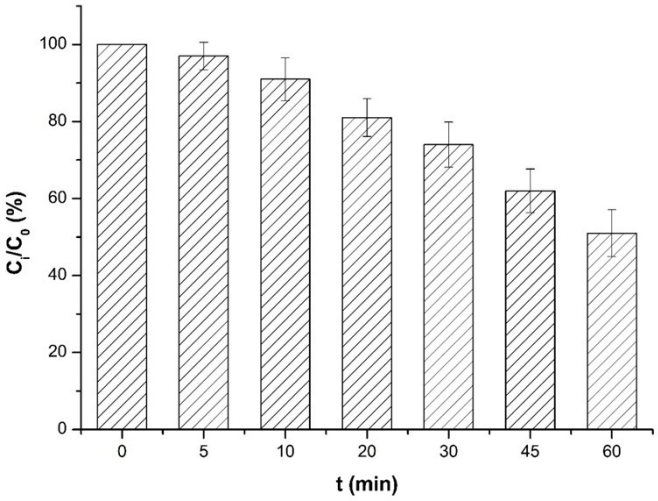

Figure S2. Variation of total organic matter.

Experimental conditions: solution temperature 25 ± 2°C, pH 6.5-7.2, $[CIP]_0$ = 3.02 μM, 254 UV irradiation intensity = 2.0 mW cm^{-2}, 185 VUV irradiation intensity = 0.12 mW cm^{-2}. All the experiments were carried out in triplicate with error bars representing the standard error of the mean.

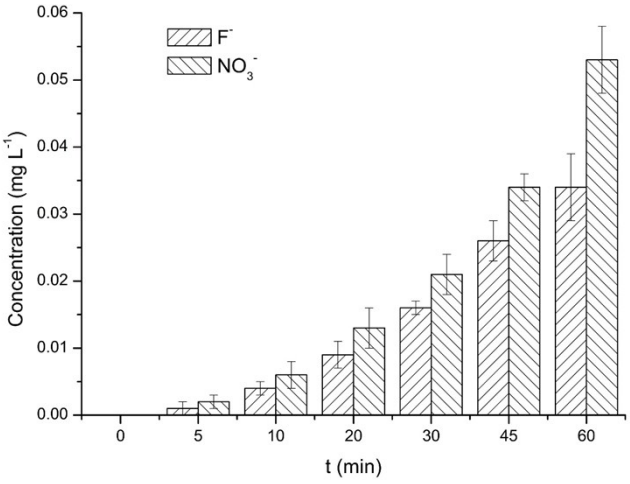

Figure S3. Variation of inorganic product anions.

Experimental conditions: solution temperature 25 ± 2°C, pH 6.5-7.2, $[CIP]_0$ = 3.02 μM, 254 UV irradiation intensity = 2.0 mW cm^{-2}, 185 VUV irradiation intensity = 0.12 mW cm^{-2}. All the experiments were carried out in triplicate with error bars representing the standard error of the mean.

References

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