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Experimental measurement and modeling of radiation fields in TiO2 nanoparticle photocatalysis

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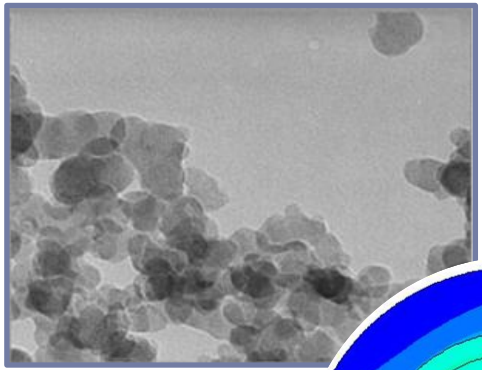

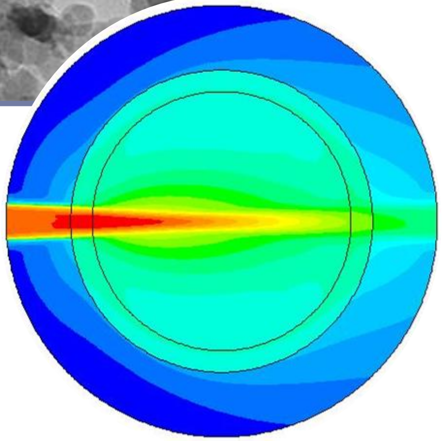

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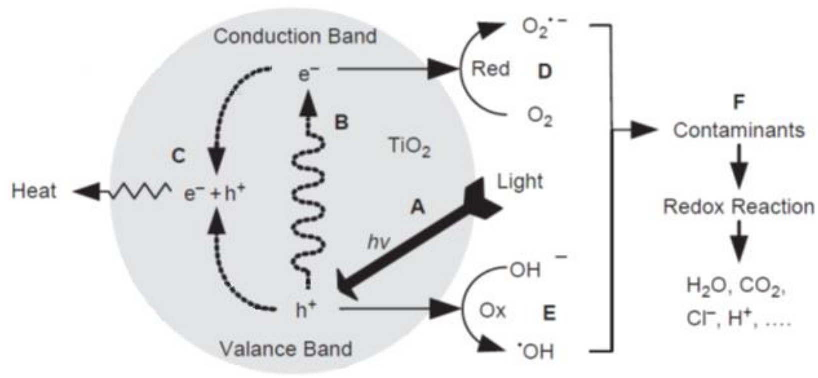
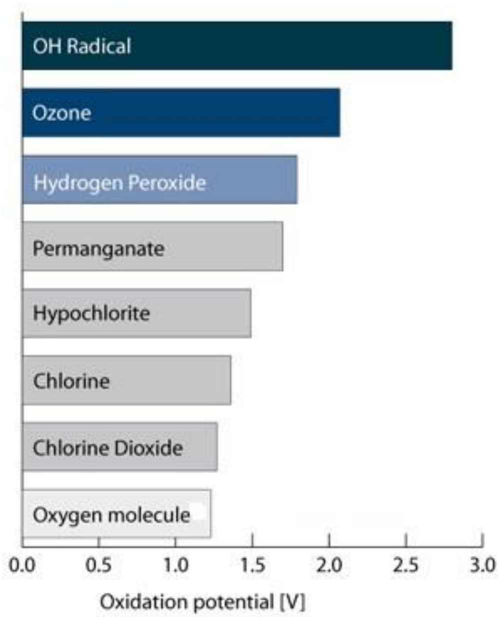
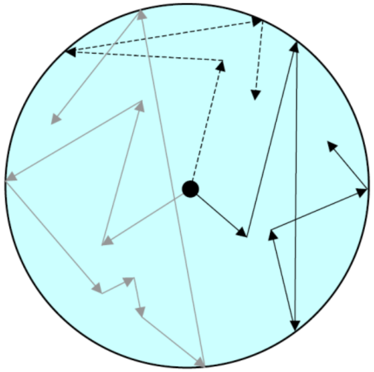
- Advanced oxidation process (AOP)
- Semiconductor band gap: 3.2 eV
  → UV radiation (λ<380 nm)
- Reactive oxygen species (ROS)
  → Hydroxyl radical ($OH^{\bullet}$)
  → Superoxide ($O_2^{\bullet -}$)





- Degradation of pollutants into lower molecular weight intermediates and damage of microorganism cells
- Many types of titanium dioxide, a few commercialized applications, not competitive with established technologies (O_3, H_2O_2/UV)
- **Strong R&D interest, multidisciplinary approach**

- Heterogeneous process involving complex optical phenomena: radiation absorption and scattering



- Understanding the interaction between nanoparticles and radiation is fundamental for process engineering

- The goal is to determine radiation fields throughout reactor volume by solving radiative transfer equation

$$\frac{dI_\lambda}{ds} = -\kappa_\lambda I_\lambda(s,\Omega) - \sigma_\lambda I_\lambda(s,\Omega) + \frac{1}{4\pi}\sigma_\lambda \int_0^{4\pi} p(\Omega' \to \Omega) I_\lambda(s,\Omega') I_\lambda(s,\Omega') d\Omega'$$

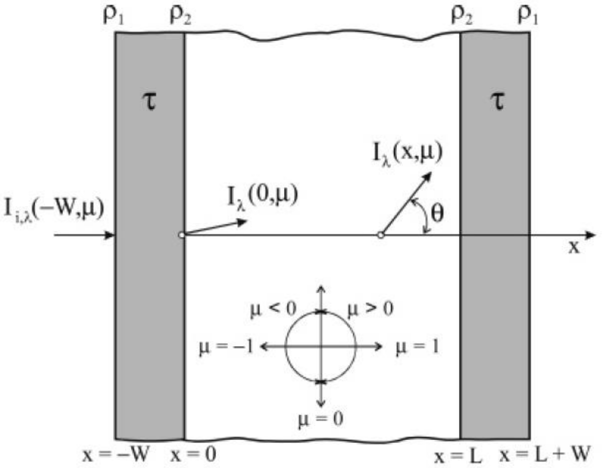
- Need for experimental characterization of optical properties
  → absorption and scattering coefficients (κ_λ,σ_λ)
  → <u>scattering phase function</u>

- Need for powerful simulation tools for modeling
  → numerical: <u>CFD codes</u>

- Scattering phase function has been never determined experimentally

- Scattering is usually considered as isotrophic or some models are assumed, such as the theory of diffusion or the Henyey-Greenstein (HG) scattering phase function

- Optical properties were estimated by solving the radiative transfer equation and deriving the two coefficients from spectrophotometric measures by numerical or statistical techniques



Satuf et al. (2005)

Satuf M.L., Brandi R.J., Cassano A.E., Alfano O.M., Experimental method to evaluate the optical properties of aqueous titanium dioxide suspensions, Ind. Eng. Chem. Res. 44 (2005) 6643-6649.

Research goals

EXPERIMENTAL

- Direct measurement of scattering phase function
- Determination of a model for scattering description
- Estimation of scattering phase function parameters

MODELING

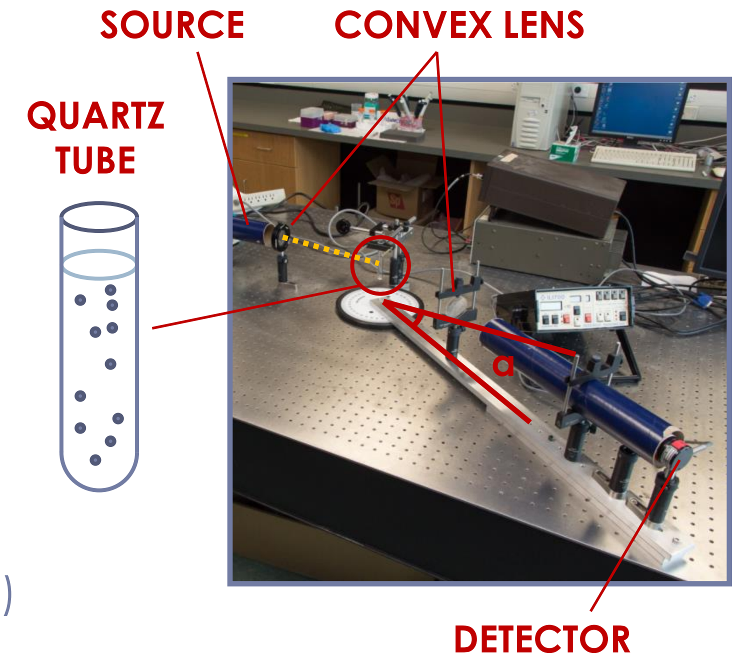
- Assessment of CFD codes as a tool for modeling the radiative transfer in TiO_2 nanoparticle photocatalysis
- Determination of optical properties of TiO_2 nanoparticle suspensions by CFD codes

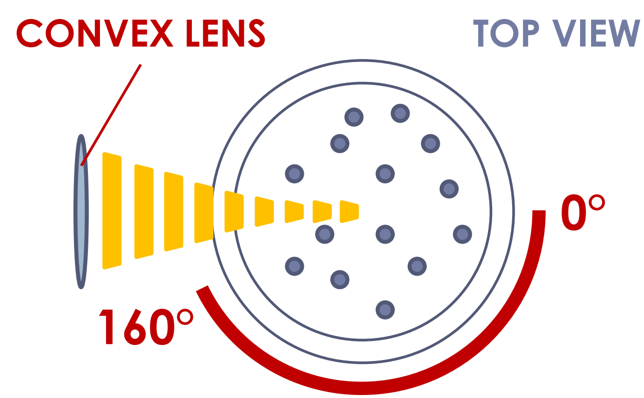
Materials and methods

Experimental

- TiO_2 nanoparticle dispersions
  - P25 Aeroxide (Evonik)
  - Non-sonicated in deionized water
  - $[TiO_2]$: 40, 100, 400 mg/L

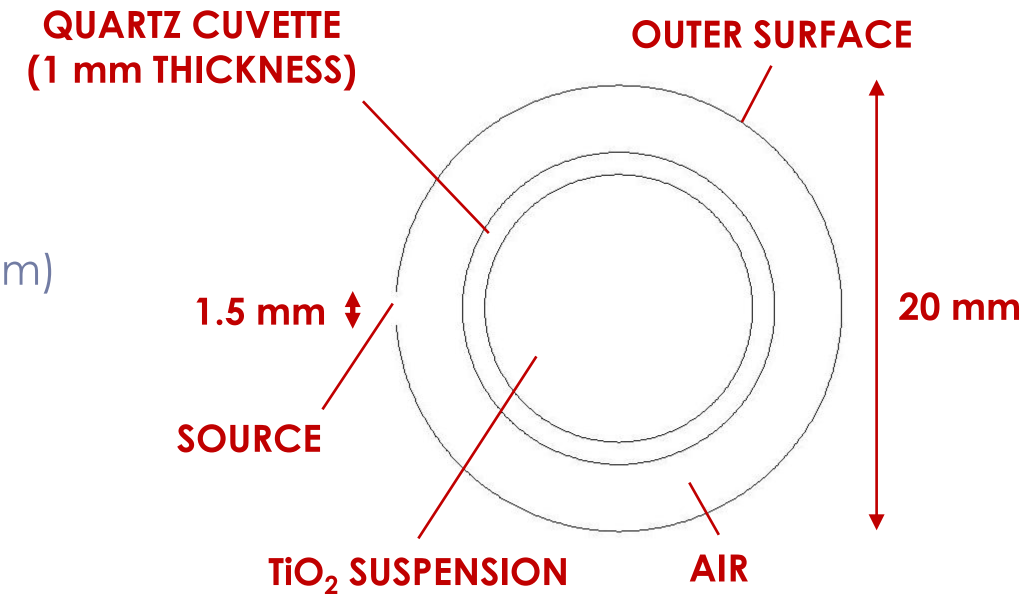
- Experimental apparatus
  - UV radiation goniometer (built in-house)
  - UV source: LEDs collimated beam (SETi)
  - UV wavelength: 254 nm, 355 nm
  - Quartz tube ($Ø_{INT}$ = 1.2 cm, $Ø_{EXT}$ = 1.4 cm)
  - Angular interval (a): 0° - 160° (step 5°)
  - Radiometer + detector (ILT1700 + SED022, International Light Technologies)

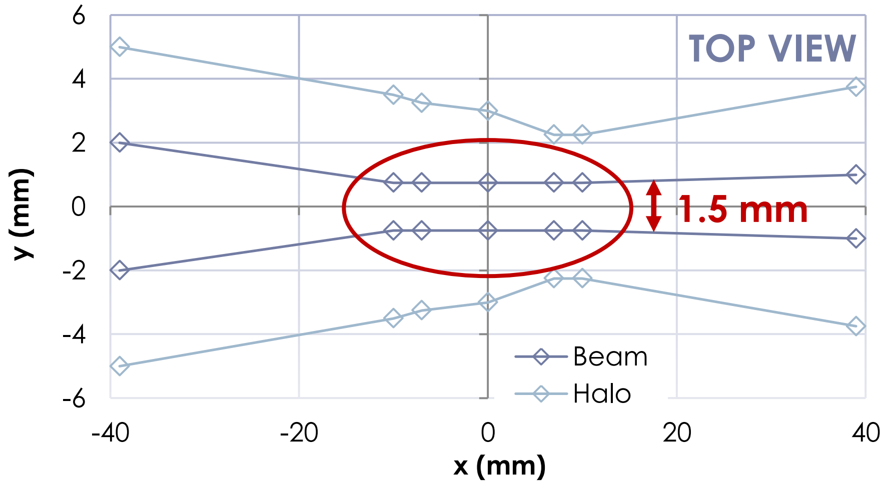




Materials and methods
Modeling

- ANSYS Fluent 15.0, Discrete Ordinates (DO) model
- 70,000 triangular elements (0.1 mm) two-dimensional planar mesh
- 1.5 mm collimated source converging on the central point
- High angular discretization Phi division / pixelation > 64 / 64
- Computed in 2 h on Intel i7-4770 processor (3.40 GHz) and 16 GB RAM
- Complete convergence at 100 iterations, residuals below 5e-05





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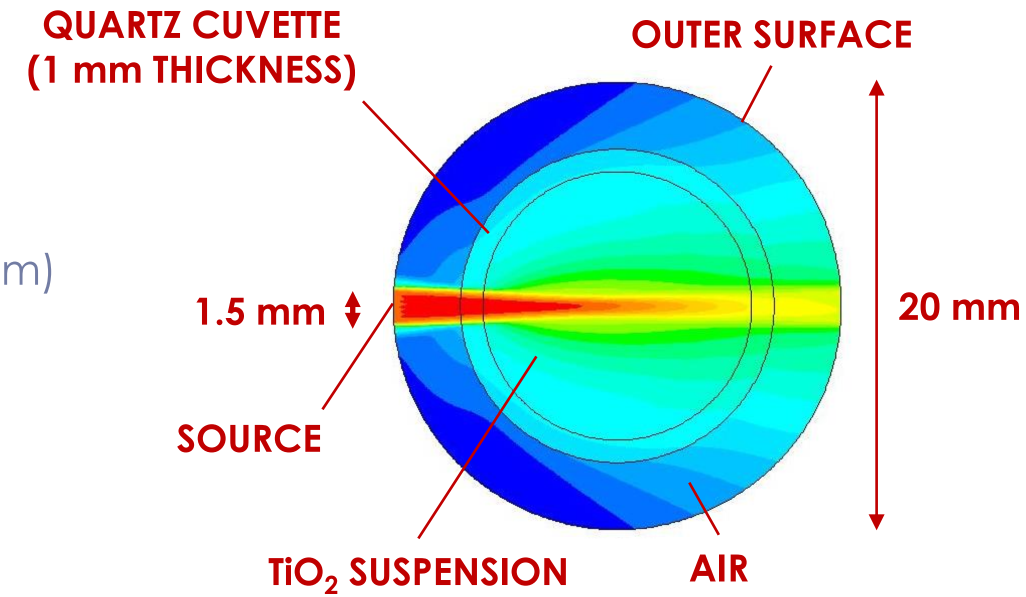
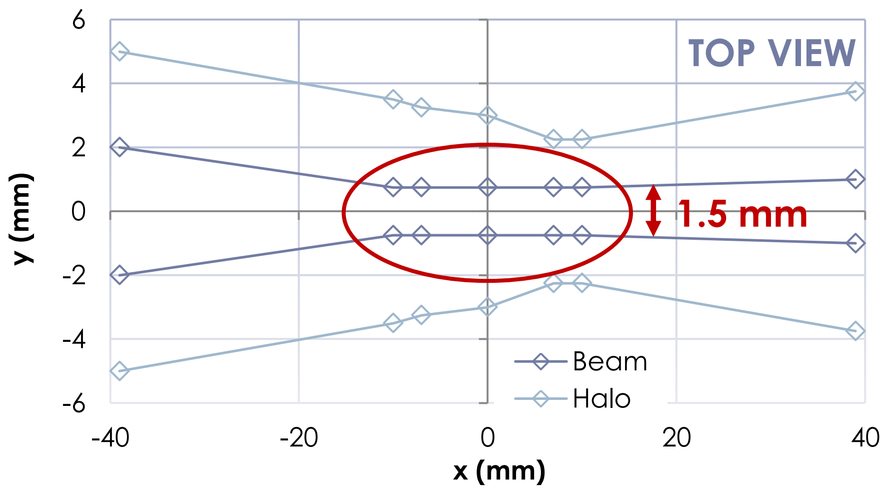
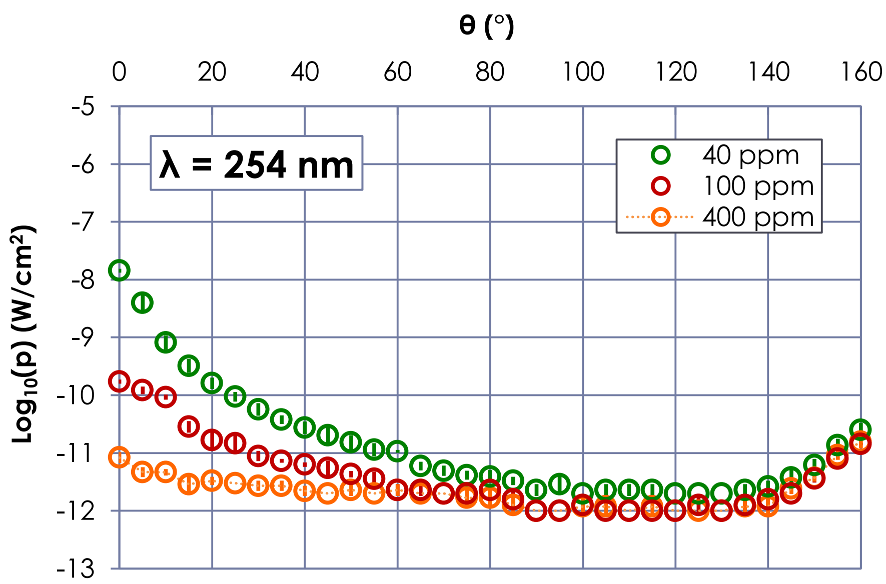
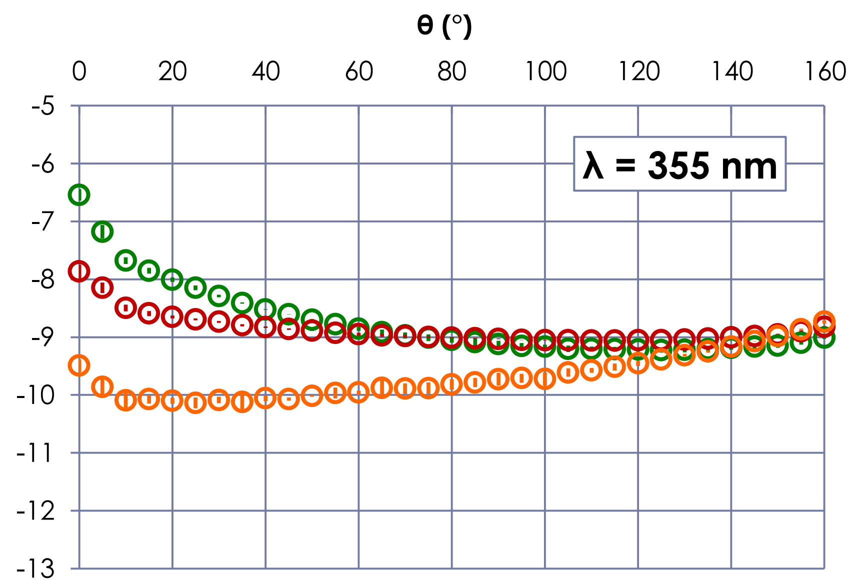




- Good data quality (four complete sets for each case, low variability)
- Data were stable over time
- Small intensities, close to sensitivity limit of the detector (10^{-13} W/cm^2)
- Different data trends depending on wavelength and TiO_2 concentration
- Unexpected increase at the highest angles (> 130°), especially at 254 nm



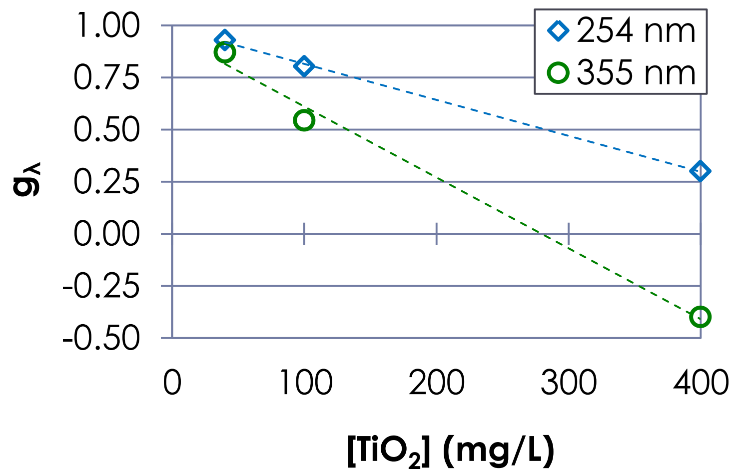


- Fitting experimental data with main scattering models reported in literature:
    - Mie theory
    - Theory of diffusion
    - Henyey-Greenstein function
- To avoid disturbances due to side optical phenomena, angular interval for fitting was limited between 5° and 120°
- Low fitting (R^2<0.4) with the exception of the Henyey-Greenstein function, that depends on a single parameter (g_λ)

$$p_\lambda(\theta) = \frac{1}{4\pi}\frac{(1-g_\lambda{}^2)}{(1+g_\lambda{}^2-2g_\lambda cos\theta)^{3/2}}$$

- g_λ decreased linearly with increasing TiO_2 concentration, moving from single to multiple scattering, and to a more uniform distribution of radiation

λ (nm)	[TiO_2] (mg/L)	g_λ (-)	R^2
254	40	0.929	0.999
	100	0.802	0.973
	400	0.299	0.865
355	40	0.870	0.976
	100	0.543	0.937
	400	-0.399	0.942



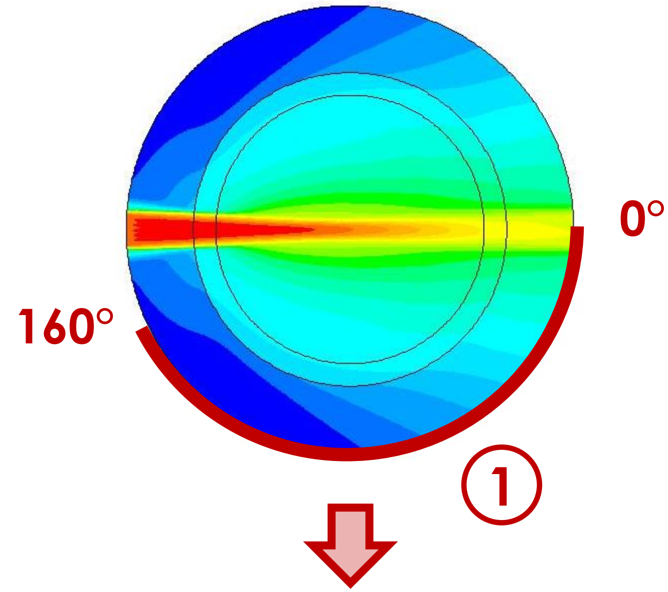
Post-processing after simulation

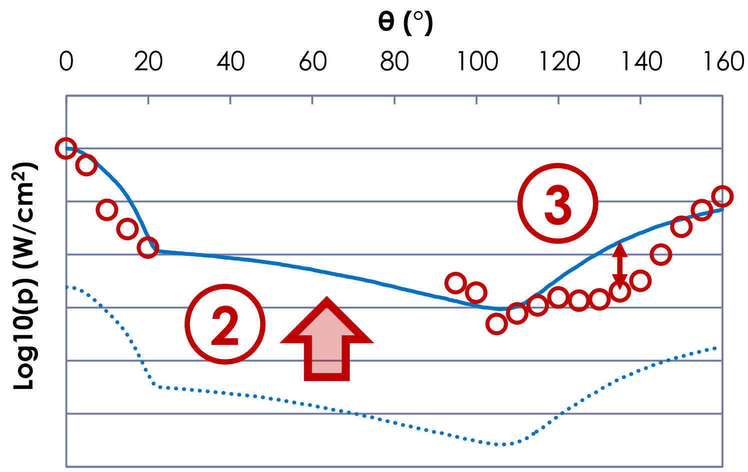
1. Incident radiation was **plotted** on outer surface, having these data the same meaning as the experimental measures

2. Since the power of UV radiation source was not calibrated, simulated datasets were **shifted** for having the coincidence with the experimental data at angle 0°

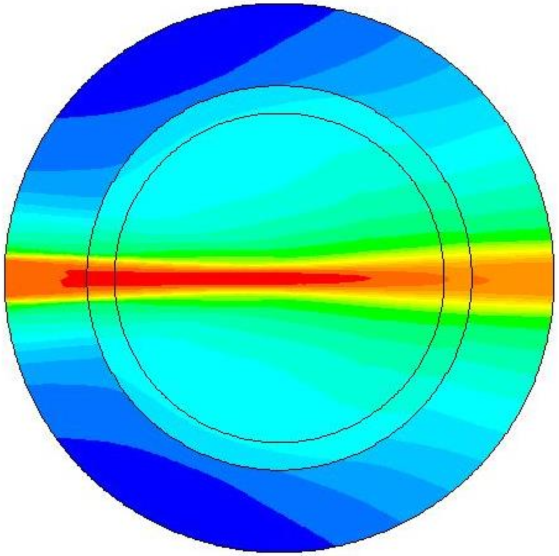
3. The **sum of the distances** between experimental data and simulated curve was used to assess the quality of fitting

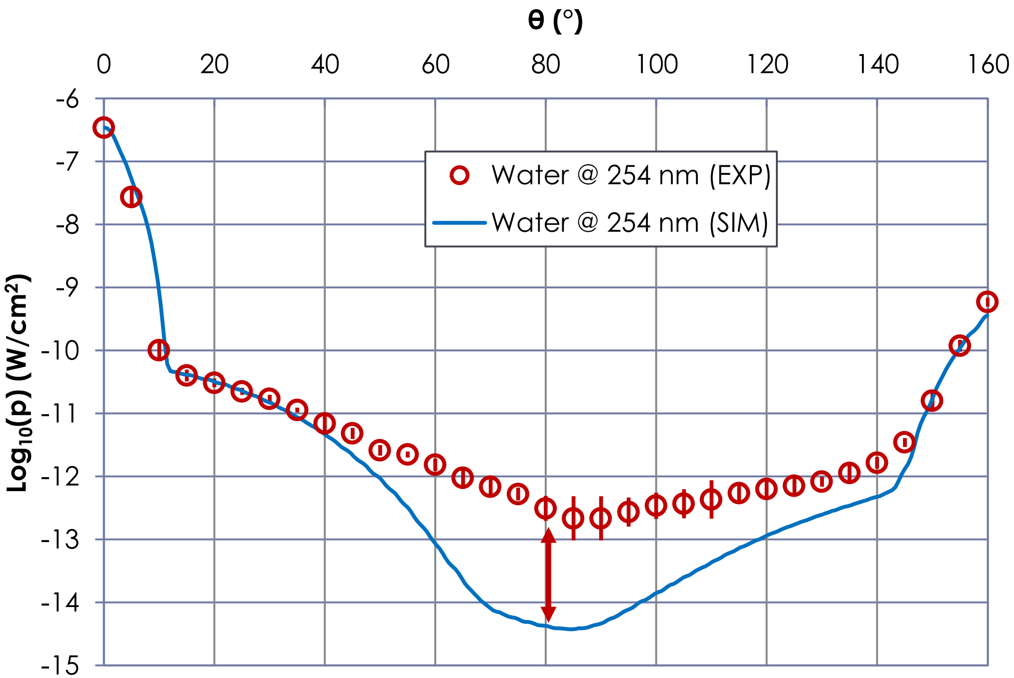
$$Error = \sum_{Angle} |Log_{10}(p)_{EXP} - Log_{10}(p)_{SIM}|$$





- The shape and the width of the beam were tuned for maximizing the fitting of experimental data obtained without TiO_2 nanoparticles at 254 nm and 355 nm
- For 1.5 mm converging beam a good fitting was achieved for low and high angles, where experimental values are much higher than radiometer sensitivity

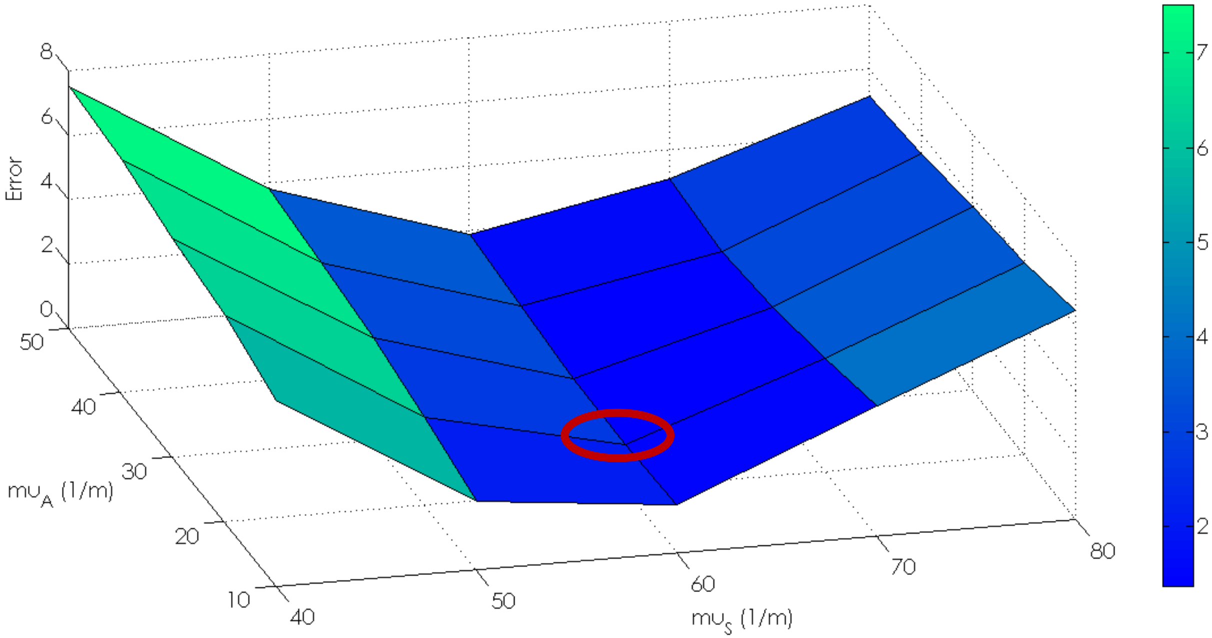




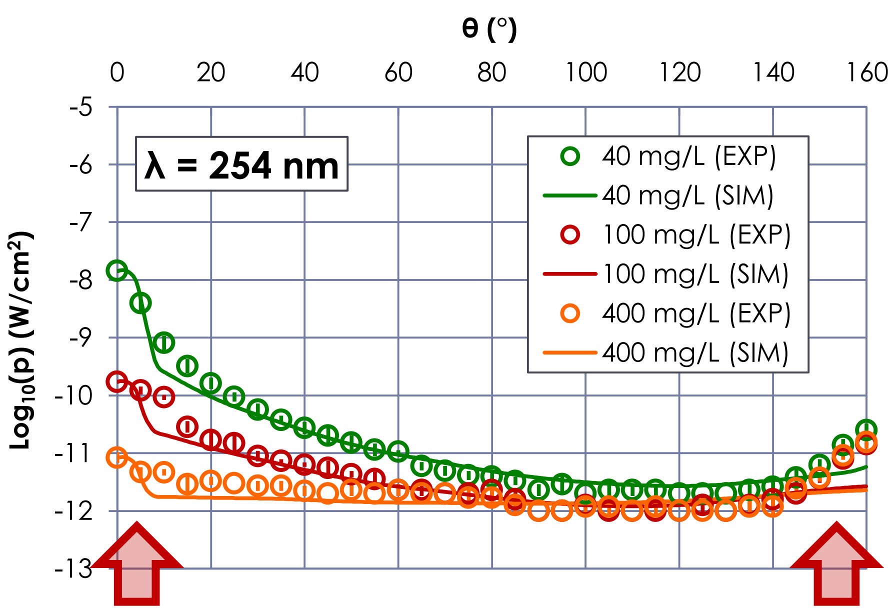
- Simulations were performed by setting the asymmetry coefficient of HG scattering phase function from experimental values, while a parametric assessment was carried out for absorption and scattering coefficients
- Absorption and scattering coefficients resulting in the lowest error were selected as optical properties at given conditions
- Results were poorly sensitive to the absorption coefficient

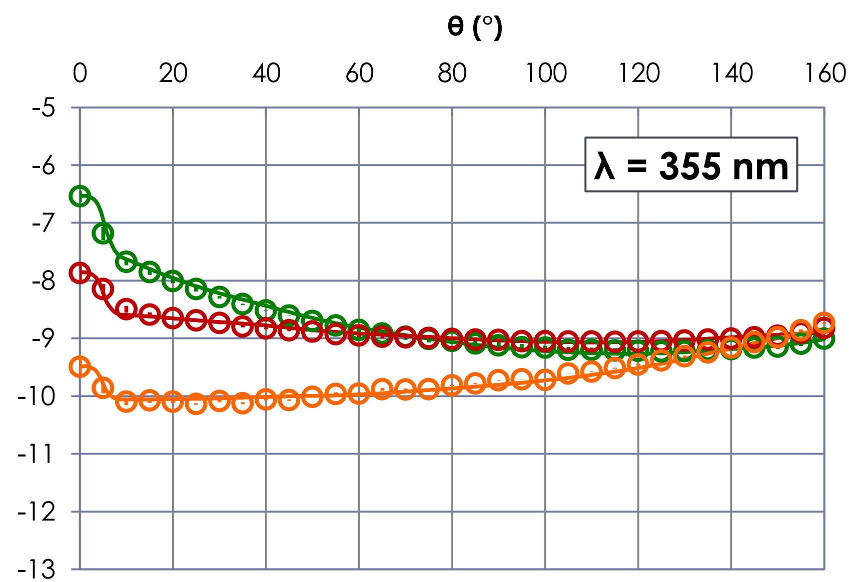
$[TiO_2]$ = 40 mg/L
λ = 355 nm

g_λ = 0.870
μ_A = 20 1/m
μ_S = 60 1/m

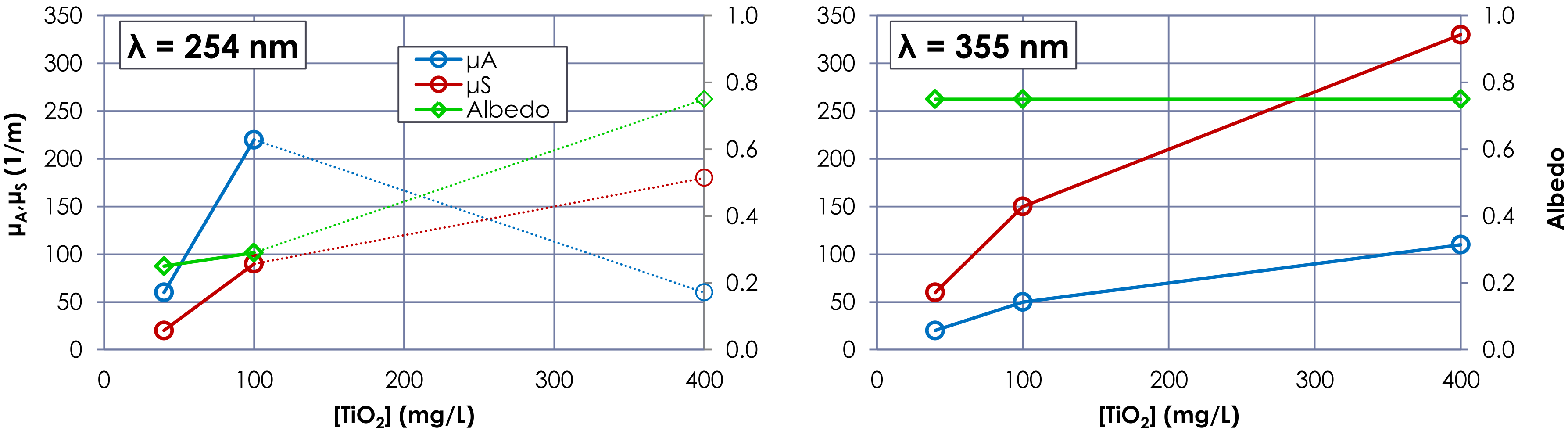


- CFD simulations were effective in reproducing the optical behavior of the three-dimensional experimental setup under different operating conditions
- Best results at 355 nm, some discrepancies from experimental data at 254 nm
- Optical properties, i.e. absorption and scattering coefficients, were determined for any combination of TiO_2 concentration and radiation wavelength





- Absorbance and scattering coefficient are supposed to grew proportionally, so that the albedo is expected to be constant, as obtained in simulations
- CFD was not effective in describing optical behavior at 400 mg/L and 254 nm
- Non-linear increase from 100 to 400 mg/L at 355 nm related to aggregation
- Good agreement at 355 nm with Satuf et al. (2005) for albedo, while values of coefficients were different > method for sample preparation (30' sonication)?



Satuf M.L., Brandi R.J., Cassano A.E., Alfano O.M., Experimental method to evaluate the optical properties of aqueous titanium dioxide suspensions, Ind. Eng. Chem. Res. 44 (2005) 6643-6649.

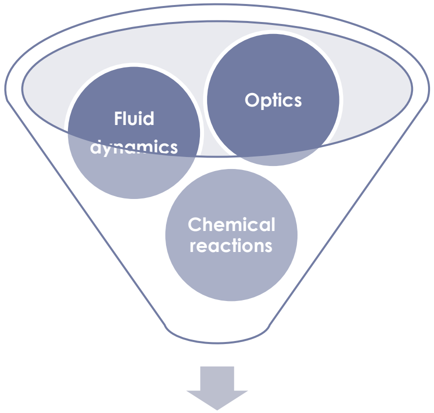
Conclusions

- Scattering in TiO_2 suspensions can be modeled by Henyey-Greenstein function
- Henyey-Greenstein function asymmetry coefficient was determined experimentally as a function of TiO_2 concentration and radiation wavelength
- CFD codes are effective tools for modeling radiation fields in three-dimensional scattering systems and for determining optical properties of TiO_2 suspensions

Future steps

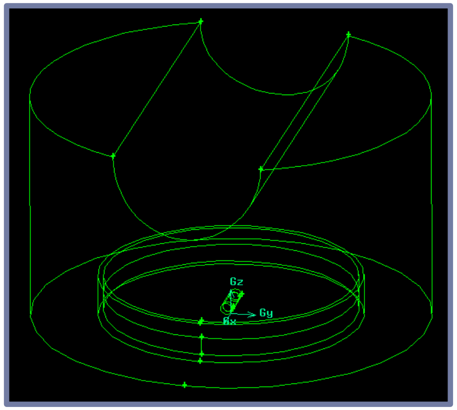
1. Optical parameters validation for the description of radiative phenomena in TiO_2 photocatalysis reactors

   > Simulation of a literature case (Grcic et Li Puma, 2013)



2. Application of CFD codes for the development of a TiO_2 photocatalysis comprehensive model, accounting for optics, fluid dynamics and chemical reactions

   > Simulation of a small scale laboratory experimental setup (10 mL) for the measurement of reactive species



Grcic I., Li Puma G., Photocatalytic degradation of water contaminants in multiple photoreactors and evaluation of reaction kinetic constants independent of photon absorption, irradiance, reactor geometry, and hydrodynamics, Environ. Sci. Technol. 47 (2013) 13702-13711.

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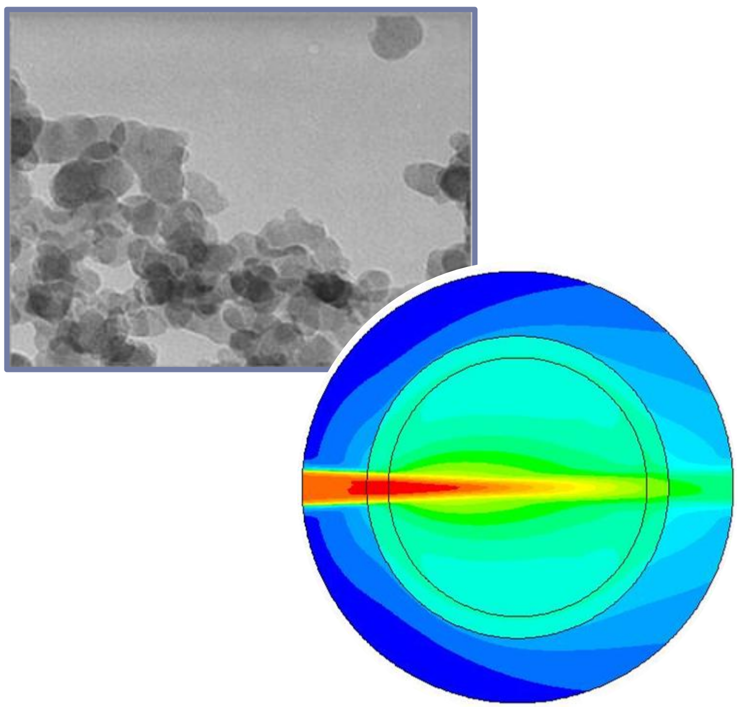

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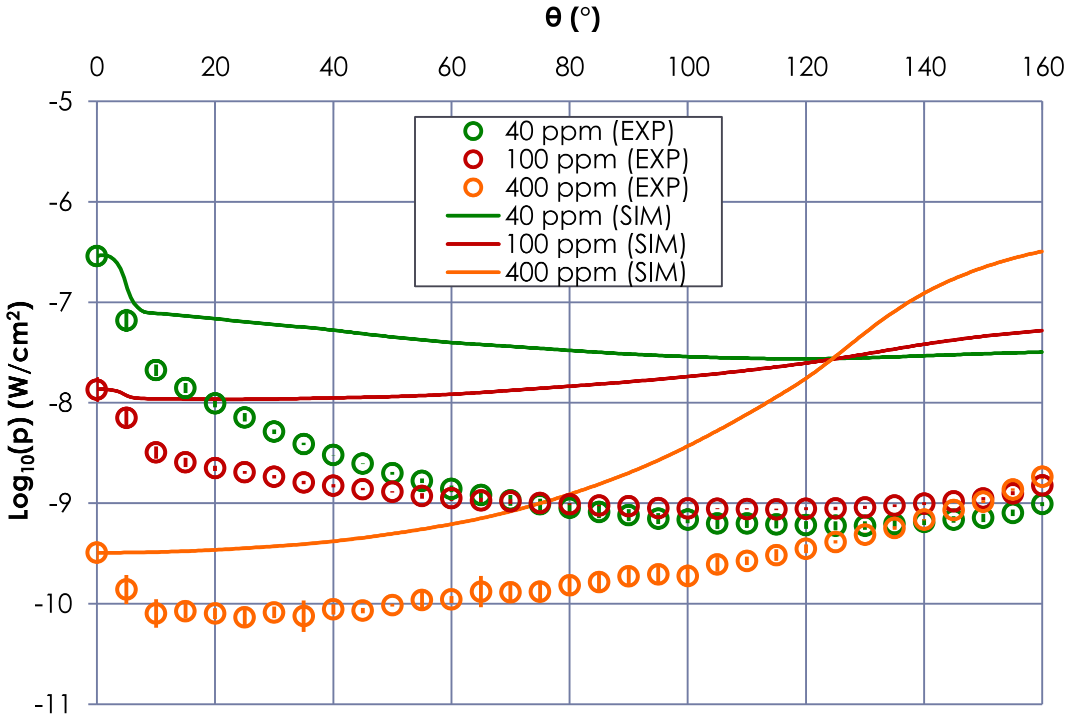
>>> THANKS FOR YOUR ATTENTION



θ (°)
0
20
40
60
80
100
120
140
160
-5
-6
-7
-8
-9
-10
-11
Log10(p) (W/cm²)
40 ppm (EXP)
100 ppm (EXP)
400 ppm (EXP)
40 ppm (SIM)
100 ppm (SIM)
400 ppm (SIM)