Supporting Information

Photocatalytic Degradation of Water Contaminants in Multiple Photoreactors and the Evaluation of Reaction Kinetics Constants Independent of Photon Absorption, Irradiance, Reactor Geometry and Hydrodynamics

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Content: **Figure S1 and S2**. Emission spectra of UV lamps. **Figure S3.** Schematic representation of the geometry of the annular photocatalytic reactor. **Figure S4.** Forward photon flux emerging from the outer wall of PR1 at different catalyst concentrations and levels of irradiance. **Figure S5.** Results of the modeling of the photocatalytic oxidation of oxalic acid in PR1 with different model assumptions. **Table S1.** Photoreactors dimensions and lamp specifications. **Table S2.** Reaction scheme for the heterogeneous photodecomposition of oxalic acid on TiO_2.

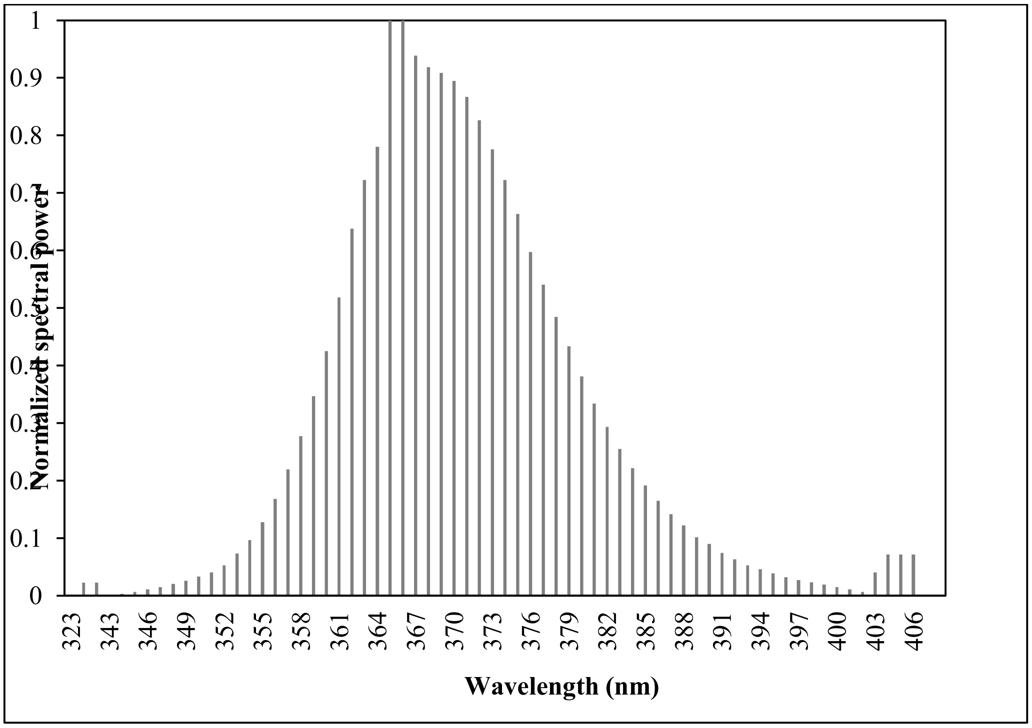


Figure S1. Emission spectrum for blacklight blue fluorescent lamps (Philips blacklight-blue TL 8W/08 F8 T5/BLB lamp).

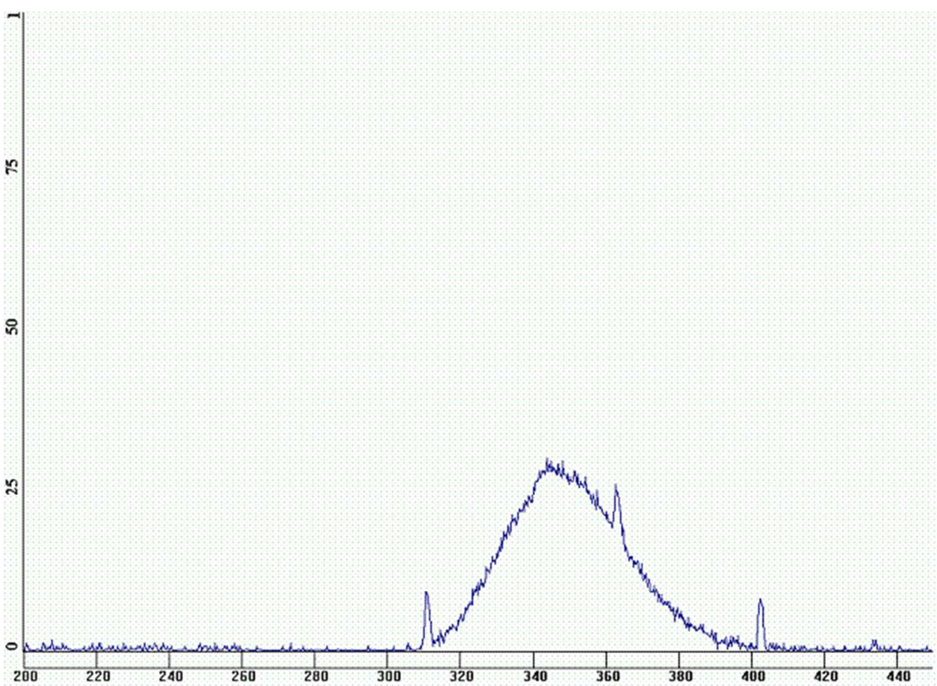


Figure S2. Emission spectrum for UVP Pen-Ray® mercury discharge lamp (model 90-0019-04) provided by UVP.

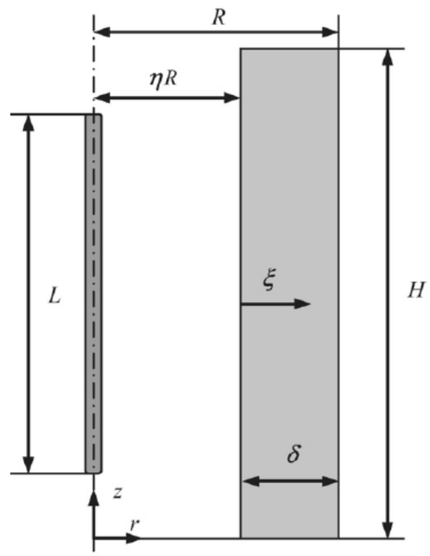
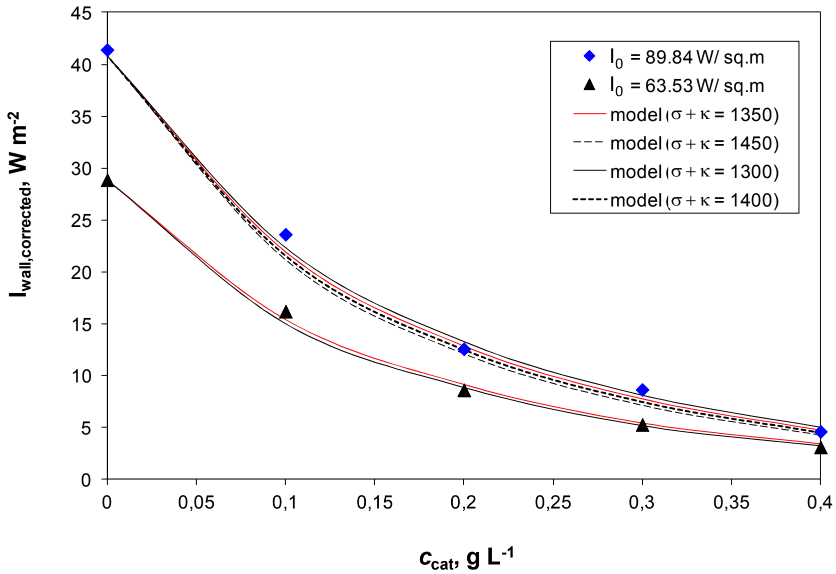
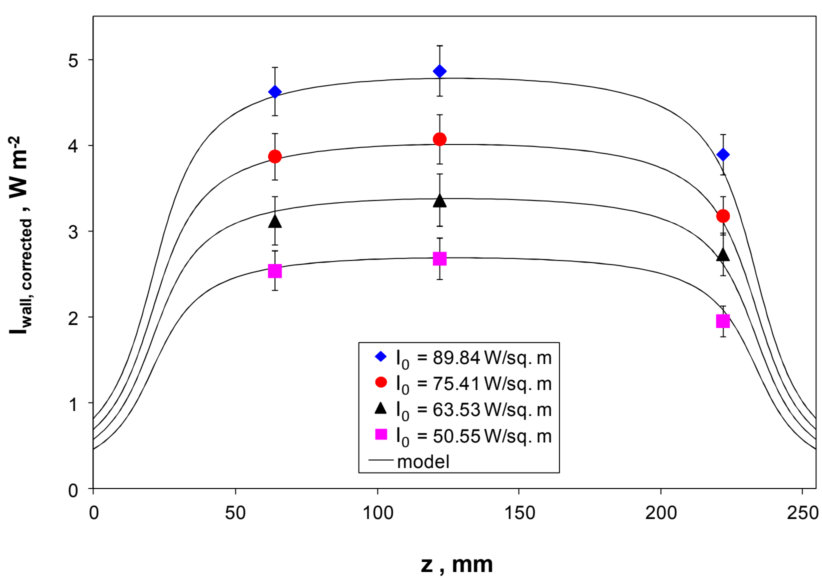


Figure S3. Schematic representation of the geometry of the annular photocatalytic reactor (reproduced from Toepfer et al.[1]).



(a)



(b)

Figure S4. Forward photon flux emerging from the outer wall of PR1. (a) At different TiO_2 powder loadings and different levels of irradiance, at z* = 0.5. Lines are the fitting of SFM with ω = 0.8617, symbols are mean values of several measurements. (b) At different positions along the axial direction varying the irradiance. Lines are the fitting of SFM with ω = 0.8617. [TiO_2] = 0.4 g/L.

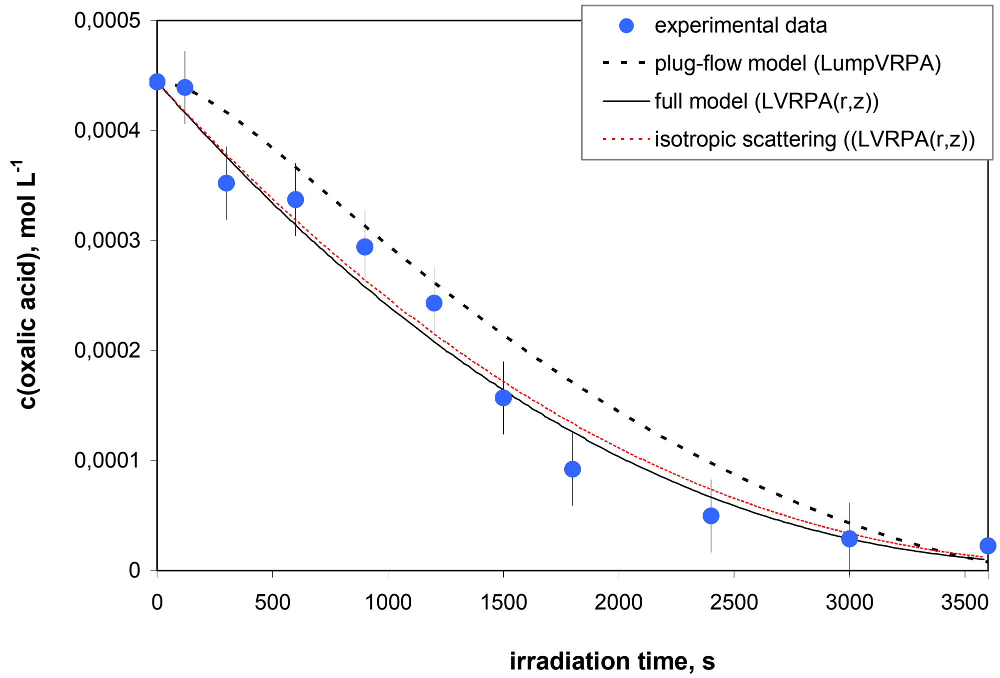


Figure S5. Results of the 5odelling of the photocatalytic oxidation of oxalic acid in PR1 with different model assumptions. pH = 4, $[TiO_2]$ = 0.4 g/L; I_0 = 89.84 W m^{-2}.

Table S1 Photoreactors dimensions and lamp specifications.

Photoreactor dimensions		PR1	PR2
Length, *H*	m	0.255	0.095
Inner radius, ηR	m	0.013	0.008
Outer radius, *R*	m	0.018	0.038
Irradiated volume, V_r	m^3	1.34×10^{-4}	5.00×10^{-4}
Lamp specifications			
Lamp type		Philips TL 8W/08 F8 T5/BLB	PenRay 90-0019-04
Irradiance at 2 cm from the source	W m^{-2}	86.75	12.55
Bulb length with uniform emission, *L*	m	0.213	0.0538
Bulb radius, r_l	m	0.00753	0.00475

Table S2. Reaction scheme for the heterogeneous photodecomposition of oxalic acid on TiO_2 according to Pozzo et al.[2]

Reaction step	
S_0	Activation (common to both pathways) $TiO_2 + h\nu \rightarrow h^+ + e^-$
S_1	Adsorption (species A) on dark/illumination conditions $[site] + C_2O_4H^-_{(sol)} \leftrightarrow C_2O_4H^-_{(ads)A}$
S_2	Adsorption (species B) on dark/illumination conditions $[site] + C_2O_4H^-_{(sol)} \leftrightarrow C_2O_4H^-_{(ads)B}$
S_3	Adsorption of oxygen $[site] + O_{2(sol)} \leftrightarrow O_{2(ads)}$
$S_{4,}$ S_5	Hole trapping (via OH^-) and *σ* bond rupture (fast kinetics) $(OH^-)_{ads} + h^+ \leftrightarrow OH^\bullet$ $C_2O_4H^-_{(ads)B} + OH^\bullet \rightarrow CO_2H^\bullet_{(ads)B} + CO_2 + OH^-$
S_6	Hole trapping (direct) and σ bond rupture (slow kinetics) $C_2O_4H^-_{(ads)A} + h^+ \rightarrow CO_2H^\bullet_{(ads)A} + CO_2$
S_7	Final mineralization (common to both mechanisms) $CO_2H^\bullet_{(ads)} + O_2 \rightarrow O_2H^\bullet + CO_2$
S_8	Electron capture $O_{2(ads)} + e^- \rightarrow O_2^{\bullet -}{}_{(ads)}$
S_9	Hole–electron recombination $e^- + h^+ \rightarrow$ heat
$S_{10\text{-}12}$	Complementary (assumed fast) reactions $O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$ $2HO_2^\bullet \rightarrow H_2O_2 + O_2$ $H_2O_2 \rightarrow H_2O + 1/2\ O_2$

References (Supporting Information)

(1) Toepfer, B.; Gora, A.; Li Puma, G. Photocatalytic oxidation of multicomponent solutions of herbicides: Reaction kinetics analysis with explicit photon absorption effects. *Appl. Catal. B: Environ.* **2006**, *68*, 171-180.

(2) Pozzo, R. L.; Brandi, R. J.; Cassano, A. E.; Baltanás, M. A. Photocatalytic oxidation of oxalic acid in dilute aqueous solution, in a fully illuminated fluidized bed reactor. *Chem. Eng. Sci.* **2010**, 65, 1345-1353