SUPPLEMENTARY MATERIAL

Photocatalytic removal of the antibiotic furazolidone using g-C_3N_4 in the presence of persulfates under lab and pilot scale conditions

Christina Efthymiou[1], Christos Lykos[1], Vasiliki Boti[1, 2, *], Ioannis Konstantinou[1, 2, *] and Triantafyllos Albanis[1,2]

[1]Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece; ch.evthymiou@uoi.gr (C.E.); c.lykos93@gmail.com (C.L.); talbanis@uoi.gr (T.A.)
[2]Unit of Environmental, Organic and Biochemical high-resolution analysis–Orbitrap-LC–MS, University of Ioannina, Ioannina, 45110, Greece

*Correspondence: vboti@uoi.gr (V.B.); iokonst@uoi.gr (I.K.)

Contents

S1 3

Table S1. Physicochemical characteristics of SWW sample used in lab and pilot-scale experiments. 4

Table S2. Gradient elution program for the separation of FZ and its TPs..... 4

Table S3. Parameters of ESI-MS for the analysis of FZ and its TPs. 4

Table S4. Removal kinetic constants (k), half-life values ($t_{1/2}$), percent removals of FZ and correlation coefficients (R^2) per applied process. 5

Table S5. Removal kinetic constants (k), half-life values ($t_{1/2}$), percent removals of FZ and correlation coefficients (R^2) for different concentrations of PS in UWW (lab-scale). 5

Table S6. Removal kinetic constants (k), half-life values ($t_{1/2}$), percent removals of FZ and correlation coefficients (R^2) for different inorganic ions in UWW (lab-scale). 5

Furazolidone (FZ) (98 %), sodium persulfate (≥ 98 %), sodium azide (NaN_3) (≥ 99.5 %), and L-histidine (≥ 99 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Potassium oxalate monohydrate ($K_2C_2O_4$) (99 %) was supplied by Fluka (Buchs, Switzerland). All solvents used (methanol (MeOH), acetonitrile (AcN) and water) were of high purity (LC-MS grade) and obtained from Fisher Chemical (Loughborough, UK). Formic acid (FA) (98-100 %) was purchased from Supelco (Bellefonte, PA, USA) and used to prepare the chromatographic mobile phases. An Evoqua water purification system (Pittsburgh, PA, USA) provided ultrapure water (UPW) and was used as an aqueous matrix for the lab-scale photocatalytic experiments. Secondary-treated municipal wastewater (SWW) was obtained from the municipal wastewater treatment plants (WWTP) of Ioannina (Epirus, Greece) and used as an aqueous matrix in both lab- and pilot-scale experiments. Bacteria in solid frozen phase (Acute Reagent) for the exotoxicological assessment using Microtox bioassay and the reconstitution solution to activate them were supplied by Modern Water (New Castle, DE, USA).

Oasis HLB (200 mg, 6 cm^3) cartridges used for solid-phase extraction (SPE) were purchased from Waters Corporation (Milford, MA, U.S.A.). The SPE procedure was performed using a Thermo Fisher Scientific HyperSep Glass Block 24-port Vacuum Manifold (Waltham, MA, USA) connected to a Rocker Scientific vacuum pump (New Taipei City, Taiwan). The extracts were condensed using a Techne Dri-Block DB-3D mild nitrogen concentrator (Staffordshire, UK) connected to a Peak Scientific NG10LA nitrogen generator (Inchinnan, UK).

Table S1. Physicochemical characteristics of SWW sample used in lab and pilot-scale experiments.

Sample	**SWW**
pH	6.94
Conductivity (μS cm^{-1})	773
Salinity (psu)	0.1
Turbidity (NTU)	7.2
Total Dissolved Solids (TDS) (mg L^{-1})	635
Chloride anions Cl^- (mg L^{-1})	52.4
Nitrate anions NO_3^- (mg L^{-1})	34.5
Sulfate anions SO_4^{2-} (mg L^{-1})	45.0

Table S2. Gradient elution program for the separation of FZ and its TPs

Time (min)	**Mobile phase**	
	A% (H_2O+0.1% FA)	**B% (MeOH+0.1% FA)**
0.0	98	2
1.0	98	2
20.0	2	98
21.0	2	98
21.1	98	2
25.0	98	2

Table S3. Parameters of ESI-MS for the analysis of FZ and its TPs.

Parameters	**Settings**
Ionization mode	Positive
Spray voltage	3.7 kV
Resolution	60,000 FWHM
Capillary voltage	50 V
Tube lens	90 V
Sheath gas flow	55 au
Auxiliary gas flow	25 au
Capillary temperature	320 °C

Table S4. Removal kinetic constants (k), half-life values ($t_{1/2}$), percent removals of FZ and correlation coefficients (R^2) per applied process.

Process	Matrix	k (min^{-1})	R^2	$t_{1/2}$ (min)	Removal (%)
Photolysis	UPW	0.038	0.9897	18.2	87.0
	SWW	0.014	0.9911	49.5	60.9
PS Photoactivation	UPW	0.043	0.9865	16.1	93.3
	SWW	0.022	0.9879	31.5	73.5
	SWW (Pilot)	0.012	0.9934	57.8	75.0
g-C_3N_4	UPW	0.073	0.9932	9.5	100
	SWW	0.020	0.9899	34.7	66.9
g-C_3N_4/PS	UPW	0.103	0.9914	6.7	100
	SWW	0.029	0.9867	23.9	86.2
	SWW (Pilot)	0.017	0.9749	40.8	86.7

Table S5. Removal kinetic constants (k), half-life values ($t_{1/2}$), percent removals of FZ and correlation coefficients (R^2) for different concentrations of PS in UWW (lab-scale).

PS concentration (mM)	k (min^{-1})	R^2	$t_{1/2}$ (min)	Removal (%)
1.00	0.103	0.9914	6.7	100
0.75	0.096	0.9926	7.14	99.3
0.50	0.093	0.9800	7.35	99.2

Table S6. Removal kinetic constants (k), half-life values ($t_{1/2}$), percent removals of FZ and correlation coefficients (R^2) for different inorganic ions in UWW (lab-scale).

Anion	Concentration ($mg\ L^{-1}$)	k (min^{-1})	R^2	$t_{1/2}$ (min)	Removal (%)
NO_3^-	34.5	0.110	0.9936	6.30	100
SO_4^{2-}	45.0	0.073	0.9881	8.73	96.6
Cl^-	52.4	0.074	0.9829	8.52	97.1