

Six Flux Model for the central lamp reactor applied to an external four-lamp reactor

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1. The function of albedo and optical density of the catalyst, $f(\omega, \tau)$ and other parameters of the SFM [1] (reference [19] in main text)

$$f(\omega, \tau) = \left(1 + \frac{1}{\omega_{cor}} \left(1 - \frac{1+\gamma}{1-\gamma} \sqrt{1-\omega_{cor}^2} \right) \right) \left(1 + \frac{4\omega p_s}{1-\omega p_f - \omega p_b - 2\omega p_s} \right) \quad (S1)$$

with

$$\gamma = \frac{1 - \sqrt{1-\omega_{cor}^2}}{1 + \sqrt{1-\omega_{cor}^2}} \exp(-2\tau_{ap}) \quad (S2)$$

$$\tau_{ap} = a\tau \sqrt{1-\omega_{cor}^2} \quad (S3)$$

$$\omega_{cor} = \frac{b}{a} \quad (S4)$$

$$a = 1 - \omega p_f \frac{(2\omega p_s)^2}{1 - \omega p_f - \omega p_b - 2\omega p_s} \quad (S5)$$

$$b = \omega p_b \frac{(2\omega p_s)^2}{1 - \omega p_f - \omega p_b - 2\omega p_s} \quad (S6)$$

$$\tau = (\kappa + \sigma) \delta C_{Cat} \quad (S5)$$

$$\omega = \frac{\sigma}{\sigma + \kappa} \quad (S6)$$

and p_f , p_b , and p_s the probabilities for the photon to follow forward, backward and side directions after colliding with a catalyst particle, respectively, σ and κ are the specific mass dispersion or scattering and absorption coefficients of the catalyst, respectively, and C_{Cat} the concentration of the catalyst. Given the polichromatic radiation of the lamps, scattering and absorption coefficients were calculated as a function of radiation intensity at wavelengths between 350 and 410 nm as follows:

$$\sigma = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} \sigma_{\lambda} I_{\lambda} d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} I_{\lambda} d\lambda} \quad (\text{S7})$$

$$\kappa = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} \kappa_{\lambda} I_{\lambda} d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} I_{\lambda} d\lambda} \quad (\text{S8})$$

Table S1. Values of parameters applied for SFM and dimensions of external lamp photoreactor

Parameter or photoreactor dimension	
R ₁ , distance from one lamp to reactor wall	8 cm
R ₂ = R ₁ plus diameter of reactor	18 cm
δ, radial distance of reaction space: R ₂ -R ₁	10 cm
H, Reactor height	14 cm
L, lamp length	43.5 cm
d _L , lamp diameter	2.5 cm
Useful emission wavelength	350-410 nm
I _w , the incident radiation at r=R ₁	100,77 Wm ⁻²
Specific absorption coefficient, κ	3630 cm ² g ⁻¹
Specific scattering coefficient, σ	56080 cm ² g ⁻¹
TiO ₂ catalyst loading, C _{cat}	Between 0,001 and 1,5 gL ⁻¹
Photon scattering probabilities	p _r =0.11 p _b =0.71 p _s =0.045

Table S2. OVRPA SFM calculated values at different catalyst concentration

C _{cat} , gL ⁻¹	OVRPA, W
0,001	0,300
0,005	0,827
0.01	1,023
0.05	1,096
0,10	1,096
0.15	1,096
0,5	1,096
1,0	1.372
1,5	1.372

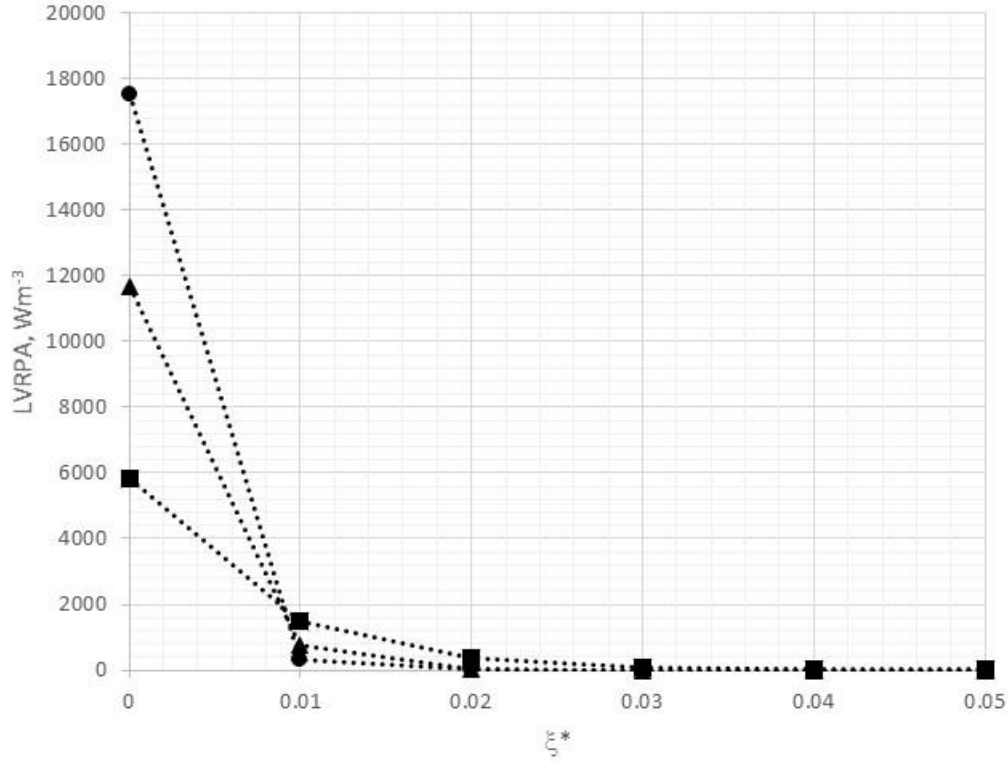


Figure S1 LVRPA vs ξ^* from SFM adapted to the external four lamp photoreactor. Variation with dimensional radial position within the reaction space and catalyst concentration. Catalyst concentration, gL⁻¹: ■ 0.5, ▲ 1, ● 1.5

2. Determination of the adsorption equilibrium constant of MCPA on TiO₂ P25

Given the fact that MCPA, although in small quantity (less than 20% [2], reference [34] of main text) adsorbs on TiO₂, the equilibrium constant, K_M , is needed to check whether or not MCPA photocatalytic oxidation follows Langmuir or pseudo first order kinetics. Equilibrium of MCPA is described by reaction (S9):



where MCPA and MCPA-S represents MCPA in water and adsorbed on TiO₂, respectively, and S is the free active site on the catalyst surface. From (S9) the adsorption equilibrium constant is:

$$K_M = \frac{C_{MCPA-S}}{C_{MCPA} C_S} \quad (S10)$$

where C means concentration and the subindex represents the corresponding species, MCPA, MCPA-S and S. From the work of Zertal et al [2] (reference [34] of main text) it can be deduced that in the presence of 1 gL⁻¹ of TiO₂, at equilibrium, C_{MCPA} and C_{MCPA-S} are 4.4x10⁻⁴ M and 1.2x10⁻⁴ mol.gcat⁻¹, respectively. On the other hand, Rodriguez et al., [3] (reference [35] of main text) have reported a total of 1.79 active sites per nm² for TiO₂ P25 which is equivalent to 1.63x10⁻⁴ mol.gcat⁻¹ once Avogadro's number and the specific surface of TiO₂ (55 m²gcat⁻¹) were taking into account. Now, the number of free active sites

can be calculated from the difference between total sites and MCPA occupied sites: $1.63 \times 10^{-4} - 1.2 \times 10^{-4} = 4.33 \times 10^{-5} \text{ mol.gcat}^{-1}$ which is C_s . Substitution of these concentrations in equation (S10) yields an estimation for the MCPA-TiO₂ adsorption equilibrium constant of 6303.3 M^{-1} . With this value the product $K_M C_{\text{MCPA}}$ is 1.57 which cannot be neglected against 1 in the denominator of the Langmuir kinetic equation. Then, MCPA photocatalytic oxidation does not follow first order kinetics.

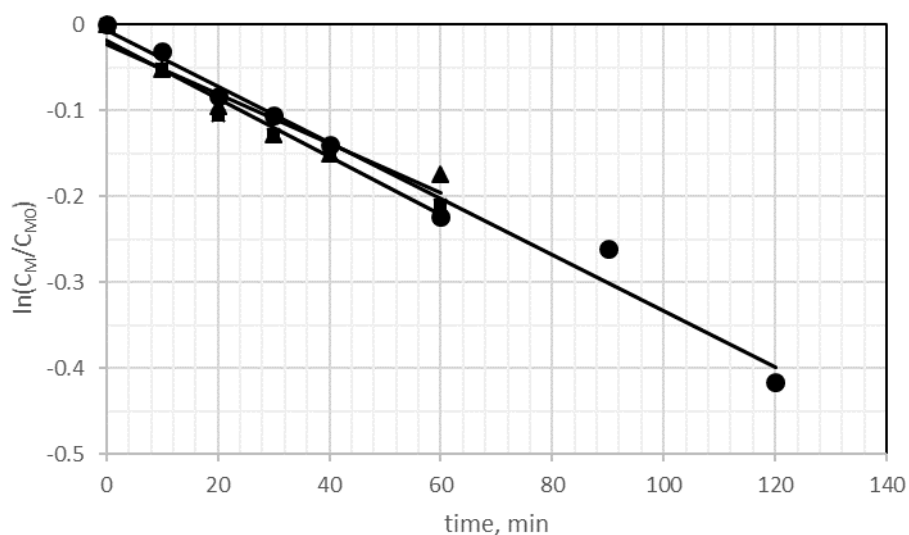


Figure S2. Confirmation of first order kinetics for KTR, DCF and MTP photocatalytic oxidation. Initial concentration of compounds: 20 mgL^{-1} . Symbols: ■ DCF, ▲ MTP, ● KTR. Experimental results deduced from [4] (reference [22] of main text)

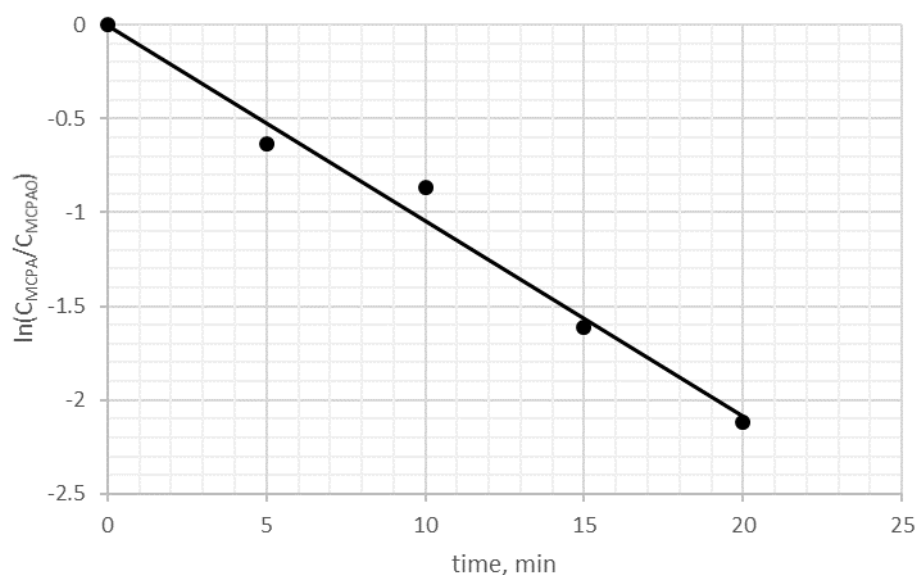


Figure S3. Assumed first order kinetics for photocatalytic oxidation of MCPA (experimental results deduced from [5], (reference [20] of main text)).

References [1] to [5] below are references [19], [34], [35], [22] and [20] of main manuscript, respectively

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