#### Supplementary material

# KINETIC MODEL BASIS OF OZONE/LIGHT BASED ADVANCED OXIDATION PROCESSES. A PSEUDOEMPIRICAL APPROACH

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#### Actinometry determination

Actinometry was performed to characterize the power of UVA LEDs of the photoreactor. Due to the  $\lambda_{max}$  (365 nm) and high irradiance of the LEDS employed, typical actinometers such as hydrogen peroxide or ferrioxalate, were not valid. Hydrogen peroxide has a very low molar absorptivity at 365 nm so its conversion during the experiment was negligible. On the other hand, due to the high molar absorptivity and quantum yield of ferrioxalate, together with the high irradiance of the LEDs, the actinometer was totally photoreduced to Fe(II) before leaving the photoreactor.

To solve this situation,  $NO_2^-$  was used as actinometer since It undergoes direct photolysis leading to production of HO· (Jankowski, Kieber, and Mopper 1999):

$$NO_2^- + hv \to NO + O^- \tag{S1}$$

$$O^- + H_2 O \to OH + OH^- \tag{S2}$$

Equation (S3) represents the photolysis rate of the actinometer at a given wavelength as a function of the irradiance per unit volume ( $I_0$ ), quantum yield ( $\Phi$ ), molar absorptivity ( $\epsilon$ ) and light path length (L).

$$-\frac{dC}{dt} = I_o \Phi (1 - e^{-2.303 \, L \,\varepsilon \, C})$$
(S3)

For low optical density, (2.303 L  $\varepsilon$  C < 0.2), equation (S3) can be simplified leading to (S4):

$$-\frac{dC}{dt} = 2.303 I_o \Phi L \varepsilon C$$
(S4)

After integration takes the form:

$$ln\frac{C}{C_0} = -2.303 I_0 \Phi L \varepsilon t$$
(S5)

Being, at 365 nm,  $\Phi_{NO2^-} = 0.02$  mol E<sup>-1</sup> and  $\varepsilon_{NO2^-} = 18.82$  M<sup>-1</sup> cm<sup>-1</sup> (Jankowski, Kieber, and Mopper 1999). For the tubular photoreactor used in this work an effective radiation pathlenght (L) of 3 cm (diameter of the tube) was considered. If the evolution of NO<sub>2</sub><sup>-</sup> concentration with time is known, from the slope of the straight line obtained from the least squares analysis of the straight line resulting from plotting the left side of equation (S5) against reaction time, I<sub>0</sub> can be determined. Fig S1 shows the fitting of two experimental data series (C<sub>0</sub> concentrations 1.56x10<sup>-4</sup> M and 1.23x10<sup>-3</sup> M) to equation (S5), from which I<sub>0</sub> resulted to be 3.92x10<sup>-5</sup> Einstein L<sup>-1</sup> s<sup>-1</sup>.



Figure S1: Determination of  $I_0$  corresponding to the UVA LED tubular photoreactor using nitrite as actinometer.

#### Non ideal flow model study

At the conditions tested (7.7 L h<sup>-1</sup> flow rate) and taking into account the characteristics of the tubular reactor (50 cm length, 3 cm diameter), the flow regime resulted to be laminar with a Reynolds number of 97.3.

Under laminar flow regime, for the experimental system used in this work a perfectly mixed condition cannot be assumed. For this reason, positive step tracer experiments (Fogler 2004) were performed using NaCl as tracer (inlet concentration of 5 g L<sup>-1</sup>). Figure S2(A) and S2(B) depicts the evolution with time of tracer normalized concentration corresponding to one of the experiments and the residence time distribution function, E(t), respectively.

Values of E(t) function leads to a mean residence time of 2.97 min and a dimensionless variance of 0.31. The inverse of this value, 3.23, yields the number (N) of perfectly mixed reactors in series simulating the actual tubular photoreactor. For calculation reasons, this value was incremented to a whole number of 4.



**Figure S2**: A: Evolution of NaCl (tracer) concentration with time in a positive step tracer experiment in the tubular photoreactor. B: Residence time distribution function obtained.

## Kinetic model of the oxidation systems studied.

Mass balance of ozone gas in the tank:

$$\frac{dC_{O_{3g}}}{dt} = \frac{1}{V_{T}(1-\beta)} \left[ Q_{g}C_{O_{3g},\text{intet}} - Q_{g}C_{O_{3g}} - V_{T}k_{1}a \left( C_{O_{3g}}\frac{RT}{He} - C_{O_{3d}} \right) \right]$$
(56)

Mass balance of dissolved ozone in the tank and in any assumed photoreactor. Note that in the photoreactors no ozone is fed and consequently  $k_La = 0$ :

$$\frac{dC_{O_{3d}}}{dt} = Q_{L}C_{O_{3d,inlet}} - Q_{L}C_{O_{3d}} + \frac{k_{1}a}{(1-\beta)} \left(C_{O_{3g}} \frac{RT}{He} - C_{O_{3d}}\right) - V_{F}C_{O_{3d}} \left(\sum_{1}^{4} k_{D_{i}}C_{TOC_{i}} + k_{RO_{3}}C_{OH} + k_{H}C_{H_{2}O_{2}} + k_{ini}C_{OH} + k_{ini2}\right)$$
(57)

Mass balances of different dissolved TOC fractions in the tank and in any assumed photoreactor:

$$\frac{dC_{\text{TOC1}}}{dt} = \frac{1}{V_{\text{F}}} \begin{bmatrix} Q_{\text{L}}C_{\text{TOC1}}^{\text{inlet}} - Q_{\text{L}}C_{\text{TOC1}} + V_{\text{F}}C_{\text{TOC1}} \left(k_{\text{D1}}C_{\text{O}_{\text{J}}\text{d}} + k_{\text{R1}}C_{\text{OH}^{\star}}\right) \\ + V_{\text{F}} \left(k_{\text{eq1}}C_{\text{TOC1}\text{ADS}} - k_{\text{eq}_{\text{I}}\text{I}}C_{\text{TOC1}}C_{\text{TiO}_{2}}\right) \end{bmatrix}$$
(S8)

$$\frac{dC_{TOC2}}{dt} = \frac{1}{V_{F}} \left[ \frac{Q_{L}C_{TOC2}^{inlet} - Q_{L}C_{TOC2} - V_{F}C_{TOC2} \left(k_{D2}C_{O_{3}d} + k_{R2}C_{OH}\right)}{+V_{F} \left(k_{eq2}C_{TOC1ADS} - k_{eq_{2}}C_{TOC2}C_{TIO_{2}}\right) + V_{F}C_{TOC1} \left(k_{D1}C_{O_{3}d} + k_{R1}C_{OH}\right) \times r - V_{F}k_{FTOC2}C_{TOC2}} \right]$$
(S9)

$$\frac{dC_{TOC3}}{dt} = \frac{1}{V_F} \begin{bmatrix} Q_L C_{TOC3}^{inlet} - Q_L C_{TOC3} - V_F C_{TOC3} \left( k_{D3} C_{O_3d} + k_{R3} C_{OH*} \right) \\ + V_F \left( k_{eq3} C_{TOC1ADS} - k_{eq_3} C_{TOC2} C_{TIO_2} \right) + V_F C_{TOC2} \left( k_{D2} C_{O_3d} + k_{R2} C_{OH*} \right) \times r - V_F k_{FTOC3} C_{TOC3} \end{bmatrix}$$
(S10)

$$\frac{dC_{TOC4}}{dt} = \frac{1}{V_{F}} \begin{bmatrix} Q_{L}C_{TOC4}^{inlet} - Q_{L}C_{TOC4} - V_{F}C_{TOC4} \left(k_{D4}C_{O_{3d}} + k_{R4}C_{OH}\right) + V_{F} \left(k_{eq4}C_{TOC1ADS} - k_{eq_{4}}C_{TOC2}C_{TO2}\right) + V_{F}C_{TOC3} \left(k_{D3}C_{O_{3d}} + k_{R3}C_{OH}\right) \\ + V_{F} \left(k_{eq4}C_{TOC1ADS} - k_{eq_{4}}C_{TOC2}C_{TO2}\right) + V_{F}C_{TOC3} \left(k_{D3}C_{O_{3d}} + k_{R3}C_{OH}\right) \\ \end{bmatrix}$$
(S11)

Mass balances of different adsorbed TOC fractions in the tank and in any assumed photoreactor:

$$\frac{\mathrm{dC}_{\mathrm{TOCIADS}}}{\mathrm{dt}} = \frac{1}{\mathrm{V}_{\mathrm{F}}} \begin{bmatrix} \mathrm{Q}_{\mathrm{L}} \mathrm{C}_{\mathrm{TOCIADS}}^{\mathrm{inlet}} - \mathrm{Q}_{\mathrm{L}} \mathrm{C}_{\mathrm{TOCIADS}} - \mathrm{V}_{\mathrm{F}} \mathrm{k}_{\mathrm{R}1} \mathrm{k}_{\mathrm{Hetero}} \mathrm{C}_{\mathrm{TOCIADS}} \\ - \mathrm{V}_{\mathrm{F}} \left( \mathrm{k}_{\mathrm{eq1}} \mathrm{C}_{\mathrm{TOCIADS}} - \mathrm{k}_{\mathrm{eq_{1}}1} \mathrm{C}_{\mathrm{TOC1}} \mathrm{C}_{\mathrm{TiO_{2}}} \right) \end{bmatrix}$$
(S12)

$$\frac{\mathrm{dC}_{\mathrm{TOC2ADS}}}{\mathrm{dt}} = \frac{1}{\mathrm{V}_{\mathrm{F}}} \begin{bmatrix} \mathrm{Q}_{\mathrm{L}} \mathrm{C}_{\mathrm{TOC2ADS}}^{\mathrm{inlet}} - \mathrm{Q}_{\mathrm{L}} \mathrm{C}_{\mathrm{TOC2ADS}} - \mathrm{V}_{\mathrm{F}} \mathrm{k}_{\mathrm{R2}} \mathrm{k}_{\mathrm{Hetero}} \mathrm{C}_{\mathrm{TOC2ADS}} \\ - \mathrm{V}_{\mathrm{F}} \left( \mathrm{k}_{\mathrm{eq2}} \mathrm{C}_{\mathrm{TOC2ADS}} - \mathrm{k}_{\mathrm{eq2}} \mathrm{C}_{\mathrm{TOC2}} \mathrm{C}_{\mathrm{TiO_{2}}} \right) + \mathrm{V}_{\mathrm{F}} \mathrm{k}_{\mathrm{R1}} \mathrm{k}_{\mathrm{Hetero}} \mathrm{C}_{\mathrm{TOC1ADS}} \end{bmatrix}$$
(513)

$$\frac{\mathrm{dC}_{\mathrm{TOC3ADS}}}{\mathrm{dt}} = \frac{1}{\mathrm{V}_{\mathrm{F}}} \begin{bmatrix} \mathrm{Q}_{\mathrm{L}} \mathrm{C}_{\mathrm{TOC3ADS}}^{\mathrm{inlet}} - \mathrm{Q}_{\mathrm{L}} \mathrm{C}_{\mathrm{TOC3ADS}} - \mathrm{V}_{\mathrm{F}} \mathrm{k}_{\mathrm{R3}} \mathrm{k}_{\mathrm{Hetero}} \mathrm{C}_{\mathrm{TOC3ADS}} \\ - \mathrm{V}_{\mathrm{F}} \left( \mathrm{k}_{\mathrm{eq3}} \mathrm{C}_{\mathrm{TOC3ADS}} - \mathrm{k}_{\mathrm{eq.3}} \mathrm{C}_{\mathrm{TOC3}} \mathrm{C}_{\mathrm{TiO_{2}}} \right) + \mathrm{V}_{\mathrm{F}} \mathrm{k}_{\mathrm{R2}} \mathrm{k}_{\mathrm{Hetero}} \mathrm{C}_{\mathrm{TOC2ADS}} \end{bmatrix}$$
(S14)

$$\frac{\mathrm{dC}_{\mathrm{TOC4ADS}}}{\mathrm{dt}} = \frac{1}{V_{\mathrm{F}}} \begin{bmatrix} Q_{\mathrm{L}} C_{\mathrm{TOC4ADS}}^{\mathrm{inlet}} - Q_{\mathrm{L}} C_{\mathrm{TOC4ADS}} - V_{\mathrm{F}} k_{\mathrm{R4}} k_{\mathrm{Hetero}} C_{\mathrm{TOC4ADS}} \\ - V_{\mathrm{F}} \left( k_{\mathrm{eq4}} C_{\mathrm{TOC4ADS}} - k_{\mathrm{eq}} C_{\mathrm{TOC4}} C_{\mathrm{TiO}} \right) + V_{\mathrm{F}} k_{\mathrm{R3}} k_{\mathrm{Hetero}} C_{\mathrm{TOC3ADS}} \end{bmatrix}$$
(S15)

Mass balance of hydroxyl radicals in the tank and in any assumed photoreactor:

$$\frac{dC_{OH}}{dt} = \frac{1}{V_{F}} \left[ Q_{L}C_{OH}^{inlet} - Q_{L}C_{OH} - V_{F}C_{OH} \left( \sum_{1}^{4} k_{R_{i}}C_{TOC_{i}} + k_{RO_{3}}C_{O_{3}d} + k_{HOH}C_{H_{2}O_{2}} \right) + V_{F}C_{O_{3}d} \left( k_{H}C_{H_{2}O_{2}} + k_{ini2} \right) \right]$$
(S16)

Mass balance of hydrogen peroxide in the tank and in any assumed photoreactor

$$\frac{dC_{H_{2}O_{2}}}{dt} = \frac{1}{V_{F}} \begin{bmatrix} Q_{L}C_{H_{2}O_{2}}^{inlet} - Q_{L}C_{H_{2}O_{2}} + V_{F} \left( \sum_{1}^{3} z_{H_{2}O_{2}i}k_{R_{i}}C_{TOC_{i}}C_{OH} + \sum_{1}^{3} z_{H_{2}O_{2}i}k_{D_{i}}C_{TOC_{i}}C_{O_{3}d} \right) \\ -V_{F}C_{H_{2}O_{2}} \left( k_{H}C_{O_{3}d} - k_{HOH}C_{OH} \right) + V_{F}k_{ini}C_{OH} - C_{O_{3}d} + z_{H_{2}O_{2}}^{Photocal}V_{F}k_{R_{1}}k_{Hetero}C_{TOC1ADS} \end{bmatrix}$$
(S17)

### References

Fogler, H Scott. 2004. Elements of Chemical Reaction Engineering. Third edition. New Delhi: Prentice Hall.

Jankowski, Joseph J., David J. Kieber, and Kenneth Mopper. 1999. "Nitrate and Nitrite Ultraviolet Actinometers." *Photochemistry and Photobiology* 70 (3): 319–28. https://doi.org/https://doi.org/10.1111/j.1751-1097.1999.tb08143.x.

# Nomenclature

C <sub>O3d</sub>	Outlet dissolved ozone concentration, mol L <sup>-1</sup>
C <sub>O3d inlet</sub>	Inlet dissolved ozone concentration, mol L <sup>-1</sup>
C <sub>O3g</sub>	Outlet gas ozone concentration, mol L <sup>-1</sup>
C <sub>O3g inlet</sub>	Inlet gas ozone concentration, mol L <sup>-1</sup>
C <sub>i</sub>	Concentration of species i, mol L <sup>-1</sup>
$C_i^{\text{inlet}}$	Inlet concentration of species i, mol L <sup>-1</sup>
Не	Henry constant, atm M <sup>-1</sup>
l <sub>o</sub>	Volumetirc radiation intensity, Einstein s <sup>-1</sup> L <sup>-1</sup>
k <sub>Di</sub>	Direct ozonation rate constant of species i, $M^{\text{-}1}\text{s}^{\text{-}1}$
k <sub>eqi</sub>	Direct adsorption of TOC <sub>i</sub> onto TiO <sub>2</sub> , $M^{-1}$ s <sup>-1</sup>
k <sub>eq_i</sub>	Desorption of $TOC_i$ from $TiO_2$ , s <sup>-1</sup>
k <sub>FTOCi</sub>	Direct photolysis of TOC <sub>i</sub> , s <sup>-1</sup>
k <sub>H</sub>	$HO_2$ radical rate constant of ozone, $M^{\text{-}1}\text{s}^{\text{-}1}$
k <sub>нон</sub>	HO radical rate constant of hydrogen peroxide, $M^{\text{-1}}\text{s}^{\text{-1}}$
k <sub>Hetero</sub>	First order rate constant of adsorbed TOC, s <sup>-1</sup>
k <sub>ini</sub>	$\rm HO^{\text{-}}$ anion rate constant of ozone, $\rm M^{\text{-}1}\rm s^{\text{-}1}$
k <sub>ini2</sub>	First order rate constant of ozone photolysis, s <sup>-1</sup>

k <sub>l</sub> a	Volumetric mass transfer coefficient, s <sup>-1</sup>
k <sub>Ri</sub>	HO radical rate constant of species i, $M^{\text{-}1}\text{s}^{\text{-}1}$
k <sub>RO3</sub>	HO radical rate constant of ozone, $M^{-1} s^{-1}$
L	Radiation path length, cm
Q <sub>L</sub>	Liquid flow rate, L s <sup>-1</sup>
Qg	Gas flow rate, L s <sup>-1</sup>
R	Universal gas constant, atm L mol <sup>-1</sup> K <sup>-1</sup>
r	TOC reduction factor, dimensionless
т	Temperature, K
V <sub>F</sub>	¼ of Volume of photolytic reactor, L
V <sub>T</sub>	Volume of tank reactor, L
Z <sub>H2O2</sub>	stoichiometric factor of $\mathrm{H}_{2}\mathrm{O}_{2}$ generation, dimensionless

# Greek letters

α	Parameter in equation 24, g $L^{-1}$ s <sup>-1</sup>
β	Gas hold up, dimensionless
γ	Parameter in equation 24, g L <sup>-1</sup>
ε <sub>i</sub>	Molar extinction coefficient of species i, M cm <sup>-1</sup>
φ <sub>i</sub>	Quantum yield of species I, mol Einstein <sup>-1</sup>