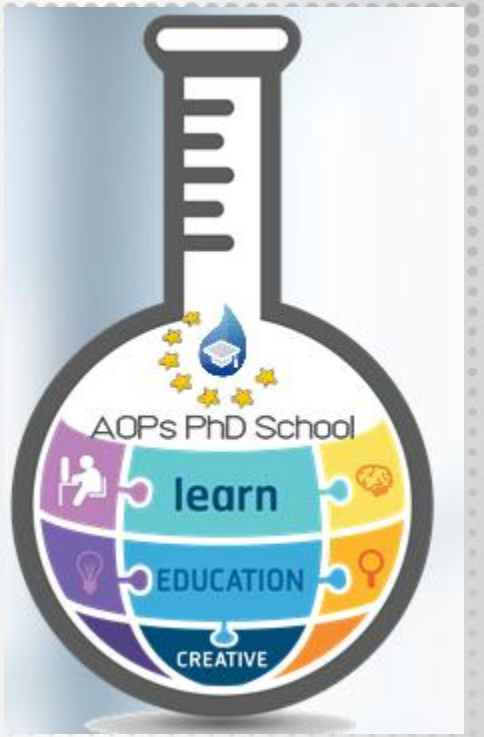
AOPs PhD School

University of Salerno

Fisciano, 15 June 2015



Western

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Modelling AOPs using Computational Fluid Dynamics: Coupling Optics, Hydraulics and Photochemistry

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Outline

- Introduction
- Part I: Mathematical Framework
- Part II: Disinfection Applications
- Part III: AOP Applications
- Conclusions
- Acknowledgements

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Introduction

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Background

- Historically, Analytical Fluid Dynamics (AFD) and EFD (Experimental Fluid Dynamics) were used.
- Computational Fluid Dynamics (CFD) has become feasible due to the advent of high speed digital computers.
- Computer simulation for prediction of fluid-flow phenomena and complex reactor behaviours.
- The objective of CFD is to model the continuous fluids (with or without sink terms) with discretized PDEs.
- Then, turn PDEs into an algebraic problem, solve it and verify it. Finally, validate it and achieve simulation based design
- Growing number of applications, including: Aerospace, Automotive, Biomedical, Chemical, Environmental, Hydraulics, Oil & Gas, Power Generation, etc.

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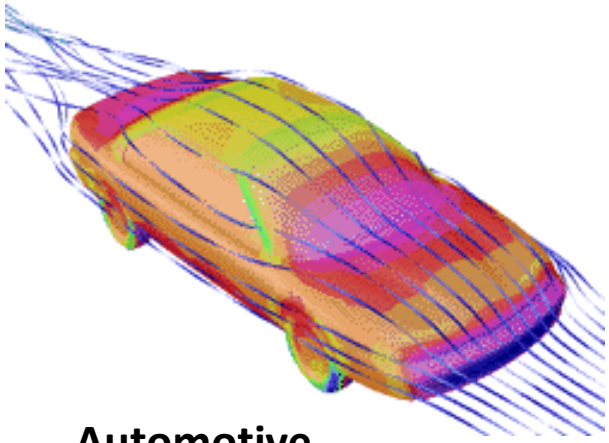
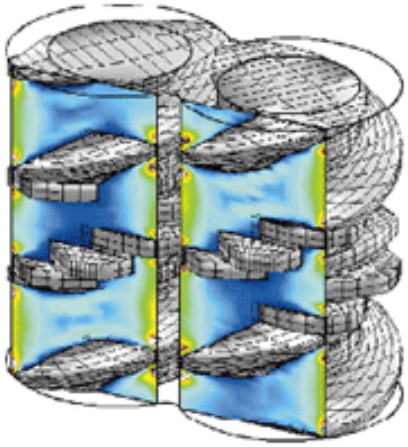
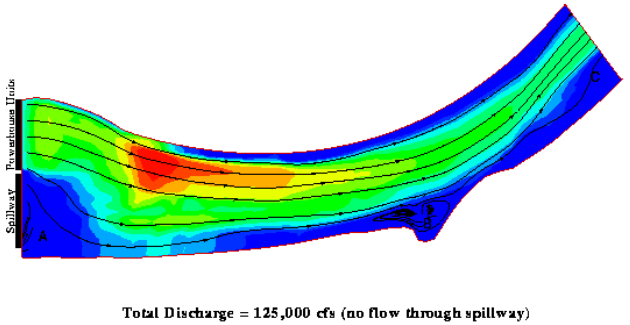
CFD = ***Colorful*** Fluid Dynamics?



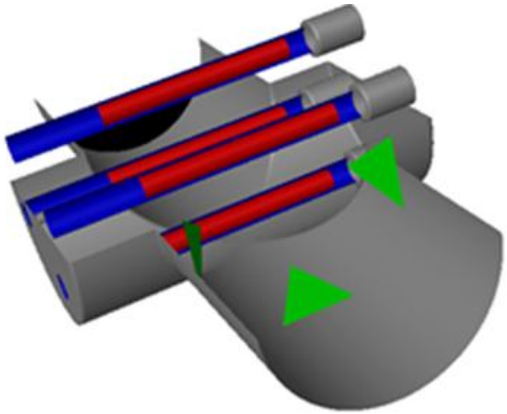
Automotive



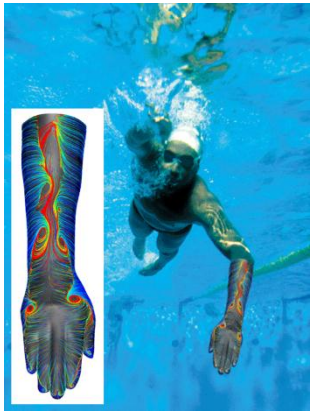
Chemical Processes



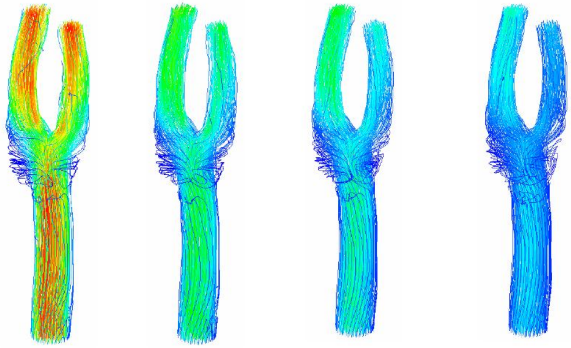
Environmental Hydraulics



Photoreactors



Sports



Biomedical

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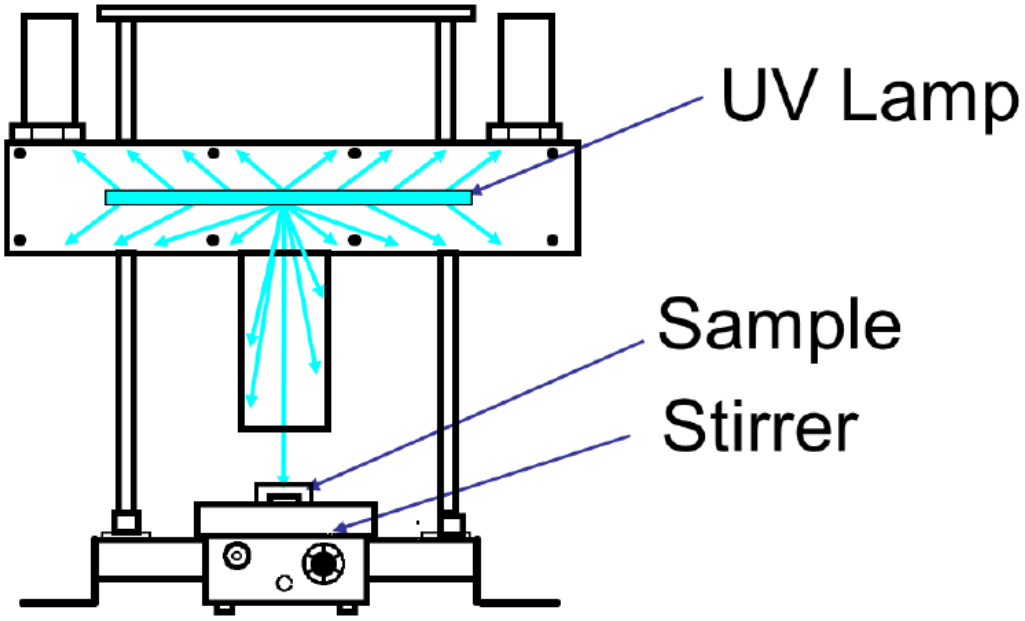
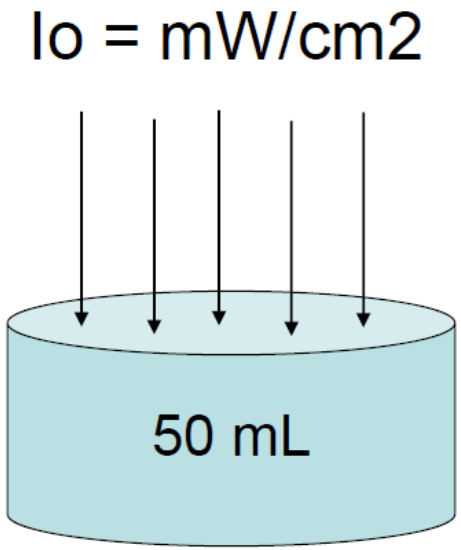
Standard Industrial Apparatus





Dose UV = Io x WF x DF x PF x RF

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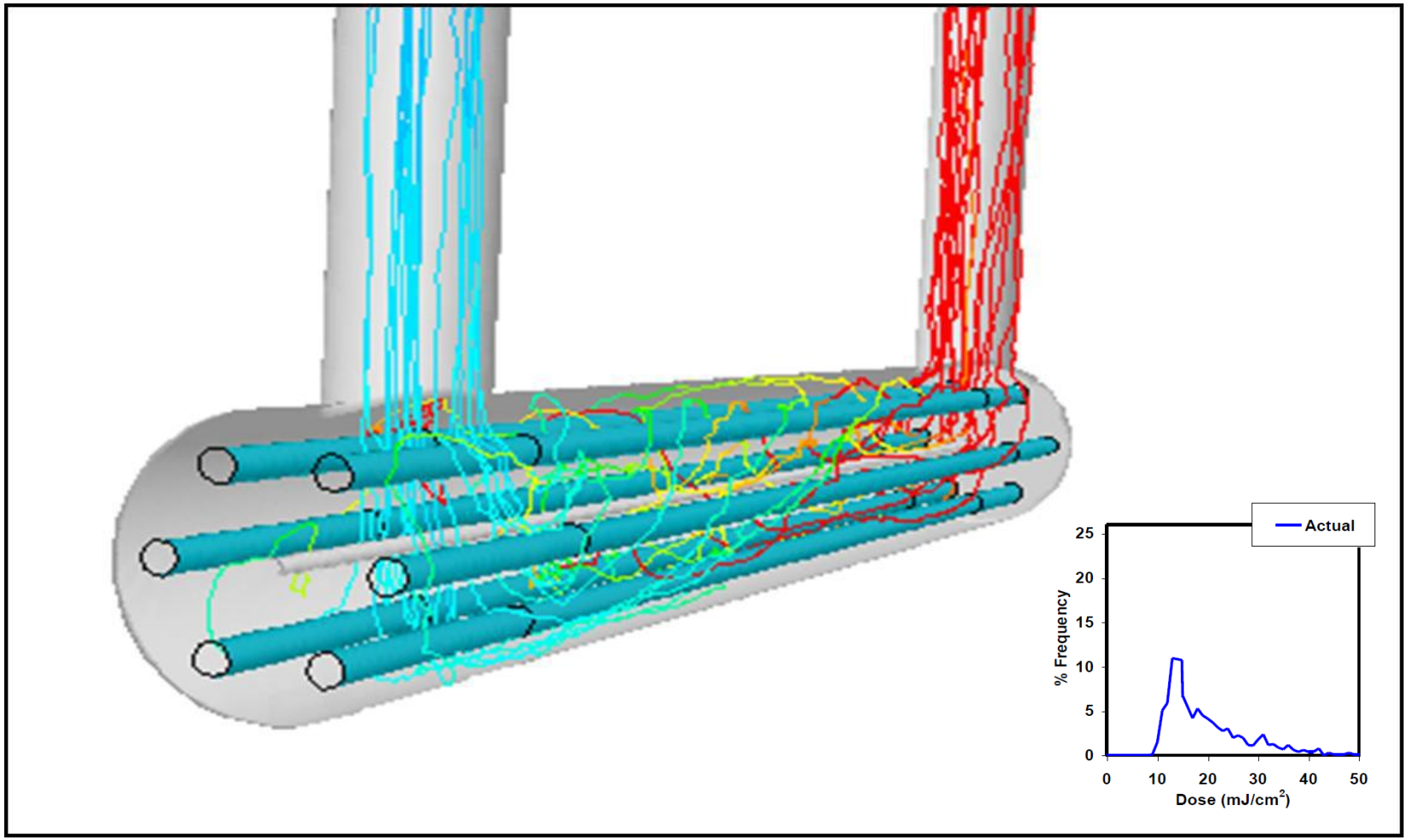
Dose Distribution Concept



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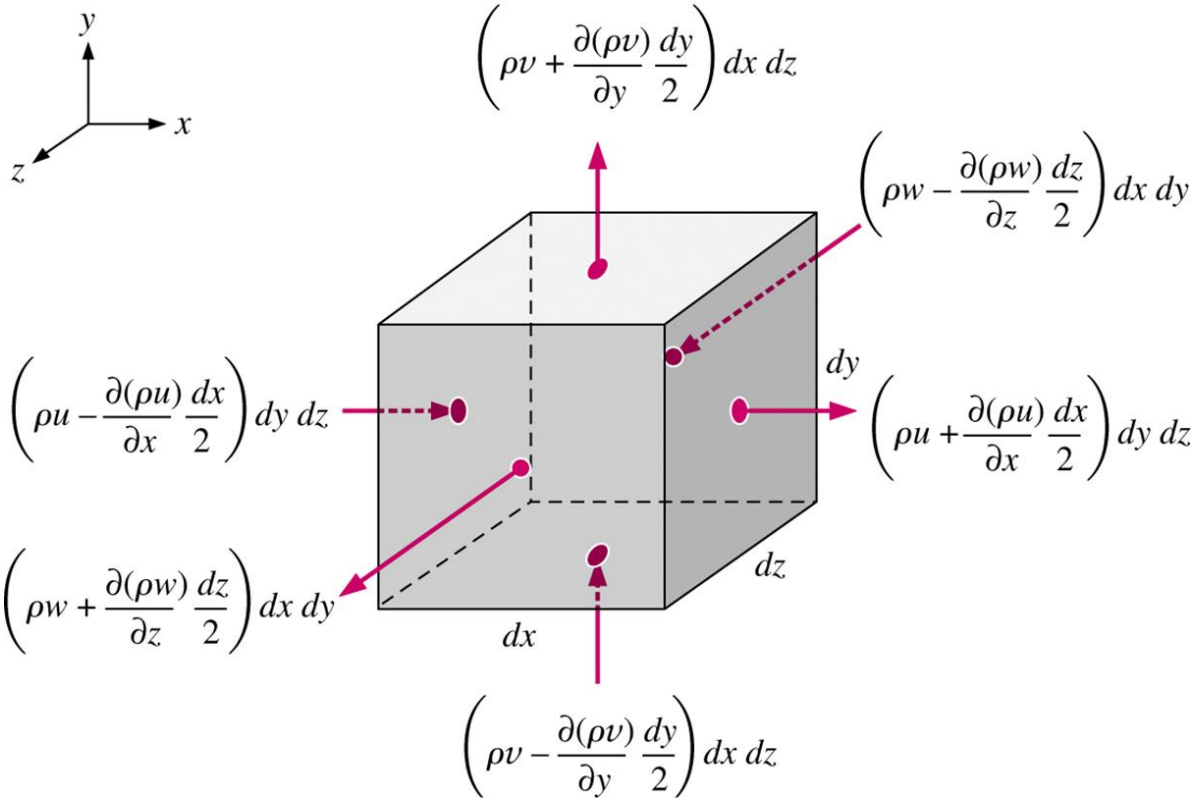
Part I: Mathematical Framework

Mathematical Framework (1)

- Control Volume (Cartesian Coordinates)



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Mathematical Framework (2)

- Vectorial form

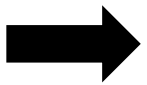
$$\frac{\partial \rho}{\partial t} + \nabla \cdot \left(\rho \vec{V}\right) = 0$$

- Steady state

$$\vec{\nabla} \cdot \left(\rho \vec{V}\right) = 0$$

- Alternative form

$$\frac{1}{\rho}\frac{D\rho}{Dt} + \nabla \cdot \vec{V} = 0$$



$$\vec{\nabla} \cdot \vec{V} = 0$$

- Incompressible fluids

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Mathematical Framework (3)

- Conservation of Momentum (Newton's 2nd law)

$$\sum \vec{F} = \underbrace{\int_{CV} \rho g \, \mathrm{d}\mathcal{V}}_{\text{Body Force}} + \underbrace{\int_{CS} \sigma_{ij} \cdot \vec{n} \, \mathrm{d}A}_{\text{Surface Force}}$$

- Cauchy's Equation

$$\frac{\partial}{\partial t}\left(\rho \vec{V}\right) + \nabla \cdot \left(\rho \vec{V} \vec{V}\right) = \rho \vec{g} + \nabla \cdot \sigma_{ij}$$

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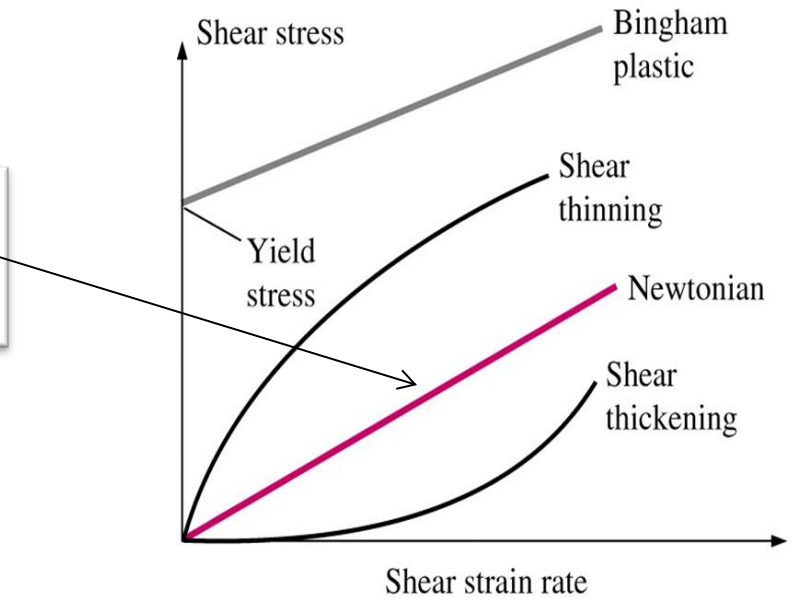
Mathematical Framework (4)

- Relating Shear-Stress to Strain-Rate
- Newtonian Closure

$$\tau_{ij} = 2\mu\epsilon_{ij}$$



- Navier-Stokes!

$$\rho\frac{D\vec{V}}{Dt} = -\nabla p + \rho\vec{g} + \mu\nabla^2\vec{V}$$

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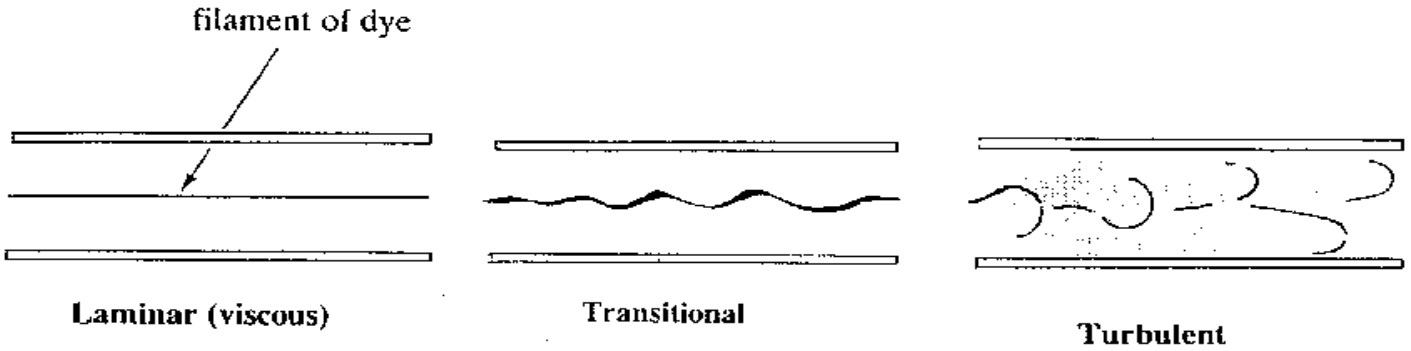
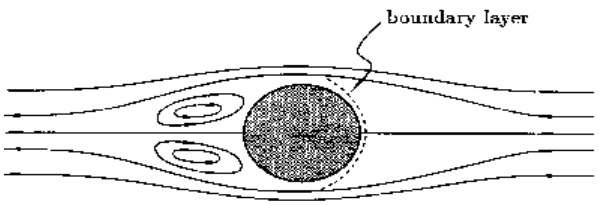
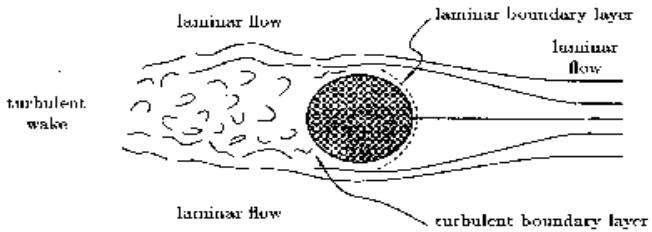
Mathematical Framework (5)

- Turbulence Models
  - It's a model within the model
  - It's a computational procedure to close the system of mean flow equations
  - How turbulence affected the mean flow?







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Mathematical Framework (6)

- State-of-the-art Turbulence Models
  - Zero equation model: mixing length model
  - One equation model: Spalart-Almaras
  - Two equation models: k-eps, k-omega model
  - Seven equation model: Reynolds stress model
  - Large Eddy Simulation (LES) model
- Boussinesq Approximation (1877)
  - Reynolds stresses could be linked to the mean rate of deformation

$$\tau_{ij} = -\rho\overline{u_i' u_j'} = \mu_t\left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i}\right)$$

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Mathematical Framework (7)

- K parameter

$$\frac{\partial(\rho k)}{\partial t} + div(\rho k \mathbf{U}) = div\left[\frac{\mu_t}{\sigma_k} grad\ k\right] + 2\mu_t E_{ij}.E_{ij} - \rho\varepsilon$$

Rate of increase | Convective transport | Diffusive transport | Rate of production | Rate of destruction

- Epsilon parameter

$$\frac{\partial(\rho\varepsilon)}{\partial t} + div(\rho\varepsilon \mathbf{U}) = div\left[\frac{\mu_t}{\sigma_\varepsilon} grad\ \varepsilon\right] + C_{1\varepsilon}\frac{\varepsilon}{k}2\mu_t E_{ij}.E_{ij} - C_{2\varepsilon}\rho\frac{\varepsilon^2}{k}$$

Rate of increase | Convective transport | Diffusive transport | Rate of production | Rate of destruction

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Mathematical Framework (8)

- Generalized Scalar Transport Equations

$$\frac{\partial u\phi}{\partial x}+\frac{\partial v\phi}{\partial y}+\frac{\partial w\phi}{\partial z}=\frac{\partial}{\partial x}\left[\Gamma_\phi\frac{\partial\phi}{\partial x}\right]+\frac{\partial}{\partial y}\left[\Gamma_\phi\frac{\partial\phi}{\partial y}\right]+\frac{\partial}{\partial z}\left[\Gamma_\phi\frac{\partial\phi}{\partial z}\right]+S_\phi$$

Table 1
Values of Φ, Γ_Φ and S_Φ for the convection and diffusion equation in Cartesian coordinate system.

#	Equation	Φ	Γ_Φ	S_Φ
a	Continuity	1	0	0
b	Momentum in x direction	u	$\nu+\nu_t$	$-\frac{1}{\rho}\frac{\partial(p+2k/3)}{\partial x}$
c	Momentum in y direction	v	$\nu+\nu_t$	$-\frac{1}{\rho}\frac{\partial(p+2k/3)}{\partial y}$
d	Momentum in z direction	w	$\nu+\nu_t$	$-\frac{1}{\rho}\frac{\partial(p+2k/3)}{\partial z}$
e	Turbulent kinetic energy	k	$\nu+\frac{\nu_t}{\sigma_k}$	$P_k-\varepsilon$
f	Dissipation rate	ε	$\nu+\frac{\nu_t}{\sigma_\varepsilon}$	$C_{\varepsilon1}\frac{\varepsilon}{k}P_k-C_{\varepsilon2}\frac{\varepsilon^2}{k}$
g	Scalar (microbial inactivation)	N	$\frac{\nu_t}{Sc_t}$	$-kIN$
h	Scalar (UV dose)	D	0	$+I$

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Crapulli et al., (2010): "Modeling virus transport and inactivation in a fluoropolymer tube UV photoreactor using Computational Fluid Dynamics", *Chemical Engineering Journal,* 161 (2010) pp. 9–18

Mathematical Framework (9)

- Radiative Transport Equation (RTE)
  - It is solved for a discrete number of angles
  - Optical properties of the fluid must be known
  - Light source emission characteristics must be known
  - Light behavior at the interface must be understood
  - Fluence rate (not irradiance) is the key variable

$$\frac{\partial I_{si}}{\partial x_i} + \underbrace{(a+\sigma_s)I(r,s)}_{\text{absorption}} = \cancel{\underbrace{an^2\frac{\sigma T^4}{\pi}}_{\text{emission}}} + \underbrace{\frac{\sigma_s}{4\pi}\int_0^{4\pi} I(r,s')\Phi(s\cdot s')d\Omega'}_{\text{scattering}}$$

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Part II: Disinfection Applications

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Monochromatic Disinfection: Teflon UV Photoreactors (1)

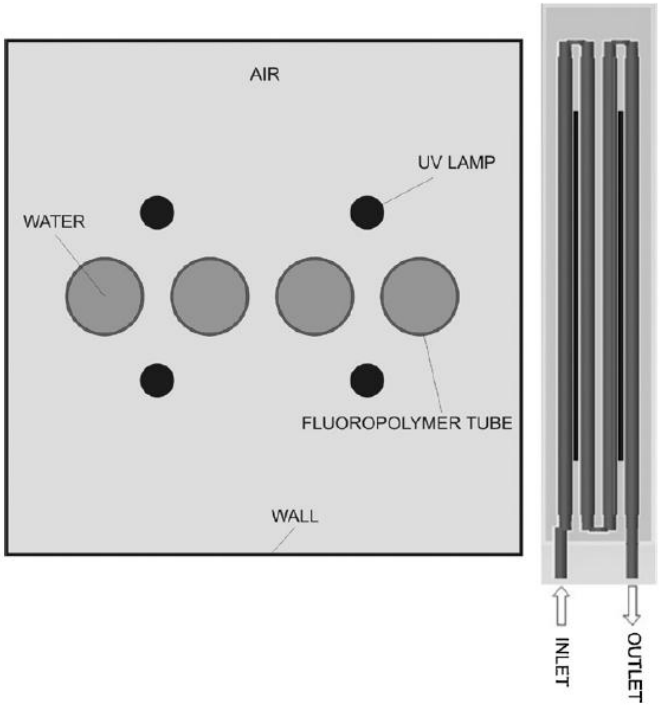

Fig. 1. Horizontal and vertical cross-sections of the fluoropolymer tube UV photoreactor.

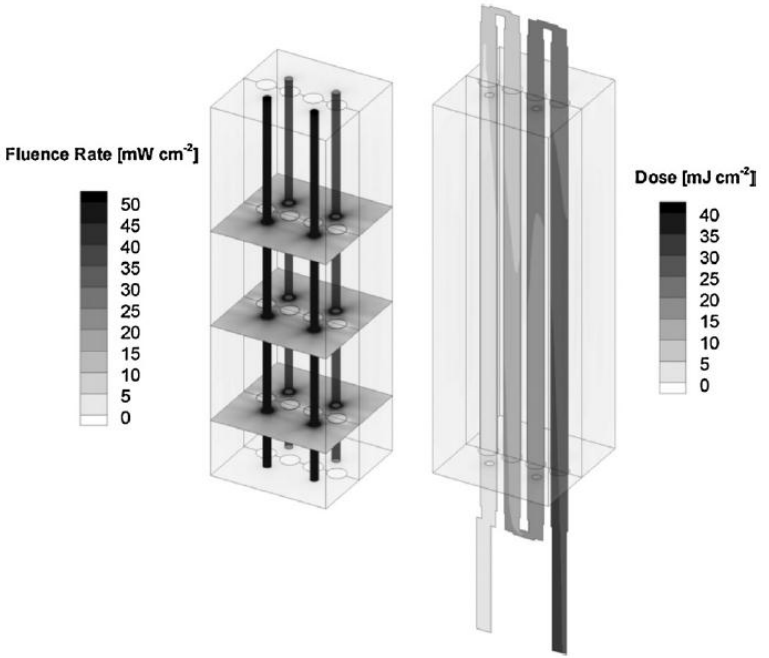

Fig. 10. Fluence rate (right) and cumulated UV dose (left) in the fluoropolymer UV photoreactor (flowrate = 1.26 l s^{-1}, UVT_{254} = 67.9% cm^{-1}).

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Monochromatic Disinfection: Teflon UV Photoreactors (2)

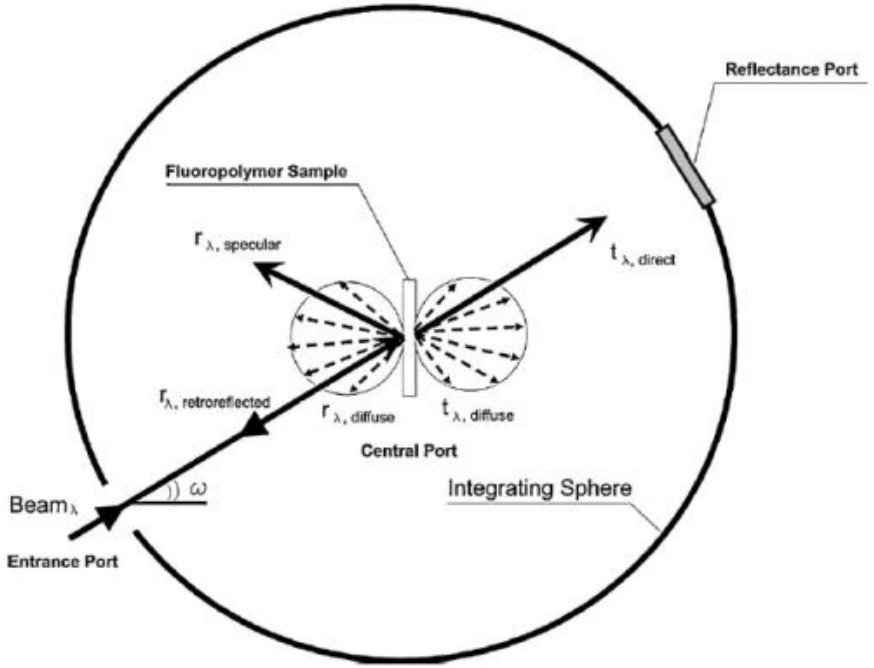

Fig. 2. Relevant light components in an integrating sphere apparatus.

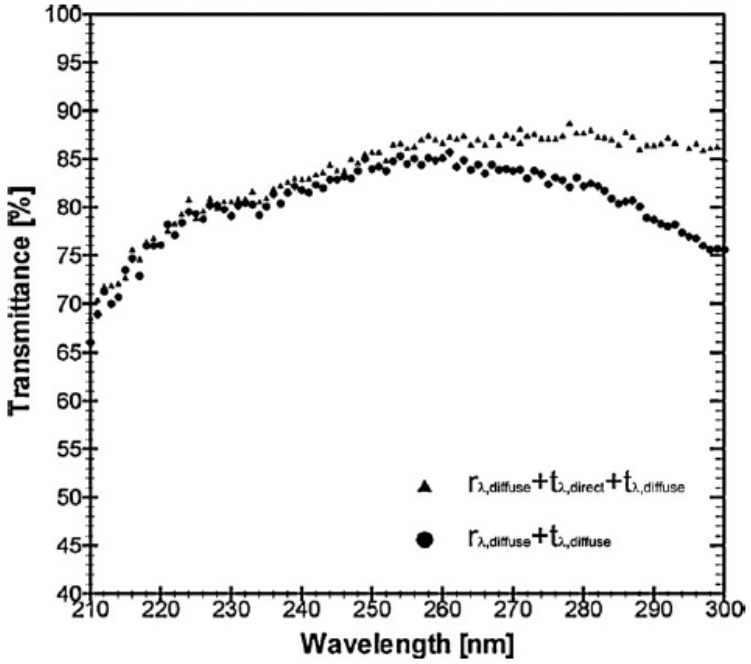

Fig. 4. Transmittance spectra of the fluoropolymer tube (1.2 mm thick sample).

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Monochromatic Disinfection: Teflon UV Photoreactors (3)

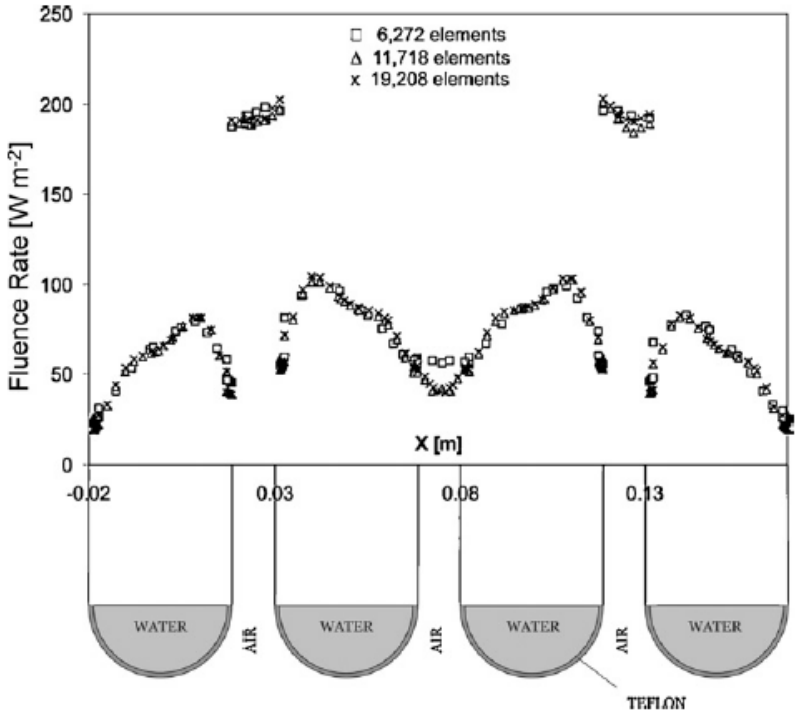

Fig. 5. Fluence rate profiles for three different computational grids.

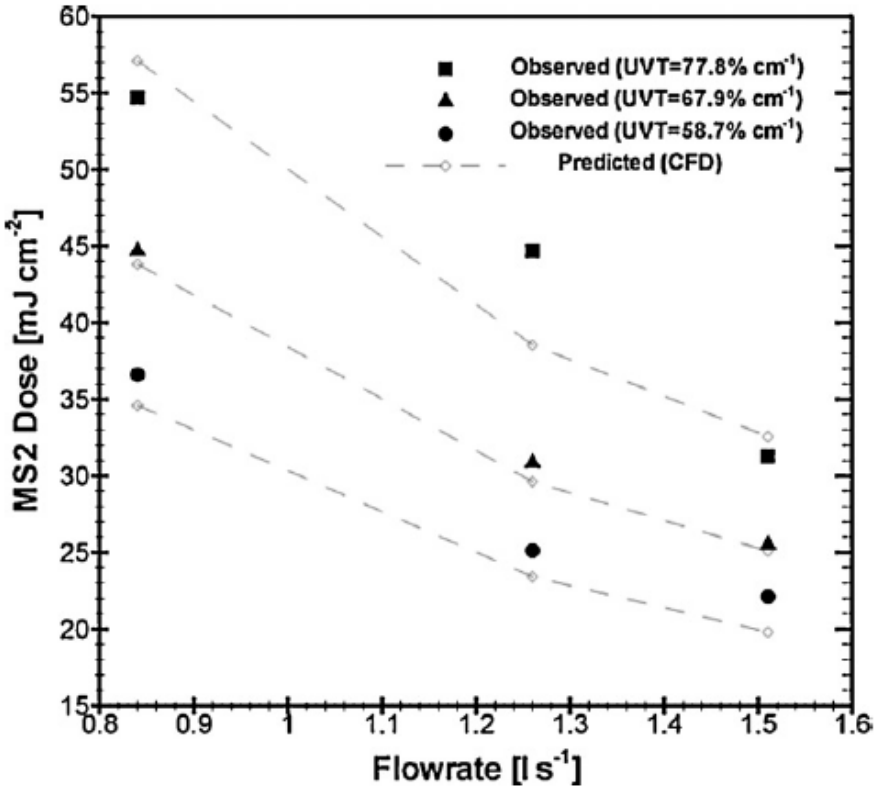

Fig. 7. Comparison between observed and predicted MS2-RED.

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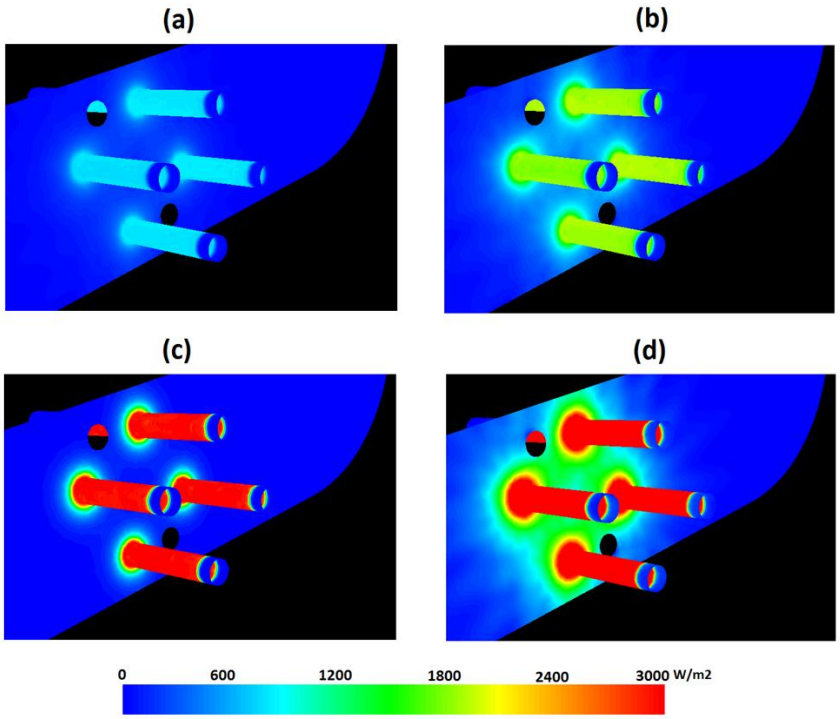
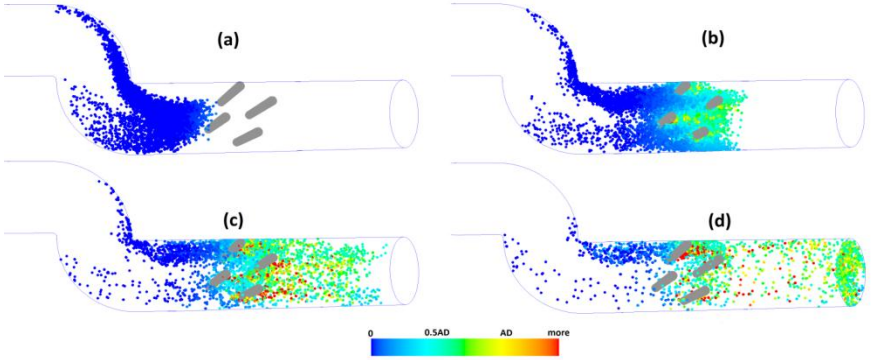
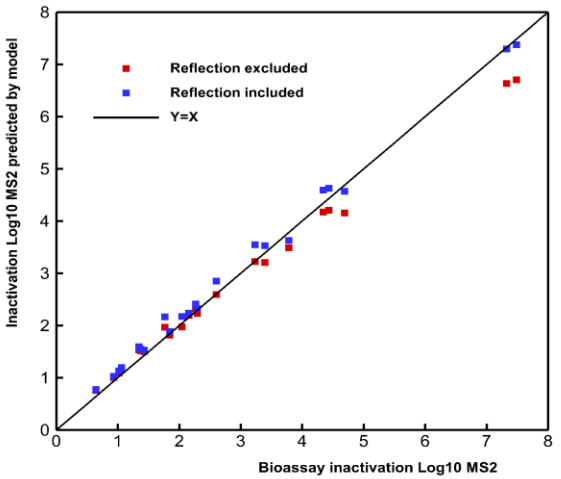
Polychromatic Disinfection: Quartz UV Photoreactors

$$D_{eff}(i) = \sum_{\lambda=200}^{300} \sum_{t=0}^{T} I_{\lambda}(x, y, z) \times \Delta t \times \varepsilon_{\lambda}$$







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Unpublished to date

Part III:
AOP Applications

UV/H2O2 AOP Photoreactors (1)

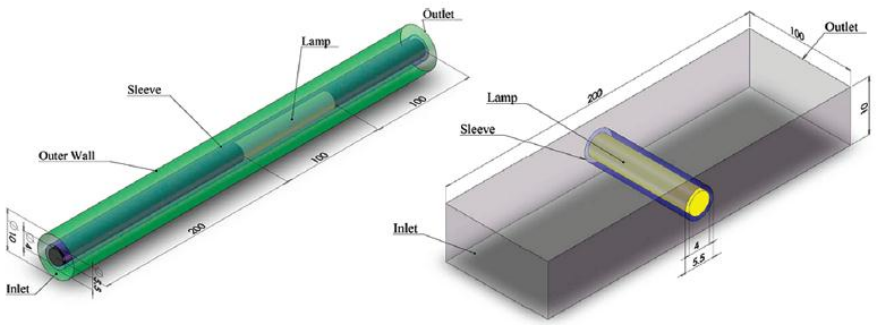


FIGURE 1. Schematic representation of the annular UV (left) and cross-flow (right) photoreactors (dimensions are given in centimeters).

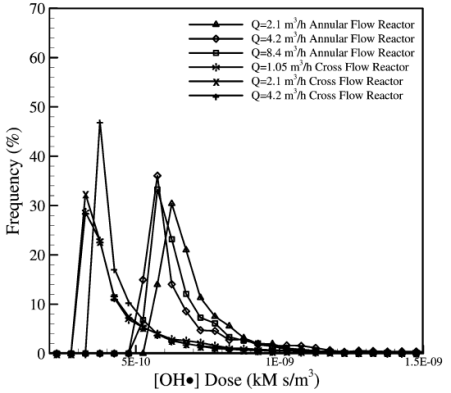


FIGURE 9. [OH•] dose distribution for annular and cross-flow photoreactors.

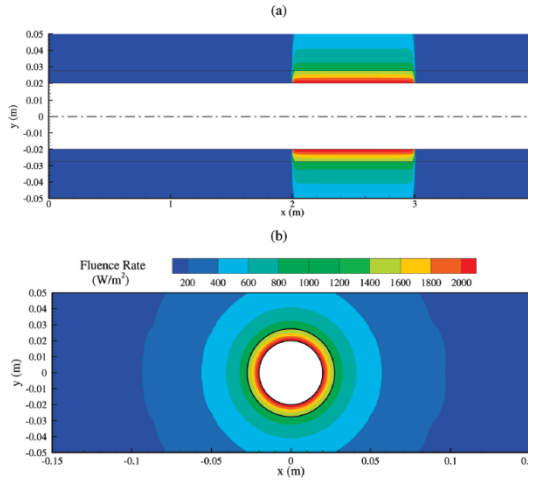


FIGURE 4. Fluence rate contours for a) annular UV reactor and b) cross-flow UV reactor.

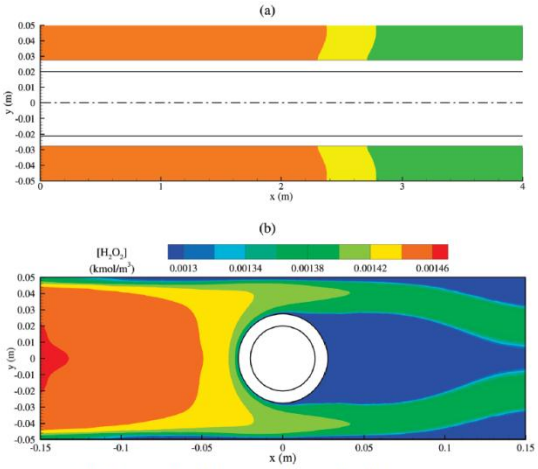
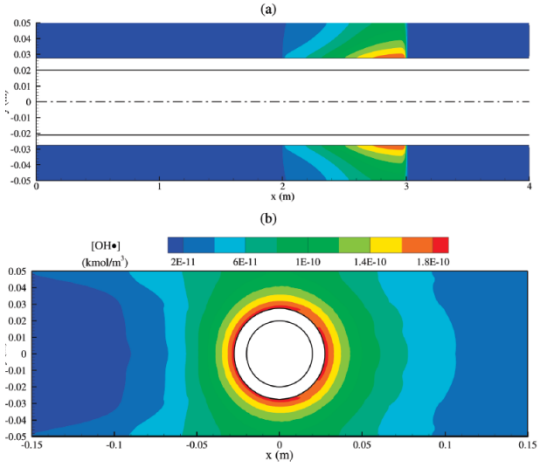


FIGURE 6. Molar concentration of H_2O_2 for a) annular UV reactor and b) cross-flow UV reactor.



centration of [OH•] through the (a) annular and (b) cross-flow reactors.

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Santoro et al., (2010): "Modeling hydroxyl radical distribution and trialkyl phosphates oxidation in UV− H2O2 photoreactors using computational fluid dynamics", *Environmental science & technology 44 (16),* pp. 6233-6241

UV/H2O2 AOP Photoreactors (2)

TABLE 1. Kinetic Model of UV–H_2O_2 Advanced Oxidation of Phosphate Esters (16)

no.	reactions	rate constants, $M^{-1} s^{-1}$	reference
1	$H_2O_2/HO_2^- + h\upsilon \rightarrow 2OH\bullet$	$r^{local}_{UV,H_2O_2} = -2.303\phi_{H_2O_2} I_{r,H_2O_2}[H_2O_2] + \varepsilon_{HO_2^-}[HO_2^-])$	Baxendale and Wilson (17)
2	$H_2O_2 + OH\bullet \rightarrow H_2O + HO_2\bullet$	$k_2 = 2.7 \times 10^7$	Buxton et al. (18)
3	$OH\bullet + HO_2^- \rightarrow HO_2\bullet + OH^-$	$k_3 = 7.5 \times 10^9$	Christensen et al. (19)
4	$H_2O_2 + HO_2\bullet \rightarrow OH\bullet + H_2O + O_2$	$k_4 = 3$	Koppenol et al. (20)
5	$H_2O_2 + O_2^-\bullet \rightarrow OH\bullet + O_2 + OH^-$	$k_5 = 0.13$	Weinstein and Bielski (21)
6	$OH\bullet + CO_3^{2-} \rightarrow CO_3\bullet + OH^-$	$k_6 = 3.9 \times 10^8$	Buxton et al. (18)
7	$OH\bullet + HCO_3^- \rightarrow CO_3\bullet + H_2O$	$k_7 = 8.5 \times 10^6$	Buxton et al. (18)
8	$H_2O_2 + CO_3\bullet \rightarrow HCO_3^- + HO_2\bullet$	$k_8 = 4.3 \times 10^5$	Draganic et al. (22)
9	$HO_2^- + CO_3\bullet \rightarrow CO_3^{2-} + HO_2\bullet$	$k_9 = 3.0 \times 10^7$	Draganic et al. (22)
10	$OH\bullet + OH\bullet \rightarrow H_2O_2$	$k_{10} = 5.5 \times 10^9$	Buxton et al. (18)
11	$OH\bullet + HO_2\bullet \rightarrow H_2O + O_2$	$k_{11} = 6.6 \times 10^9$	Sehested et al. (23)
12	$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$	$k_{12} = 8.3 \times 10^5$	Bielski et al. (24)
13	$HO_2\bullet + O_2^-\bullet \rightarrow HO_2^- + O_2$	$k_{13} = 9.7 \times 10^7$	Bielski et al. (24)
14	$OH\bullet + O_2^-\bullet \rightarrow O_2 + OH^-$	$k_{14} = 7.0 \times 10^9$	Beck (25)
15	$OH\bullet + CO_3\bullet \rightarrow ?$	$k_{15} = 3.0 \times 10^9$	Holeman et al. (26)
16	$CO_3\bullet + O_2^-\bullet \rightarrow CO_3^{2-} + O_2$	$k_{16} = 6.0 \times 10^8$	Eriksen et al. (27)
17	$CO_3\bullet + CO_3\bullet \rightarrow ?$	$k_{17} = 3.0 \times 10^7$	Huie and Clifton (28)
18	$OH\bullet + TCEP \rightarrow TCEP_{products}$	$k_{18} = k_{TCEP} = 5.6 \times 10^8$	Watts and Linden (29)
19	$OH\bullet + TBP \rightarrow TBP_{products}$	$k_{19} = k_{TBP} = 6.4 \times 10^9$	Watts and Linden (29)
20	$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	$pK_{a1} = 6.3$	Stumm and Morgan (30)
21	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$pK_{a2} = 10.3$	Stumm and Morgan (30)
22	$H_2O_2 \leftrightarrow H^+ + HO_2^-$	$pK_{a3} = 11.6$	Perry et al. (31)
23	$HO_2\bullet \leftrightarrow H^+ + O_2^-\bullet$	$pK_{a4} = 4.8$	Perry et al. (31)

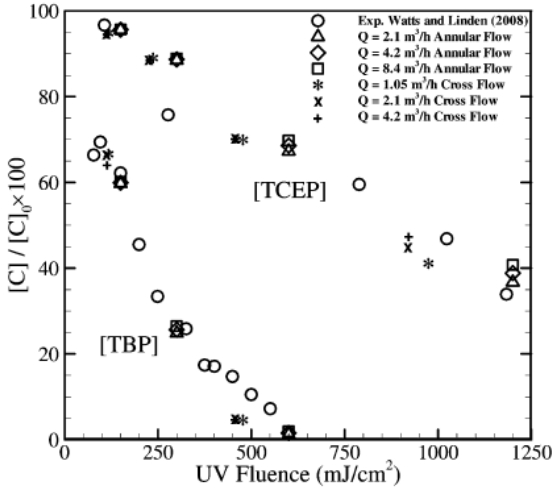

FIGURE 2. Comparison of numerical and experimental removal yield for TCEP and TBP.

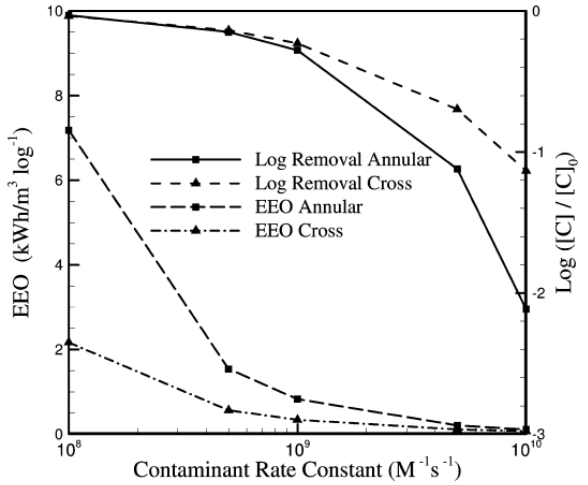

FIGURE 10. Impact of hydroxyl radical rate constant on EEO and reactor log removal.

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VUV/H2O AOP Photoreactors (1)

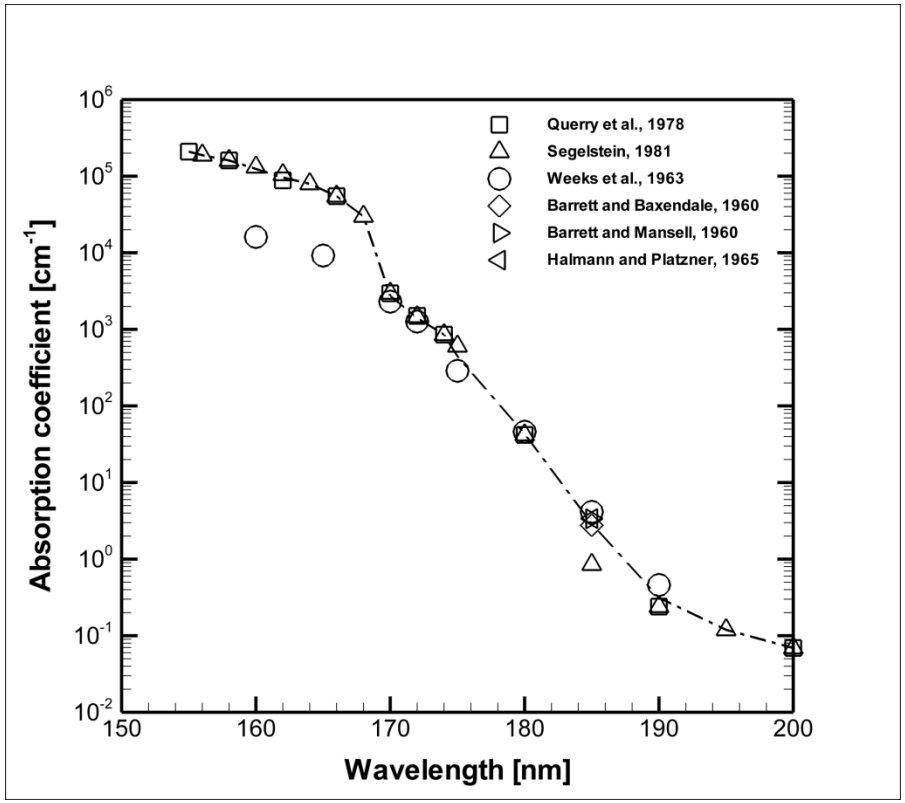

Table 1 – List of elementary reactions and rate constants (compiled from primary and secondary sources) for the 172 nm, 185 nm and 253.7 nm AOP.

Symbol and units	Elementary reaction	Value and reference
Φ_1 [mol einstein^{-1}]	$H_2O + h\nu_{172nm} \rightarrow HO^{\bullet} + H^{\bullet}$	0.42 [Azrague et al., 2005] 0.45 [Gonzalez and Braun, 1995] 0.42 [Gonzalez et al., 2004] 0.42 [Sosnin et al., 2006] 0.37 [Zvereva, 2010]
Φ_2 [mol einstein^{-1}]	$H_2O + h\nu_{172nm} \rightarrow HO^{\bullet} + H^{+} + e^{-}_{aq}$	0.05 [Gonzalez and Braun, 1995] 0.045 [Gonzalez et al., 2004] 0.05 [Sosnin et al., 2006] 0.05 [Zvereva, 2010]
Φ_3 [mol einstein^{-1}]	$H_2O_2 + h\nu_{172nm} \rightarrow HO^{\bullet} + HO^{\bullet}$	0.5 [Zvereva, 2010]
k_4 [m^3 mol^{-1} s^{-1}]	$e^{-}_{aq} + H^{+} \rightarrow H^{\bullet}$	$2.3 \cdot 10^7$ [Gonzalez and Braun, 1995] $2.2 \cdot 10^7$ [Gonzalez et al., 2004] $2.3 \cdot 10^7$ [Imoberdorf and Mohseni, 2011] $2.3 \cdot 10^7$ [Zvereva, 2010] $2.14 \cdot 10^7$ [Manion et al. – NIST Database]
k_5 [m^3 mol^{-1} s^{-1}]	$HO^{\bullet} + H_2 \rightarrow H^{\bullet} + H_2O$	$6.0 \cdot 10^4$ [Gonzalez and Braun, 1995] $6.0 \cdot 10^4$ [Gonzalez et al., 2004] $6.0 \cdot 10^4$ [Imoberdorf and Mohseni, 2011] $4.2 \cdot 10^4$ [Zvereva, 2010] $4.6 \cdot 10^4$ [Manion et al. – NIST Database]
k_6 [m^3 mol^{-1} s^{-1}]	$O^{\bullet -} + H_2 \rightarrow H^{\bullet} + OH^{-}$	$8.0 \cdot 10^4$ [Zvereva, 2010]
k_7 [m^3 mol^{-1} s^{-1}]	$H_2 + O^{\bullet -}_3 \rightarrow O_2 + OH^{-} + H^{\bullet}$	$2.5 \cdot 10^2$ [Zvereva, 2010]
k_8 [m^3 mol^{-1} s^{-1}]	$e^{-}_{aq} + H_2O \rightarrow H^{\bullet} + OH^{-}$	$1.9 \cdot 10^{-2}$ [Imoberdorf and Mohseni, 2011] $1.9 \cdot 10^{-2}$ [Zvereva, 2010]
k_9 [m^3 mol^{-1} s^{-1}]	$H^{\bullet} + H_2O \rightarrow H_2 + HO^{\bullet}$	$1.0 \cdot 10^{-2}$ [Zvereva, 2010]
k_{10} [m^3 mol^{-1} s^{-1}]	$H^{\bullet} + H^{\bullet} \rightarrow H_2$	$1.0 \cdot 10^7$ [Gonzalez and Braun, 1995] $1.0 \cdot 10^7$ [Gonzalez et al., 2004] $1.0 \cdot 10^7$ [Imoberdorf and Mohseni, 2011] $1.0 \cdot 10^7$ [Robl et al., 2012] $1.5 \cdot 10^7$ [Zvereva, 2010] $7.8 \cdot 10^6$ [Manion et al. – NIST Database]
k_{11} [m^3 mol^{-1} s^{-1}]	$HO^{\bullet} + H^{\bullet} \rightarrow H_2O$	$2.4 \cdot 10^7$ [Gonzalez and Braun, 1995] $2.4 \cdot 10^7$ [Gonzalez et al., 2004] $7.0 \cdot 10^6$ [Heit et al., 1998] $7.0 \cdot 10^6$ [Imoberdorf and Mohseni, 2011] $1.5 \cdot 10^7$ [Robl et al., 2012] $7.0 \cdot 10^6$ [Zvereva, 2010] $7.0 \cdot 10^6$ [Manion et al. – NIST Database]

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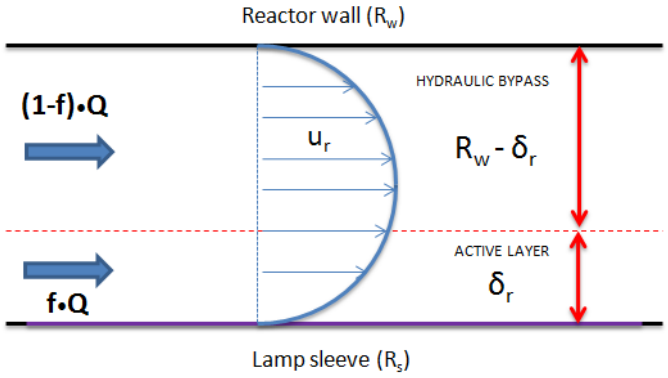
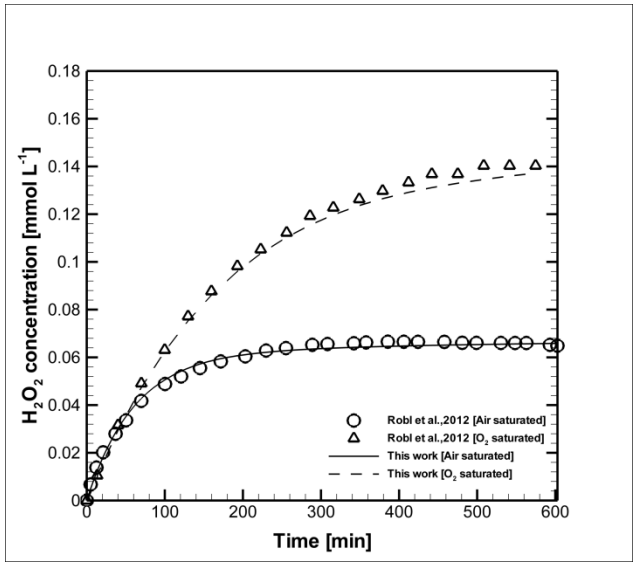
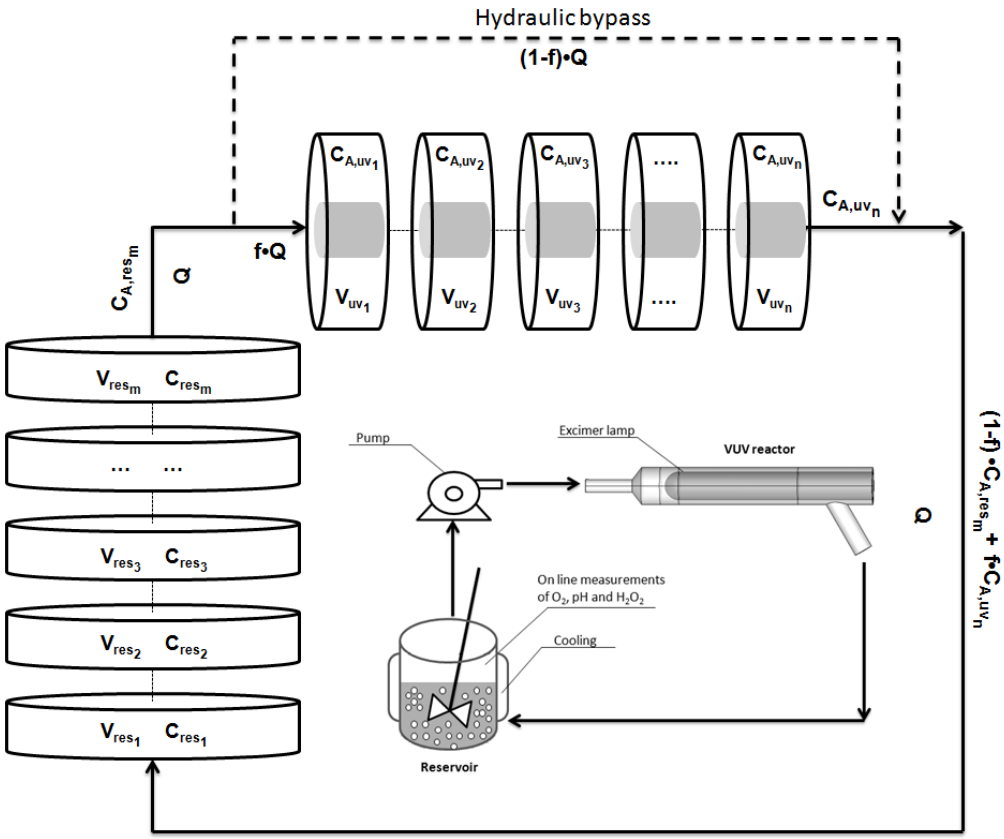
Crapulli et al., (2014): "Mechanistic modeling of vacuum UV advanced oxidation process in an annular photoreactor", *Water Research 64,* pp. 209-22

VUV/H2O AOP Photoreactors (2)







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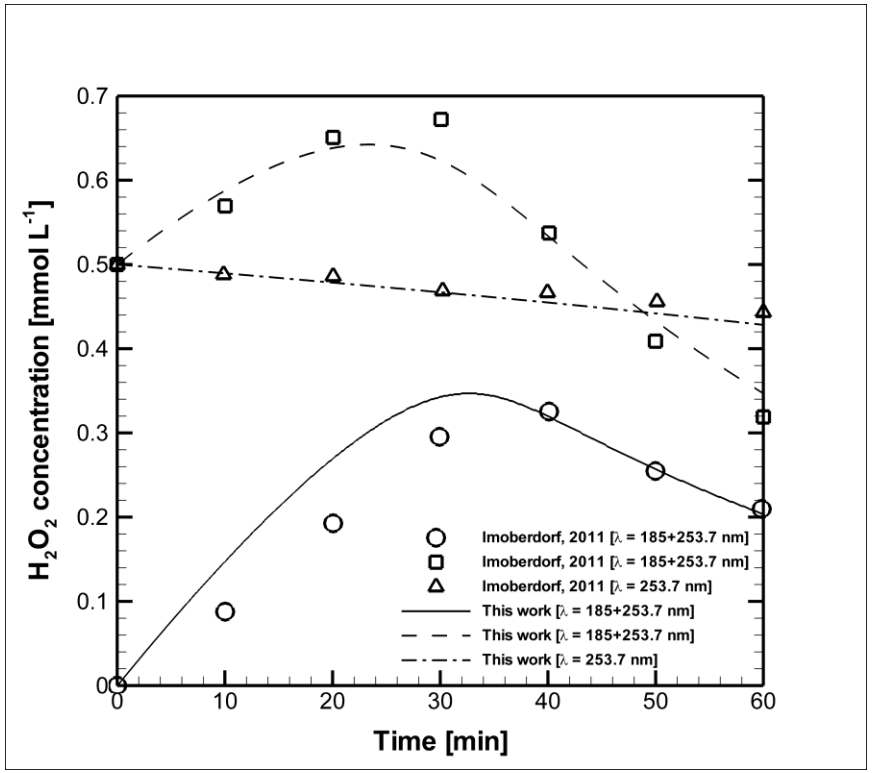
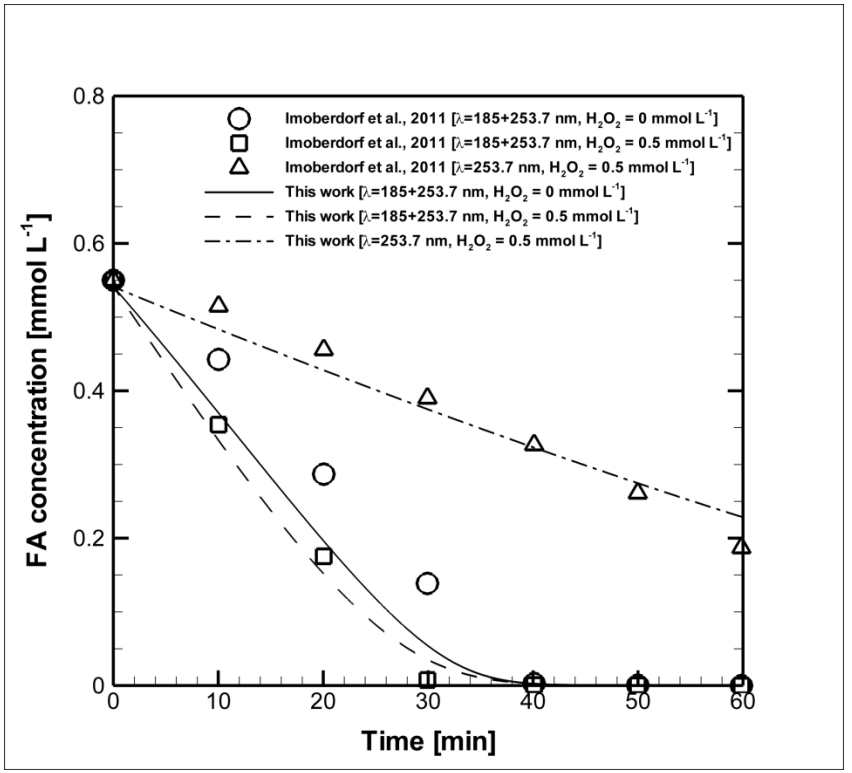
VUV/H2O AOP Photoreactors (3)





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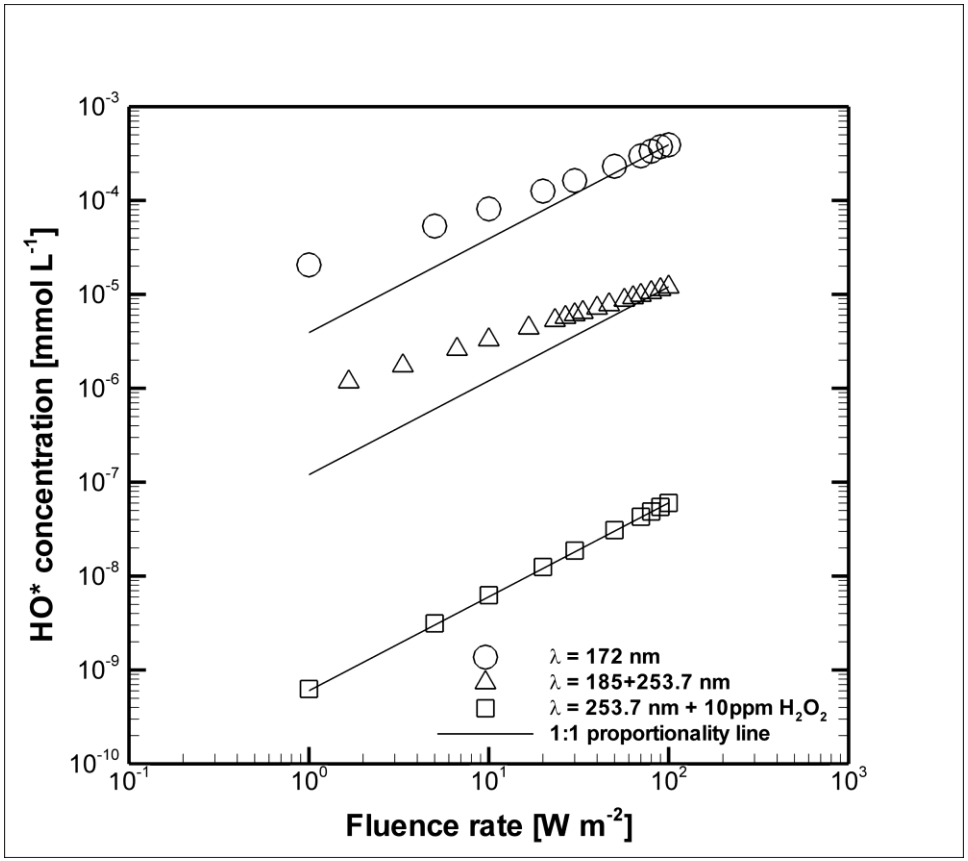
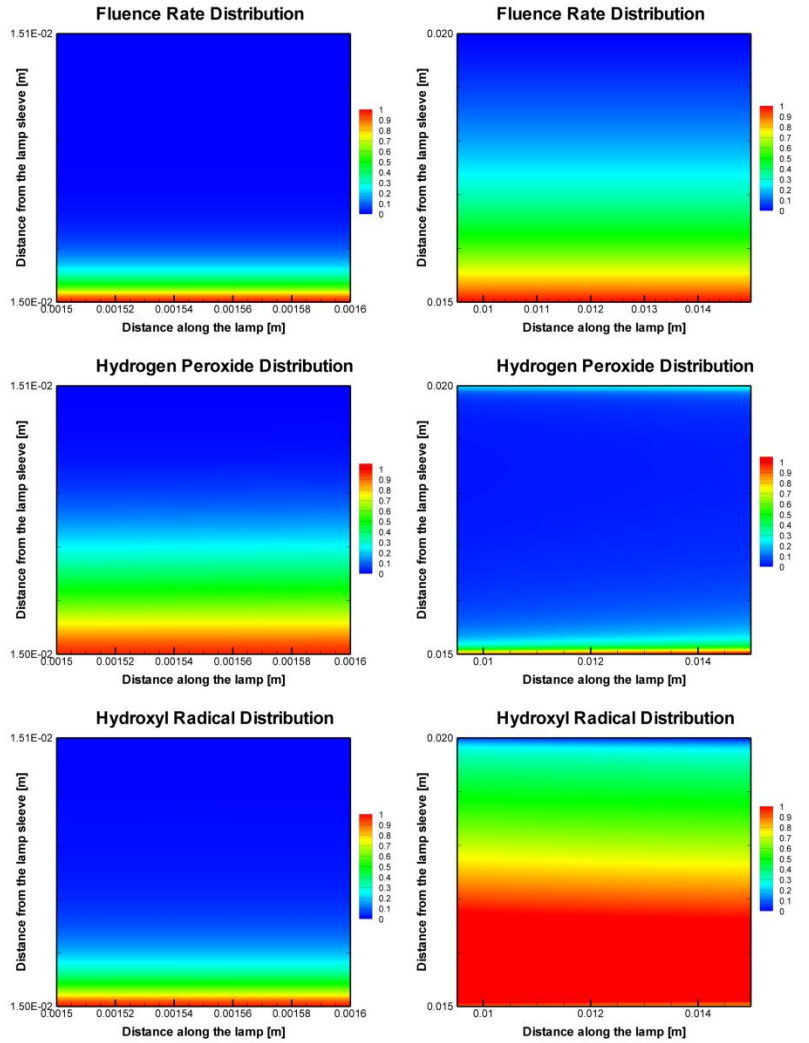
VUV/H2O AOP Photoreactors (4)





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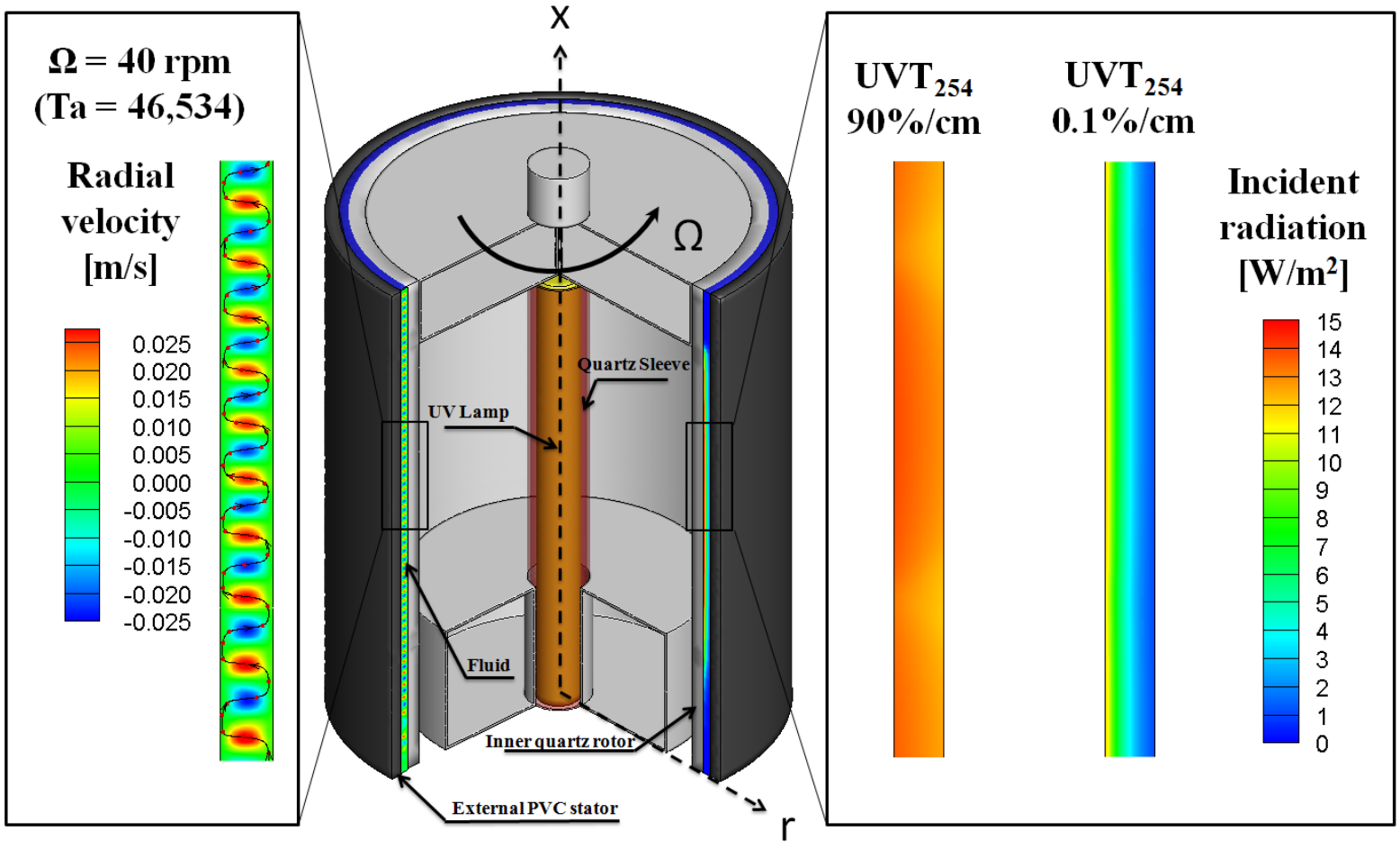
Rotating Photoreactors (1)



Crapulli et al., (2015): "Quantifying ultraviolet inactivation kinetics in nearly opaque fluids", *Water Quality Research Journal of Canada,* 75 (2), pp. 97-103

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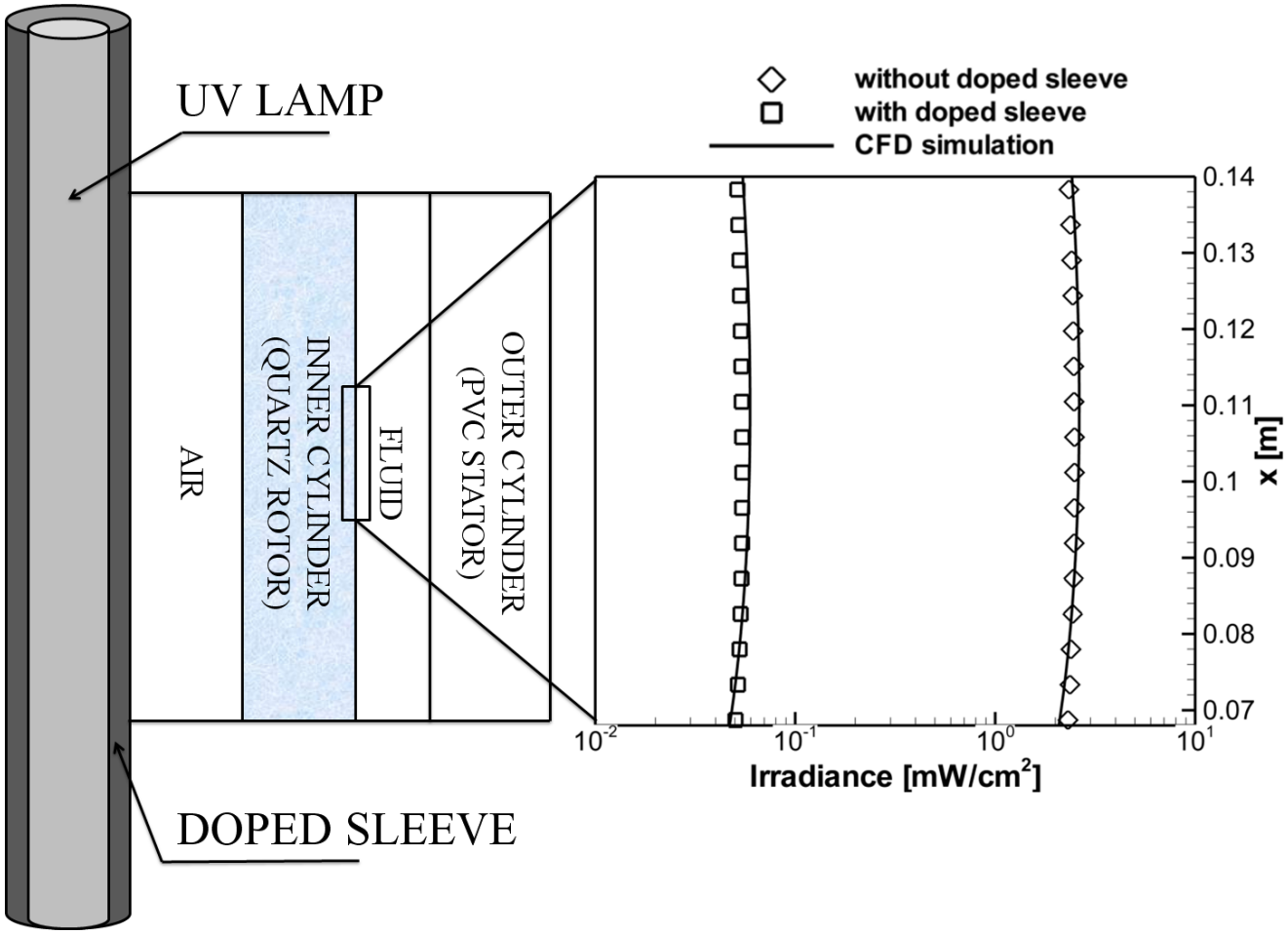
Rotating Photoreactors (2)



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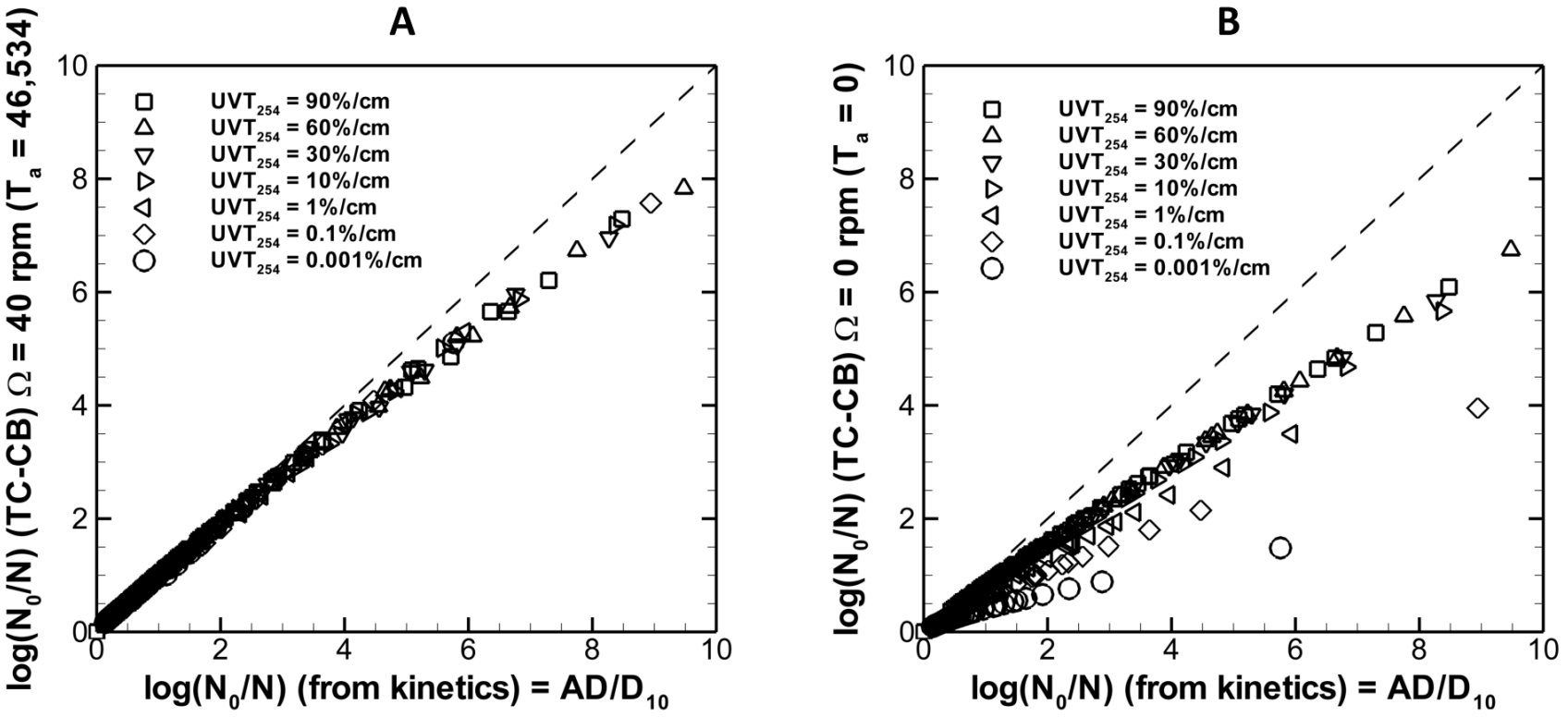
Rotating Photoreactors (3)



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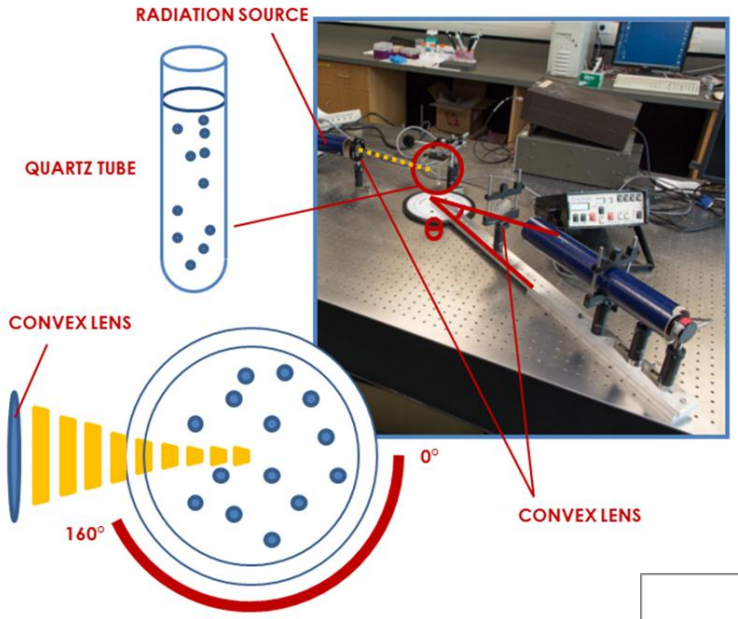
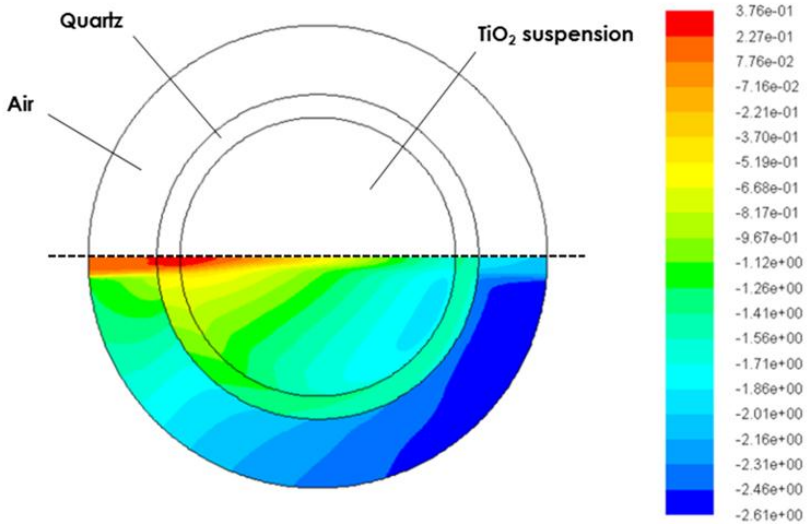
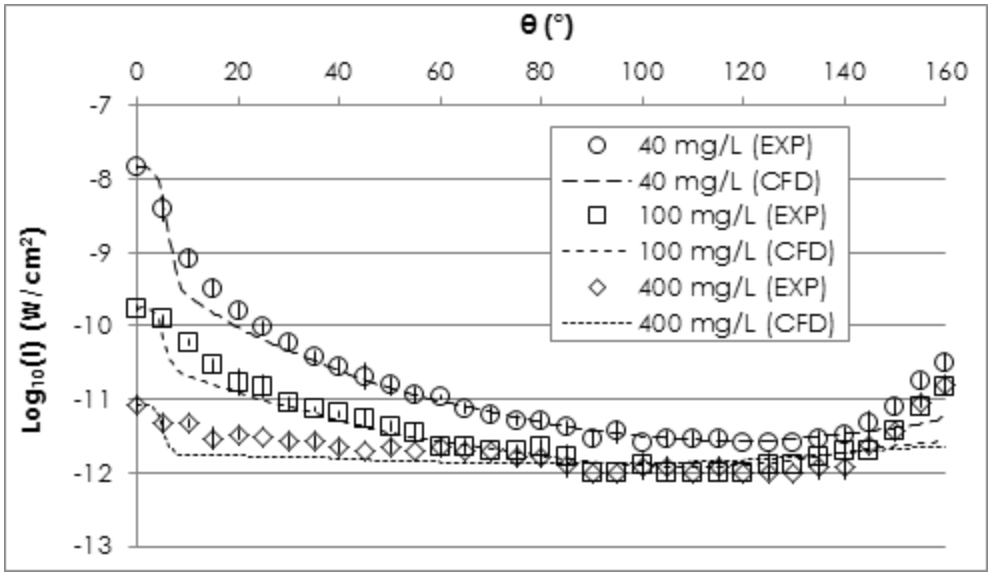
TiO2/UV AOP Photoreactors (1)





Unpublished to date. Work conducted in collaboration with Prof. Antonelli and Dr. Turolla (Polytechnic of Milan)



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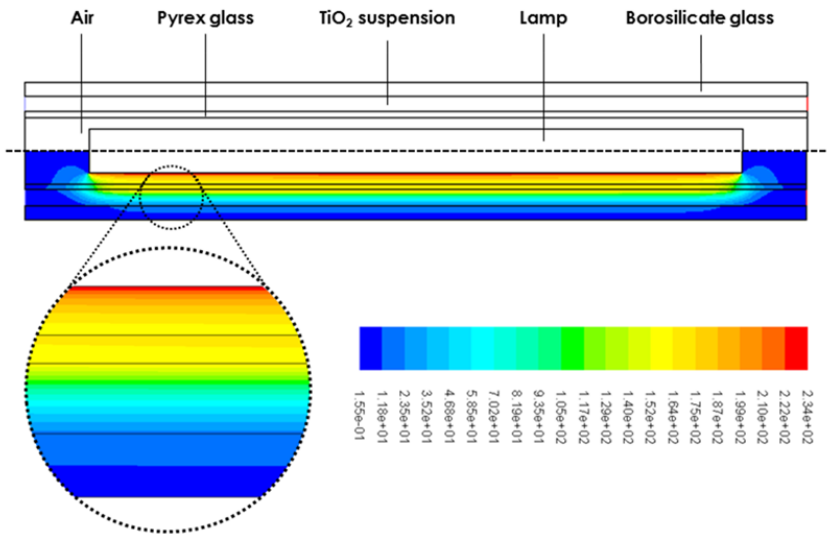
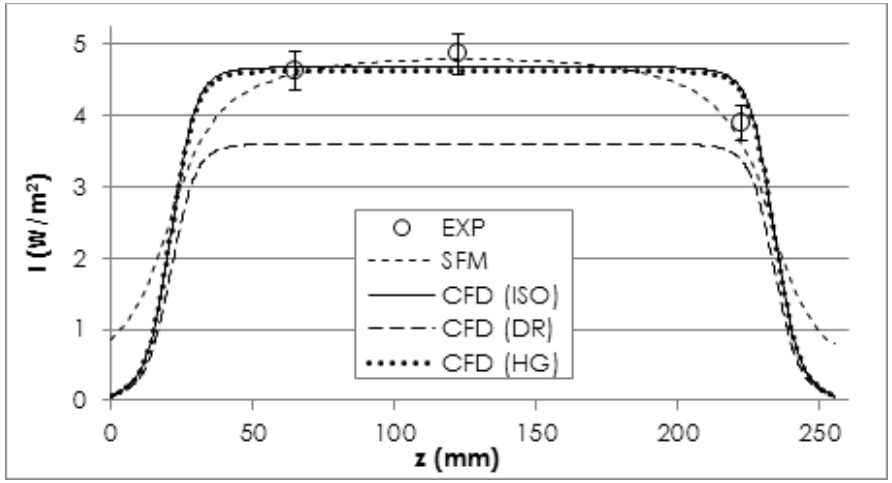
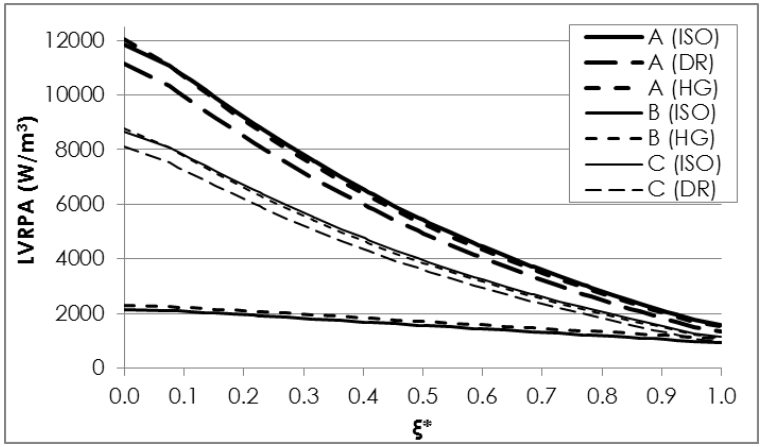
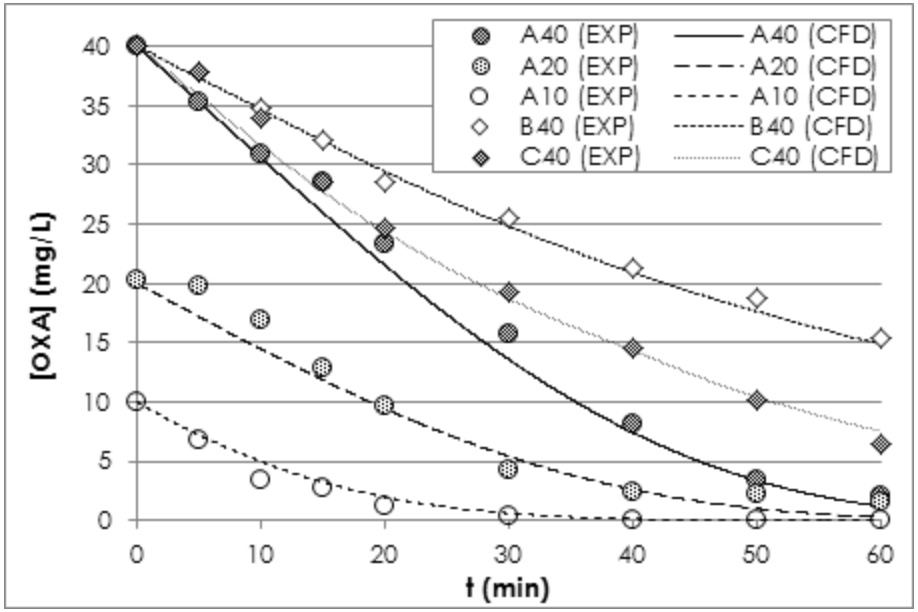
TiO2/UV AOP Photoreactors (2)









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Conclusions

- CFD is a mature methodology for (photo)reactor analysis; AOP applications are already successfully reported both by academia and industry.
- AOP modeling revealed numerous features otherwise impossible to observe;
- CFD is not a magic tool. Extensive verification and validation is still required before its use;
- CFD can be learned in a matter of weeks; the issue is how to use it. Understanding physics and chemistry is more important than mastering mathematics.

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Acknowledgements

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