

Supplementary material

Removal of Organic Micropollutants From a Municipal Wastewater Secondary Effluent by UVA-LED Photocatalytic Ozonation

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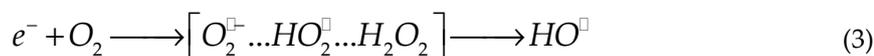
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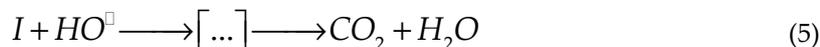
S1. Simplified reaction mechanisms of oxidation processes studied [1]

Photocatalytic oxidation:



Initiation steps for HO[•] formation: reactions (2) (main pathway) and (3).

Removal of organic matter (M) and intermediates (I): reactions (4) and (5):



M and I could also be removed by direct photolysis:

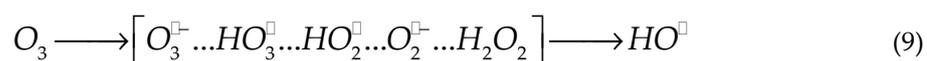


Ozonation:

Removal of organic matter (M) and intermediates (I) by free radical and direct ozone reactions: reactions (4), (5), (7) and (8).

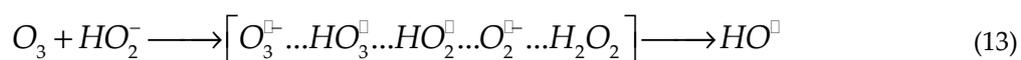


Main initiation step for HO• formation:



Photoozonation:

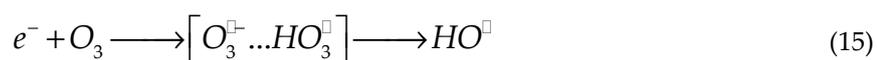
Reactions (4) to (9) and:



Main initiation steps for HO• formation: reactions (9), (11), and (13)

Photocatalytic Ozonation:

Reactions (1) to (13) and:



Initiation steps for HO• formation: reactions (2), (3), (9), (11), (13), (14), and (15)

Synergism between ozone and photocatalytic oxidation due to reactions (14) and (15).

S2. Additional Tables and Figures.

Table S1. Main characteristics of wastewater samples (WW).

	pH	DOC (mg/L)	IC (mg/L)
WW1	7.6 ± 0.2	22.2 ± 1.0	69.6 ± 1.6
WW2	7.6 ± 0.2	26.6 ± 1.0	74.2 ± 1.6

IC, inorganic carbon; DOC, Dissolved organic carbon.

Table S2. List of compounds: (i) that can be identified by the SPE-UHPLC-MS/MS method; (ii) listed in 2013/39/EU Directive and/or (iii) 2018/840/EU Decision; and (iv) detected in WW samples.

Pesticides	Detected by SPE-UHPLC-MS/MS	Directive 2013/39/EU	Decision 2018/840/EU	Detected in WW
Alachlor	X	X		
Atrazine	X	X		
Chlorfenvinphos	X	X		
Clofibric acid	X			
Acetamiprid	X		X	
Clothianidin	X		X	
Diuron	X	X		
Imidacloprid	X		X	
Isoproturon	X	X		X
Methiocarb	X		X	
Pentachlorophenol	X	X		
Simazine	X	X		
Thiacloprid	X		X	
Thiamethoxam	X		X	

Industrial Compounds	Detected by SPE-UHPLC-MS/MS	Directive 2013/39/EU	Decision 2018/840/EU	Detected in WW
Perfluorooctanesulfonic acid (PFOS)	X	X		

UV Filter
2-Ethylhexyl 4-methoxycinnamate (EHMC)

Pharmaceuticals				
Atenolol	X			
Atorvastatin	X			
Azithromycin	X		X	
Bezafibrate	X			X
Carbamazepine	X			X

Cefalexin	X		
Ceftiofur	X		
Ciprofloxacin	X	X	X
Citalopram	X		
Clarithromycin	X	X	X
Clindamycin	X		
Clopidogrel	X		X
Diclofenac	X		X
Diphenhydramine	X		
Enrofloxacin	X		
Erythromycin	X	X	
Fluoxetine	X		X
Hydrochlorothiazide	X		
Ketoprofen	X		
Metoprolol	X		X
Norfluoxetine	X		
Ofloxacin	X		
Propranolol	X		X
Sulfamethoxazole	X		
Tetracycline	X		
Tramadol	X		X
Trimethoprim	X		
Venlafaxine	X		X
Warfarin	X		

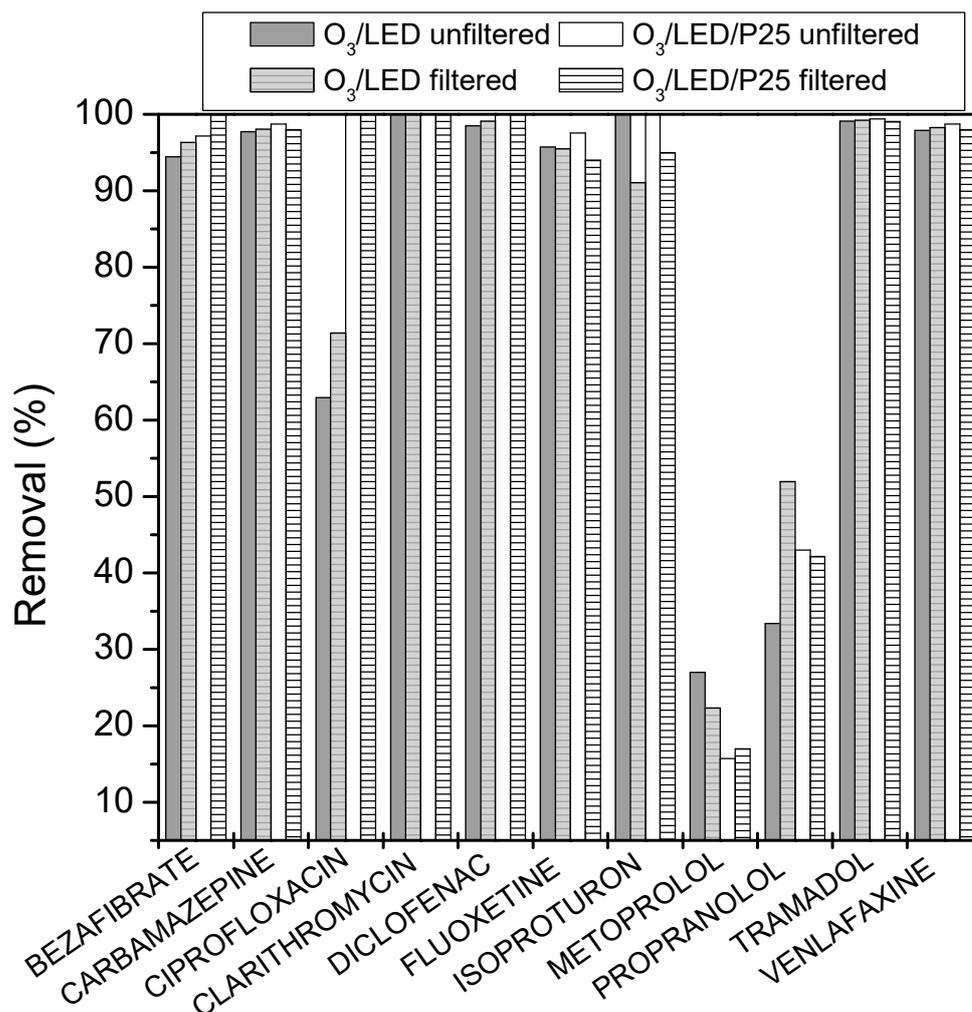


Figure S1. Comparison of removal percentage between WW1 filtered and unfiltered in different semi-batch experiments. Conditions: reaction time = 10 min; gas flow rate = 150 mL·min⁻¹; P25 loading (when applied) = 0.5 g·L⁻¹; ozone concentration = 50 mg·L⁻¹.

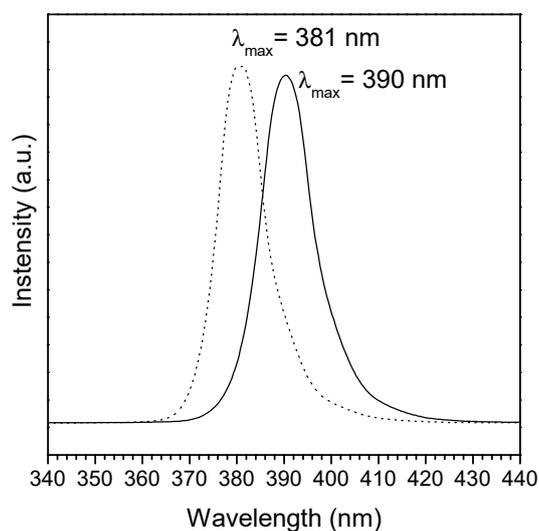


Figure S2. Irradiance spectra of UVA LEDs used for semi-batch (solid line) and continuous operation (dotted line).

S3. Mathematical Models

This part of the study focuses on matching the continuous system to a reactor flow model, taking into consideration two different reactor models. For this purpose, the normalized concentration of the tracer (F function) was determined from step-tracer (NaCl solution 2 g·L⁻¹) as described in section 2 of the manuscript.

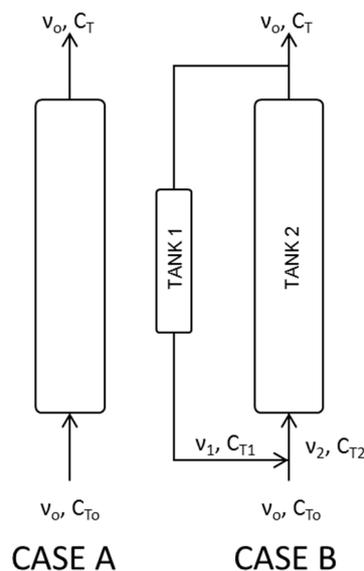


Figure S3 Case A: The system behaves as one perfectly mixed reactor. Case B: The system behaves as two perfectly mixed reactors in series due to the reaction column and the recirculation column.

Case A: Perfectly mixed reactor model.

The F function is related to residence time distribution (RTD) (also known as E function) through equation (1), [1].

$$F = \frac{C_T}{C_{T0}} = \int_0^t E dt \quad (1)$$

The E function for perfect mixing conditions is described as follows:

$$E = \frac{1}{t_m} e^{-t/t_m} \quad (2)$$

Then, taking into account both equations (1) and (2):

$$F = \frac{C_T}{C_{T0}} = 1 - e^{-t/t_m} \quad (3)$$

where the hydraulic residence time (HRT, τ) is defined as:

$$\tau = \frac{V}{V_o} \quad (4)$$

Case B: Two independent perfectly mixed reactors in series:

In this case, considering the scheme of the set-up, the tracer concentration at the inlet of the main column is described as:

$$C_{T_2} = \frac{C_T v_1 + C_{T_0} v_0}{v_2} \quad (5)$$

The outlet tracer concentration in tank 1 (C_T) and tank 2 (C_{T_1}) are described as follows:

$$C_T = C_{T_2} \left(1 - e^{-\left(\frac{t}{\tau_2}\right)} \right) \quad (6)$$

$$C_{T_1} = C_T \left(1 - e^{-\left(\frac{t}{\tau_1}\right)} \right) \quad (7)$$

Where, τ_1 and τ_2 being the hydraulic residence times in tank 1 and 2, respectively. Therefore, the F function can be obtained by combining equations (5), (6) and (7):

$$F = \frac{C_T}{C_{T_0}} = \frac{v_0 \left(1 - e^{-\left(\frac{t}{\tau_2}\right)} \right)}{v_2 - v_1 \left(1 - e^{-\left(\frac{t}{\tau_1}\right)} \right) \left(1 - e^{-\left(\frac{t}{\tau_2}\right)} \right)} \quad (8)$$

Finally, since the packed bed reactor agrees with a perfectly mixed tank model as shown in **Figure S3**, the experimental HRT can be guessed through the linear adjustment of the neperian logarithm form of equation (3).

$$\ln \left(1 - \frac{C_T}{C_{T_0}} \right) = -\frac{t}{\tau} \quad (9)$$

Thus, the inverse of the negative slope gives a result of 39 min for the HRT.

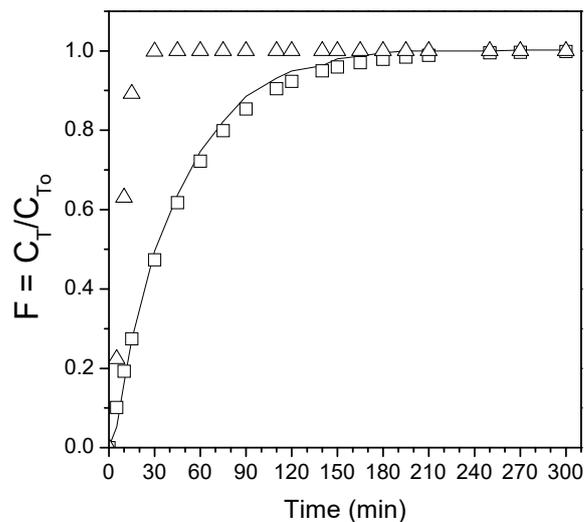


Figure S4. F curve versus time from tracer experiment (solid line) and simulated F curves for the reactor set-up in case A (□) and B (Δ).

S4. P25R Photocatalyst Characterization: scanning electron microscopy (SEM) and wavelength dispersive X-ray fluorescence (WDXRF)

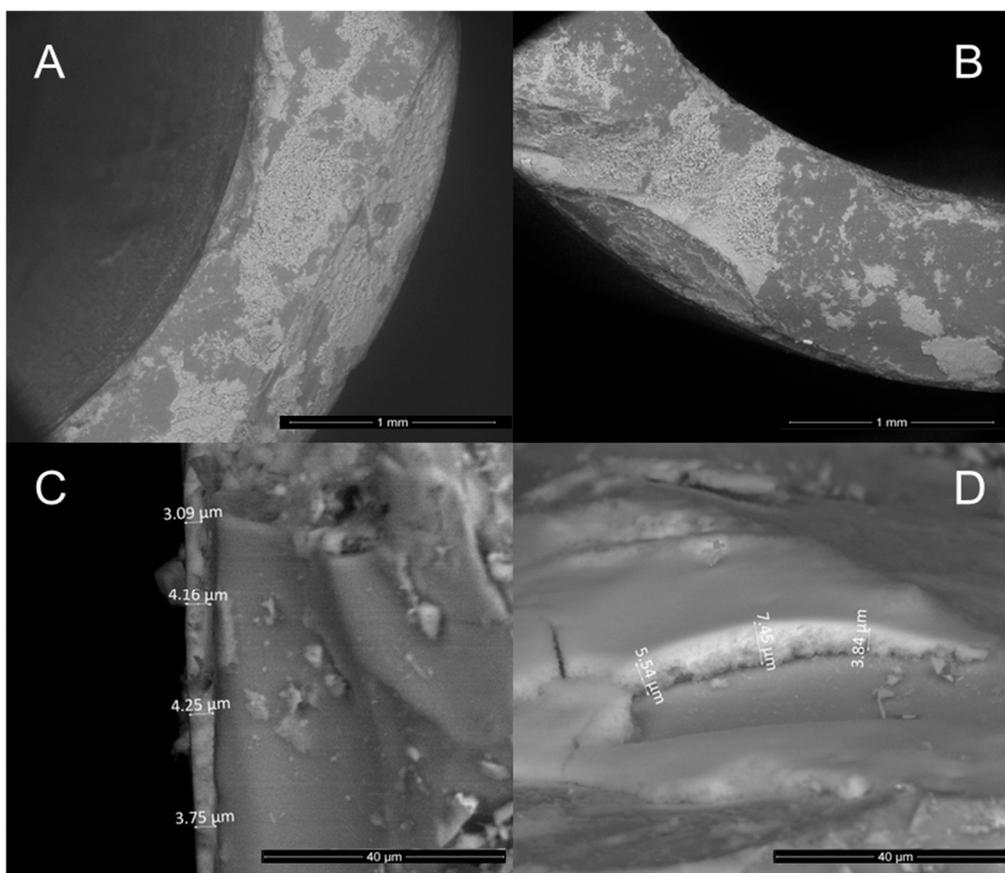


Figure S5. SEM images of fresh coated glass rings surface (A and B). Layer thickness measurements in a polished coated glass ring (C) and in a scratched coated glass ring surface (D).

Table S3. WDXRF results of uncoated glass rings (R), coated glass rings before treatment (P25R) and after photocatalytic oxidation (O₂/LED/P25R) and photocatalytic ozonation (O₃/LED/P25R).

Oxide	Concentration (weight %)			
	R	P25R	O ₂ /LED/P25R	O ₃ /LED/P25R
SiO ₂	79.9	79.8	80.0	79.5
B ₂ O ₃	13.0	13.0	13.0	13.0
Na ₂ O	3.8	3.8	3.7	3.9
Al ₂ O ₃	2.5	2.4	2.4	2.5
K ₂ O	0.65	0.65	0.68	0.69
TiO ₂	0.03	0.16	0.15	0.16
Impurities	0.07	0.14	0.05	0.24

S5. Reference

1. Beltrán, F.J., *Ozone reaction kinetics for water and wastewater systems* Lewis Publishers: Florida, U.S. 2004; pp. 1-358.