Disinfection and advanced oxidation of highly absorbing fluids by UV/VUV light: process modeling and validation

Ferdinando Crapulli
The University of Western Ontario

Supervisor
Dr. Ajay K. Ray
The University of Western Ontario

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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DISINFECTION AND ADVANCED OXIDATION OF HIGHLY ABSORBING FLUIDS
BY UV/VUV LIGHT: PROCESS MODELING AND VALIDATION

(Thesis format: Monograph)

by

Ferdinando Crapulli

Graduate Program in Engineering Science
Department of Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment
of the requirements for the degree of
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The University of Western Ontario
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Abstract

One of the limitations in treating highly absorbing fluids with ultraviolet photoreactors is the short light penetration into the fluid leading to the following issues: (a) if not engineered properly, ultraviolet photoreactors dealing with highly absorbing fluids are likely to be energy-inefficient due to a non-ideal use of emitted photons and non-uniform dose distribution (b) the quantification of photo-chemical rate constants could be a challenging task due to the severe mixing-limited conditions of the experimental apparatus used during the investigation. As a result, new lab-scale apparatus (alternative to the conventional collimated beam system) and modeling approaches are needed in order to overcome such technical limitations.

The aim of this thesis is two-fold: firstly, to develop and validate lab-scale apparatus and standard operating procedures suitable for investigating the disinfection and the advanced oxidation processes (AOPs) initiated by short-penetrating wavelengths; secondly, to apply such newly developed methodologies for quantifying microbial inactivation kinetics in liquid foods by 253.7 nm light as well as total organic carbon (TOC) removal from ultrapure water by Vacuum-UV-initiated (VUV) AOPs employing the 172 and the 185 nm wavelengths.

For quantifying microbial inactivation kinetics in liquid foods, a Taylor-Couette (TC) apparatus can be used for fluids with ultraviolet transmittance as low as ~0.001% cm$^{-1}$. A computational fluid dynamics (CFD) model was used to optimize the TC system, indicating that a Taylor number of ~46,500 was sufficient to overcome the very short UV light penetration.

For the TOC removal from ultrapure water by AOPs employing VUV light a mechanistic VUV-AOP model was developed by incorporating the vacuum UV-AOP kinetics into the theoretical framework of in-series continuous stirred tank reactors (CSTRs). Experimental trials were conducted using an annular photoreactor equipped with VUV lamps able to emit the 185 nm and 172 nm radiation revealed that, at the investigated conditions, the 185 nm AOP process gave three times better TOC degradation performance than the 172 nm AOP process.
Keywords

Ultraviolet disinfection, VUV light, advanced oxidation processes, highly absorbing fluids, ultrapure water, numerical modeling, inactivation kinetics, computational fluid dynamics.
Co-Authorship Statement

The journal articles used in some chapters of the present thesis are listed below. The individual contributions of all members are also indicated.

### Chapter 2

<table>
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<th>Article title:</th>
<th>Quantifying Ultraviolet Inactivation Kinetics in Nearly Opaque Fluids</th>
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<tr>
<td><strong>Authors:</strong></td>
<td>Ferdinando Crapulli, Domenico Santoro, Michael R. Sasges, Shaunak Ray, Housyn Mahmoud, Ajay K. Ray</td>
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<td><strong>Status:</strong></td>
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<tr>
<td><strong>Individual contributions:</strong></td>
<td>The manuscript was written by Ferdinando Crapulli who also conducted the numerical analysis on Fluent. Shaunak Ray and Housyn Mahmoud conducted several experimental tests on Taylor-Couette collimated beam apparatus. Various drafts of the article were reviewed by Domenico Santoro, and Michael Sasges. The work was supervised by Ajay Ray.</td>
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Nomenclature

\[ A_A \] Absorption coefficient of the solution at specified wavelength \([\text{m}^{-1}]\)

\[ a, b, c, d \] Generic stoichiometric coefficients

\[ C_0, C \] Initial and final concentration of the species \([\text{mol m}^{-3}]\)

\[ C_{A, B, C, D} \] Concentration of the generic species A, B, C, and D \([\text{mol m}^{-3}]\)

\[ C_{A, \text{res}} \] Concentration of the generic species A in the reservoir \([\text{mol m}^{-3}]\)

\[ C_{A, \text{uv}} \] Concentration of the generic species A in the photoreactor \([\text{mol m}^{-3}]\)

\[ c_L \] Light speed in vacuum \((2.99\times10^8 \text{ m s}^{-1})\)

\[ C_p \] Center point

\[ D \] UV dose \([\text{J m}^{-2}]\)

\[ D_{10} \] UV dose required for 1 log_{10} inactivation \([\text{J m}^{-2}]\)

\[ f \] Fraction of flowrate entering in the active layer of the photoreactor

\[ h \] Plank's constant \((6.626\times10^{-34} \text{ J s})\)

\[ I \] Fluence rate \([\text{W m}^{-2}]\)

\[ K \] Number of factors

\[ k \] Microbial inactivation constant \([\text{m}^2 \text{ J}^{-1}]\)

\[ k_x \] Reaction rate constant, second order \([\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}]\) or first order \([\text{s}^{-1}]\)

\[ L \] Lamp arc length \([\text{m}]\)

\[ MW_A \] Molecular weight of the generic species A \([\text{g mol}^{-1}]\)

\[ N \] Concentration of cells \([\text{cfu m}^{-3}]\)

\[ n \] Number of CSTRs in series in the photoreactor zone

\[ N_A \] Avogadro's number \((6.022\times10^{23} \text{ molecules mol}^{-1})\)

\[ m \] Number of CSTRs in series in the reservoir zone

\[ P \] Electrical lamp power \([\text{W}]\)

\[ P_a \] Pressure \([\text{Pa}]\)

\[ P_{\text{abs}} \] UV power absorbed by the solution \([\text{W}]\)

\[ P_{\text{UV}} \] UV power emitted from the sleeve \([\text{W}]\)

\[ p \] Total number of absorbing light species

\[ Q \] Flowrate \([\text{m}^3 \text{s}^{-1}]\)

\[ R_d \] Generic light-independent reaction rate \([\text{mol m}^3 \text{s}^{-1}]\)

\[ R_i \] Inner Taylor-Couette cylinder radius \([\text{m}]\)

\[ R_t \] Generic light-dependent reaction rate \([\text{mol m}^3 \text{s}^{-1}]\)

\[ R_o \] Outer Taylor-Couette cylinder radius \([\text{m}]\)

\[ R_S \] Sleeve radius \([\text{m}]\)

\[ R_W \] Reactor wall radius \([\text{m}]\)

\[ r \] Radial direction \([\text{m}]\)

\[ \tilde{r} \] Position of vector \([\text{m}]\)

\[ Re_{\text{axial}} \] Axial Reynolds number \([-]\)

\[ Re_{\text{radial}} \] Radial Reynolds number \([-]\)

\[ S \] Strain rate \([\text{s}^{-1}]\)
\( S_{\phi}, S_{c_A} \)  
Source term \([\phi \text{ s}^{-1}]\)

\( \vec{s} \)  
Direction vector [m]

\( S_c \)  
Schmidt number [-]

\( T_a \)  
Taylor number [-]

\( t \)  
Time [s]

\( \vec{u} \)  
Fluid velocity vector \([\text{m s}^{-1}]\)

\( u_i \)  
Fluid velocity components in Cartesian coordinates \([\text{m s}^{-1}]\)

\( u_r \)  
Fluid velocity (radial component) \([\text{m s}^{-1}]\)

\( u_x \)  
Fluid velocity (axial component) \([\text{m s}^{-1}]\)

\( u_\theta \)  
Fluid velocity (azimuthal component) \([\text{m s}^{-1}]\)

\( V_{\text{res}} \)  
Reservoir volume \([\text{m}^3]\)

\( V_{\text{uv}} \)  
Photoreactor volume \([\text{m}^3]\)

\( x \)  
Axial direction [m]

\( x_1, x_2, x_3 \)  
Independent variables

\( x_i \)  
Cartesian components [m]

\( Y \)  
Response variable

**Abbreviations**

- **AD**  Average UV dose \([\text{J m}^{-2}]\)
- **AOP**  Advanced Oxidation Process
- **BBD**  Box-Behnken Design
- **CFD**  Computational Fluid Dynamics
- **CFSTR, CSTR**  Continuous (Flow) Stirred Tank Reactor
- **DO**  Discrete Ordinate
- **EEO**  Electrical Energy per Order \([\text{W min L}^{-1} \text{ log}^{-1}]\)
- **FA**  Formic acid
- **MB**  Methylene blue
- **pCBA**  Para-chlorobenzoic acid
- **RTE**  Radiative Transport Equation
- **TC-CB**  Taylor-Couette Collimated Beam
- **TOC**  Total Organic Carbon
- **UV**  Ultraviolet Light
- **UVT_{253.7}**  Ultraviolet Transmittance at 253.7 nm \([\% \text{ m}^{-1}]\)
- **VUV**  Vacuum Ultraviolet Light

**Greek letters**

\( \beta_i \)  Regression coefficients
\( \Gamma, \Gamma_{CA} \) Diffusion coefficient \([m^2 s^{-1}]\)

\( \delta \) Annulus width \([m]\)

\( \delta_r \) Depth of photoactive layer \([m]\)

\( \Delta_{CA,kx} \) Relative error in predicting the scalar \( C_A \) when the reaction \( k_x \) is omitted from the kinetic model \([\text{mol m}^{-3}]\)

\( \varepsilon_{A,\lambda} \) Molar absorption coefficient for the generic species \( A \) at a given wavelength \( \lambda \) \([m^3 \text{mol}^{-1} m^{-1}]\)

\( \varepsilon \) Turbulent dissipation rate \([m^2 s^{-3}]\)

\( \kappa \) Turbulent kinetic energy \([m^2 s^{-2}]\)

\( \lambda \) Wavelength \([m]\)

\( \mu \) Dynamic viscosity \([\text{kg m}^{-1} s^{-1}]\)

\( \mu_t \) Turbulent dynamic viscosity \([\text{kg m}^{-1} s^{-1}]\)

\( \rho \) Density \([\text{kg m}^{-3}]\)

\( \nu \) Kinematic viscosity \([m^2 s^{-1}]\)

\( \nu_t \) Turbulent kinematic viscosity \([m^2 s^{-1}]\)

\( \Phi_l \) Quantum yield \([\text{mol einstein}^{-1}]\)

\( \phi \) Generic scalar

\( \Omega \) Rotational speed \([\text{rad s}^{-1}]\)
Chapter 1

1 INTRODUCTION

The research presented in this thesis focuses on two distinct problems entailing the use of short-penetrating UV wavelengths for treating a contaminated fluid, namely the inactivation of specific microorganisms in highly absorbing fluids such as liquid foods by the 253.7 nm ultraviolet (UV) wavelength and the oxidation of model pollutants in ultrapure water by advanced oxidation processes initiated by vacuum ultraviolet (VUV) wavelengths (172 and 185 nm). In both cases, due to a very short light penetration into the fluid, an effective photoreactor design requires a deep understanding of the reactor hydraulics, the optics, and the reaction mechanisms involved, which can be taken into account by coupling reaction kinetics, optics, and hydraulics through the use of numerical models and computational fluid dynamics (CFD). Thus, a key aspect of this research is to understand and explore different photoreactor configurations in order to identify their industrial potential as well as their limitations.

More specifically, the first investigation presented hereafter focuses on the Taylor-Couette apparatus as an alternative collimated beam reactor to quantify the intrinsic inactivation kinetics of microorganisms in high absorbing fluids irradiated by 253.7 nm UV light. Then, the attention was directed towards the advanced oxidation processes (AOPs) initiated by short wavelengths (λ<200 nm) for the removal of total organic carbon (TOC) from ultrapure water. As known, at 185 and 172 nm pure water exhibits high absorbance leading, as in the first example of an application, to short penetration of the light in the treating fluid.

1.1 UV for the inactivation of pathogens in nearly-opaque fluids

After more than a century since its first documented application (Downes and Blunt, 1877), the use of ultraviolet light (UV) to inactivate pathogens can be considered a cost-effective and environmentally-friendly solution to disinfect contaminated fluids. The primary mechanisms of disinfection are also well understood: DNA or RNA absorption
of UV photons cause the formation of pyrimidine dimers and other structural changes that ultimately prevent cell replication and lead to cell death (Miller et al., 1999).

Many successful UV applications were documented (Severin et al., 1985; Hijnen et al., 2006; Gori and Caretti, 2008; Santoro et al., 2010; Blatchley III et al., 2012), in which monochromatic or polychromatic UV reactors were applied to disinfect fluids having an ultraviolet transmittance at 253.7 nm (UVT\(_{253.7}\)) ranging from nearly opaque (UVT\(_{253.7}\)<10% cm\(^{-1}\)) to nearly transparent (UVT\(_{253.7}\)>30% cm\(^{-1}\)). Recently, the use of UV light was considered as a possible alternative to chemical and thermal treatments of liquid foods although carefully reactor design was identified as critical step to overcome the high UV absorptivity of these fluids (Forney et al., 2004; Koutchma, 2009). It is also well established that experimentally determined UV dose-response curves are essential for accurate reactor sizing (U.S.EPA, 2003b). For relatively transparent fluids (UVT\(_{253.7}\)>30% cm\(^{-1}\)), such as municipal water and wastewater, such experiments are typically carried out in an industry standard apparatus known as a collimated beam (Bolton and Linden, 2003). It consists of a UV lamp, with emission characteristics similar to those used in the full-scale UV reactor, installed in an opaque housing equipped with an open, vertically mounted tube. The sample is located at a prescribed distance underneath the tube end such that only the quasi-collimated component of the emitted light is delivered to the irradiated sample. This way, assuming perfect mixing in the crystallization dish, controlled and quantifiable UV doses (which can be estimated using average dose calculations) can be delivered to the sample.

Given the potentially complex photochemistry associated with the UV treatment of nearly opaque fluids, it is often required to irradiate larger volumes in order to be able to use the same sample to investigate multiple aspects such as possible side-effects caused by the interaction of the absorbed light and the mixture constituents. In such circumstances, a standard collimated beam apparatus, as described by Bolton and Linden (2003), may not be the appropriate choice due to the violation of the ideal mixing assumption required during conventional collimated beam studies. Indeed, lack of sufficient mixing would result in a deviation from the desired kinetically-controlled irradiation regime; as a result, the observed performance, being mass-transfer controlled,
would not be representative of intrinsic inactivation kinetics. The limitations in this type of process consist in both photon short-penetration in the liquid and lack of sufficient mixing in order to provide a uniform dose distribution to the microorganisms and, subsequently, obtain an intrinsic inactivation kinetics.

1.2 AOP processes for degradation of chemical pollutants

One of the major threats to environmental and potable water quality is chemical pollution. These chemicals can be either dumped directly into the environmental waters as constituents of industrial or municipal wastewater effluents from treatment plants that do not fulfill the discharge limit rules, or indirectly as soil runoff or leachate of agricultural chemicals such as biocides and fertilizers. Generally, water-soluble substances can be transported and distributed easily in the water cycle.

In the past, attention was paid to studying the impact of direct effects of individual pollutants on the ecosystems. But with the advancement of scientific understanding, a considerable number of chronic effects that can only be detected after a long period of time were documented (Pal et al., 2013). Furthermore, larger quantities of recalcitrant substances are being found at long distances from their sources of discharge (Oller et al., 2011).

A feasible option for treating such persistent recalcitrant compounds is the use of the advanced technologies based on chemical oxidation, such as the Advanced Oxidation Processes (AOPs), widely recognized as highly efficient treatments. AOPs were studied intensively for decades. Various combinations of oxidants, radiation and catalysts such as $O_3/H_2O_2$, $UV/H_2O_2$, $UV/O_3$, $UV/TiO_2$, $Fe^{2+}/H_2O_2$, $Fe^{2+}/H_2O_2 + hv$, vacuum ultraviolet radiation (VUV) and ionizing radiation were developed for the removal of pollutants. These processes involve the generation of highly reactive radical intermediates, especially the hydroxyl (HO$^*$) radical (Glaze et al., 1987). The appeal of AOPs is the possibility of achieving complete mineralization of organic contaminants through a process that operates near ambient temperature and pressure.
1.2.1 The role of hydroxyl radical (HO\(^*\))

The HO\(^*\) is one of the most powerful oxidants known with oxidation potential 2.7 eV, second only after fluorine (Table 1.1).

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation potential [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>3.6</td>
</tr>
<tr>
<td>HO(^*)</td>
<td>2.7</td>
</tr>
<tr>
<td>Cl</td>
<td>2.2</td>
</tr>
<tr>
<td>O(_3)</td>
<td>2.1</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>1.8</td>
</tr>
<tr>
<td>ClO(_2)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The reaction rate constants between HO\(^*\) and organic species are in the range of 10\(^8\)-10\(^{10}\) L mol\(^{-1}\) s\(^{-1}\). Once free radical reaction was initiated by photolysis, ozone, hydrogen peroxide, etc., a series of reactions will ensue providing the oxidation or degradation of recalcitrant compounds present in water. The reactions of HO\(^*\), that is non-selective oxidant, with chemical compounds can proceed in mainly three different ways: 1) by the addition of HO\(^*\) to double bonds, 2) by H-atoms abstraction, which yields carbon centered radical and 3) by reaction mechanisms where HO\(^*\) acquires an electron from an organic substance (Matilainen et al., 2010).

1.3 Vacuum-UV light

Among several advanced oxidation processes one involves the use of vacuum-UV, which relies on the high energy photons generated by VUV lamps that emit radiation at wavelengths lower than 190 nm. Such short wavelengths are most commonly produced by xenon excimer lamps (excilamps). The photonic energy produced by these lamps is greater than that of the 253.7 nm wavelength produced by conventional low pressure mercury lamp. This high energy is transferred to the water molecule that is split resulting
in the HO* production without adding any other chemical reagent. The cost of excimer
lamps that can emit a quasi-monochromatic VUV radiation, depending on the type of the
gas used, is greater than that of low pressure mercury lamps providing similar electrical
efficiency (Oppenländer, 2003). Moreover, even ultrapure water exhibits high absorption
at these low wavelengths and so the penetration of UV light is confined in millimeters for
the case of 185 nm, or fraction of a millimeter for the case of 172 nm. The following
Figure 1.1 shows the absorption coefficient of ultrapure water (in napierian base),
measured by different authors, in a wavelength range of 155-200 nm (Barrett and
Baxendale, 1960; Barrett and Mansell, 1960; Halmann and Platzner, 1965; Querry et al.,

Figure 1.1: Absorption coefficient of distilled water at short wavelengths
1.3.1 Lab-scale experiments using vacuum-UV light

Numerous papers are available in the scientific literature focusing on lab scale experiments involving the degradation of chemicals due to direct photolysis of the compounds as well as oxidation of organic species in water resulting from reaction with reactive oxygen species (ROS) such as HO\(^{•}\) created from the photolysis of water and subsequent reactions initiated by short wavelengths light. For example in the publication by Gonzalez (Gonzalez and Braun, 1994) the effect of depletion of nitrite and nitrate, in aqueous solutions, initiated by the VUV photolysis of water under different experimental conditions was measured. A cylindrical Xe excimer lamp of 25 cm length and 3 cm external diameter developed by ABB (Baden, Switzerland) emitting 172 nm was used as the irradiation source. The photochemical reactor was of annular geometry with volume 220 mL. It was noted that the depletion of nitrate depends strongly on the presence of dissolved oxygen and on temperature; higher rates of nitrate depletion were observed for argon saturated solutions at 60 °C. In their work also a numerical code was developed in order to simulate the elementary reactions involved in VUV irradiation of aqueous solutions of nitrite and nitrate at 20 and 25 °C. In the case of irradiation of ultrapure water, 12 different species were considered: HO\(^{•}\), H\(^{+}\), e\(_{aq}\)\(^{-}\), HO\(_2\)\(^{•}\), O\(_2\)\(^{•}\), H\(_2\), O\(_2\), H\(_2\)O\(_2\), HO\(_2\)\(^{-}\), H\(^+\), OH\(^{-}\) and H\(_2\)O ending up with 28 total reactions. In a more recent work Gonzalez (Gonzalez et al., 2004) considered methanol (CH\(_3\)OH) as a simple model pollutant of natural water and its oxidation was investigated in a pH range of 1-12 ending up with 14 different species (HO\(^{•}\), H\(^{+}\), e\(_{aq}\)\(^{-}\), HO\(_2\)\(^{•}\), O\(_2\)\(^{•}\), H\(_2\), O\(_2\), H\(_2\)O\(_2\), HO\(_2\), H\(^+\), OH\(^{-}\), O\(_3\)\(^{•}\), HO\(_3\)\(^{•}\) and H\(_2\)O) and a minimum set of 25-30 reactions and acid-base equilibria for a complete reaction scheme.

The PhD thesis of Jakob (1992, and subsequent paper published in 1993) focused on oxidative degradation of 4-chlorophenol (4-CP) in aqueous solution using a lab scale annular reactor with the following geometric configuration: internal diameter of 4.5 cm, a Xe-excimer lamp, emitting monochromatic light at 172 nm, with 3 cm diameter and 13 out of 24 cm total length immersed in an annular reactor. The total volume of treated solution was 220 mL. The study concluded that neither oxygen concentration nor the presence of carbonates or nitrates affected the rate of 4-CP degradation.
An actinometric experimental method was developed by Heit (Heit et al., 1998) using cis-trans isomerisation of cyclooctene solution in a lab scale apparatus with a VUV lamp at 172 nm. The production rate of hydroxyl radicals was determined from the rate of degradation of methanol dissolved in the aqueous reaction system. Once the rates of production of hydroxyl radicals and methanol degradation were determined, the quantum yield of the homolysis of water by VUV irradiation was calculated.

From all these papers, based on the experimental works presented, it can be noticed the inadequacy of the VUV photoreactors used due to a mismatch between reactor gap and light penetration. These annular photoreactors have an inner space (gap) of millimeters, where the fluid resides, meanwhile the light, at that wavelength, has a penetration of a fraction of a millimeter thereby only a small amount of the total fluid is treated. Moreover there is no agreement among these authors on the complete set of elementary chemical equations involved in the process of photolysis of pure water and, sometimes, the values of the rate constants are in disagreement. Due to the above issues, a better understanding of the hydraulic and chemical phenomena that take place would be required to provide a more definitive understanding of the process. This understanding cannot be achieved with experimental campaigns using an annular photoreactor with gap of few micrometers, due to manufacturing limitations, but it is possible by developing a numerical kinetic model which involves hydraulic, UV radiation, mass transfer and kinetic equations; however, modeling VUV processes may present some challenging tasks for a number of reasons. First of all, several reactions occur during VUV photolysis of liquid water only involving several radical and stable species. These photogenerated radicals can react with other species present in the system. Second, kinetics of photoreactions depend strongly on the radiation field in the reactor, and steep gradients are present in VUV systems due to the high absorption coefficient of water at short wavelength, which produces steep gradients in the reaction rate of photoreactions and in the concentration of photogenerated radicals. In particular, the ultrapure water absorption coefficient at 172 nm is about 555.5 cm\(^{-1}\) (base 10) and so 90% of photons are absorbed in an 18 µm layer close to the lamps. On the other hand, VUV-Hg lamps have an efficiency around 30-40% at 253.7 nm and 5-10% of UV power is emitted at 185 nm. The absorption coefficient of pure water at 185 nm is 1.8 cm\(^{-1}\) (base 10) much lower than 172 nm so that 90% of photons are absorbed in
a 5.5 mm layer. The radiation profile, for these types of lamps, is less steep and more uniform. Due to the better penetration of the light at this wavelength in the solution, the advanced oxidation at 185 nm can be competitive with the VUV process at 172 nm.

### 1.3.2 Mechanistic AOP models based on water photolysis by low wavelengths

Few mechanistic models were proposed in the literature to describe the degradation of pollutants at low wavelength radiation in aqueous solutions. Zvereva (2010) modeled the concentration of products of liquid and gaseous water decomposition under the action of VUV radiation at 172 nm. The water decomposition resulted in the formation of the following main products: H\(^{+}\), HO\(^{+}\), e\(_{aq}^{-}\), H\(_2\), OH\(^{-}\), O\(^{2-}\), H\(^{+}\), H\(_2\)O\(_2\), O\(_2\)\(^{2-}\), HO\(_2\)\(^{+}\), HO\(_2\)\(^{-}\) and O\(_3\)\(^{-}\). She composed and solved a system of 53 total kinetic equations with respect to the concentration of these components. The author neglected the diffusion term of the products because diffusion rates were smaller than the time scale considered (\(10^{-5}\)-\(10^{-4}\) cm\(^2\) s\(^{-1}\) versus \(10^{-2}\)-\(10^{-1}\) s). In the second part of the study the author used the model to estimate the decomposition of PCBs under the action of HO\(^{+}\). Zvereva showed that the VUV radiation causes efficient formation of highly reactive HO\(^{+}\) which were able to oxidize the polychlorinated biphenyl, starting from a concentration of its average solubility in the water, in less than 0.004 s in liquid water.

Another kinetic model was developed by Imoberdorf (Imoberdorf and Mohseni, 2012) considering the most important reactions involved in photolysis of water at 185 nm with presence of 2,4-dichlorophenoxyacetic acid (2,4-D) as a model micropollutant: 32 main reactions and 4 reactions of pollutant oxidation were included. They discovered that the initial degradation rate of 2,4-D in ultrapure water was not dependent on the initial concentration of the contaminant, and the presence of alkalinity and natural organic matter (NOM) reduced the degradation rate by up to 72%. The kinetic model developed in that work included also the propagation and absorption of radiation in the reactor. The kinetic model was verified by comparing the predicted data with experimental results.
1.4 Thesis objectives and outline

The main objective of this thesis is to evaluate the efficiency and limitations of different annular photoreactor configurations where the highly absorbing fluid is irradiated by UV/VUV lamps. To achieve this, the following steps were undertaken and discussed in the following chapters:

- In Chapter 1, a literature review was presented. The focus was directed towards reviewing the documented applications and process performance of fluids irradiated by 253.7 nm light for the quantification of intrinsic inactivation kinetics highlighting the limitations of a specific device when the fluids exhibited high UV absorption. Then, the attention was paid to the previously published papers describing mechanistic models for advanced oxidation processes initiated by short wavelengths (172 and 185 nm) for degradation of chemical pollutants in ultrapure waters. Available experimental and numerical studies were summarized and reported in this chapter.

- In Chapter 2, a modeling and experimental study was carried out using a Taylor-Couette apparatus as an alternative to a collimated beam reactor. CFD simulations were first verified, and then passive and active tracer tests were experimentally conducted in order to calibrate and validate the model. Finally, the validated CFD model was used for a sensitivity study using hypothetical fluids with varying absorption coefficients in order to identify a criterion for the accurate quantification of microbial inactivation rate constants.

- In Chapter 3, a novel mechanistic model is presented to simulate the process performance and reactor hydraulics of VUV photolysis at 172 nm and 185 nm on ultrapure water with hydrogen peroxide and formic acid (as investigated target micropollutant). The mechanistic model was validated with previously published data and used to investigate the role of HO* in these different processes.

- In Chapter 4, data collected from experimental campaigns using VUV reactors are reported. The studies were conducted on annular thin-film photoreactors where the lamp is placed parallel to the main direction of the fluid and emitting 172 nm, or 185/253.7 nm wavelengths. Specific pollutants such as para-chlorobenzoic acid
and methylene blue were used. Different concentrations of pollutants as well as flowrates and annular gaps were investigated. Subsequently, the previous validated mechanistic model (discussed in Chapter 3) was extended to other elementary reactions in order to take into account the degradation mechanism of para-chlorobenzoic acid. The tested annular photoreactor geometries were modeled in MATLAB and, subsequently, a more detailed model was carried out using CFD. The model was validated after a careful calibration and finally applied to the exploration of different baffled annular photoreactor configurations by changing variables such as annular gap, flowrate and initial concentration of target model pollutants.

1.5 References


Chapter 2

2 QUANTIFYING ULTRAVIOLET INACTIVATION KINETICS IN NEARLY OPAQUE FLUIDS

2.1 Introduction

An alternate design to the standard collimated beam apparatus is proposed for advanced kinetic studies in low transmittance and nearly opaque fluids. The design is based on the use of the well-known Taylor-Couette flow (Karpel et al., 1997; Prigent and Dauchot, 2000) established between rotating cylinders, with UV light delivered through the inner one made of quartz, irradiated by an axially mounted UV lamp. This new Taylor-Couette collimated beam (TC-CB) apparatus exploits the fluid instabilities resulting in the formation of toroidal, counter-rotating pairs of vortices, and the axi-symmetric fluence rate generated by the central position of the 253.7 nm UV lamp.

Specifically, the disinfection performance of a TC-CB system is investigated using computational fluid dynamics (CFD). First, CFD simulations were verified by comparing the numerical solutions obtained from the current CFD model with analytical equation and previously published information. Then, passive and reactive tracer experiments were conducted in order to macroscopically calibrate and validate the CFD model. Finally, the validated CFD model was used to conduct a sensitivity study using hypothetical fluids (with varying absorption coefficients) and hypothetical inactivation kinetics (with various inactivation rate constants, or \( D_{10} \)) as listed in Table 2.1) to determine a generalized criterion for accurate kinetic studies of nearly opaque fluids using a TC-CB apparatus.

Table 2.1: \( D_{10} \) [mJ cm\(^{-2}\)] measured at 253.7 nm for various pathogen types

<table>
<thead>
<tr>
<th>Pathogen type</th>
<th>( D_{10} ) [mJ cm(^{-2})]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Escherichia coli</em> O25:K98:NM</td>
<td>5</td>
<td>Sommer et al., 2000</td>
</tr>
<tr>
<td><em>Murine norovirus</em></td>
<td>10</td>
<td>Lee et al., 2008</td>
</tr>
<tr>
<td>Virus/Organism</td>
<td>Time (min)</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Coxsackie B3</td>
<td>15</td>
<td>Gerba et al., 1996</td>
</tr>
<tr>
<td>MS2 (Phage)</td>
<td>20</td>
<td>Lazarova and Savoye, 2004</td>
</tr>
<tr>
<td>Adenovirus 41 ATCC TAK</td>
<td>25</td>
<td>Meng and Gerba, 1996</td>
</tr>
<tr>
<td>Adenovirus 40 ATCC Dugan</td>
<td>30</td>
<td>Meng and Gerba, 1996</td>
</tr>
<tr>
<td>Adenovirus type 2</td>
<td>35</td>
<td>Ballester and Malley, 2004</td>
</tr>
<tr>
<td>Acanthamoeba spp.</td>
<td>40</td>
<td>Hijnen et al., 2006</td>
</tr>
</tbody>
</table>

2.2 Materials and Methods

2.2.1 The Taylor-Couette collimated beam apparatus

The TC-CB apparatus used in this study is schematically represented in Figure 2.1. It consists of a low pressure mercury vapor UV lamp (UV Max Pro, Trojan Technologies, Canada) emitting 253.7 nm radiation, positioned along the vertical axis of the apparatus, two concentric cylinders (an inner quartz rotor and an outer polyvinyl-chloride stator), and an optional doped sleeve to control the incident radiation entering the fluid region.

The physical dimensions of TC-CB apparatus are as follows: the inner and the outer cylinders have radii of 73.8 mm and 77.1 mm respectively, leaving a net annulus of 3.3 mm between cylinders. The inner quartz rotor and the polyvinyl-chloride (PVC) stator have thicknesses of 5 mm and 6 mm, respectively. The total vertical length of the system is 198.6 mm of which 123.7 mm is directly exposed to UV light. The TC flow is generated by rotating, via a motor, the inner quartz cylinder while keeping the outer cylinder stationary.

The TC-CB is connected to a 40 L reservoir via a Masterflex L/S HV-07523-80 peristaltic pump (Cole-Parmer, Canada) which can be used to control flow in the 100-1000 mL min$^{-1}$ range. The treated fluid, consisting in a 0.6 M potassium iodate
actinometer (Rahn et al., 2003), diluted in Milli-Q water (dilution factor 1:20, absorbance at 253.7 nm ~ 1.9 measured with a 1 cm cuvette), exits the TC-CB annulus via an overflow weir and is continuously collected in sterile vials. Absorbance measures were conducted, at the wavelength of interest (352 nm to detect the photoproduct of potassium iodate actinometry and 664 nm to quantify methylene blue concentration), using a Cary50 UV-Vis spectrophotometer (Agilent, USA).

A doped quartz sleeve with reduced transmittance at 253.7 nm (GE Type 214) was optionally mounted co-axially to the UV lamp to control the fluence rate distribution inside the fluid domain.

Figure 2.1: Schematic representation of the flow loop used for TC-CB experiments
2.2.2 Irradiance measurements

A X9\textsubscript{11} radiometer equipped with an UV-3718-4 detector (Gigahertz-Optik, Germany) was used to measure the radiation emitted by the 253.7 nm UV lamp, with and without doped sleeve, at the outer surface of the rotating quartz cylinder, that is, the cylindrical face exposed to the fluid without the presence of any liquid in the annulus. Measurements were conducted in triplicate in order to determine the mean and standard deviation. The sensor was installed using a vertical stand placed besides a graduated tape to allow irradiance measurements at different vertical positions. The position of the sensor was kept perpendicular to the vertical lamp axis and at constant distance from the surface of the lamp (~7.4 cm). Irradiance measurements were taken also in presence of a low transmittance quartz sleeve which was used to adjust the average dose of the apparatus.

2.2.3 CFD governing equations

Two dimensional axi-symmetric CFD simulations were carried out to solve the Taylor-Couette flow established in the annulus of the TC-CB apparatus. Ansys Fluent 12.1.4 (Ansys Fluent, Canonsburg) was used in order to numerically solve the governing equations in cylindrical coordinates.

- **Continuity equation**
  
  The continuity equation for an incompressible, constant-density fluid is given by
  
  \begin{equation}
  \frac{\partial(\rho u_x)}{\partial x} + \frac{\partial(\rho u_r)}{\partial r} + \frac{\rho u_r}{r} = 0
  \end{equation}

  where \(x\) and \(r\) are the axial and radial coordinates, respectively, and \(u_x\) and \(u_r\) are the axial and radial velocities.

- **Navier-Stokes equations**
  
  The Navier-Stokes equations for a 2D incompressible, constant viscosity fluid can be written in cylindrical coordinates as follows:

  \[
  \frac{1}{r} \frac{\partial(r \rho u_x u_x)}{\partial x} + \frac{1}{r} \frac{\partial(r \rho u_r u_x)}{\partial r} = \]
The tangential momentum is given by:

\[
- \frac{\partial P_a}{\partial x} + \frac{1}{r} \frac{\partial}{\partial x} \left[ r \mu \left( 2 \frac{\partial u_x}{\partial x} - \frac{2}{3} (\nabla \cdot \bar{u}) \right) \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ r \mu \left( \frac{\partial u_x}{\partial r} + \frac{\partial u_r}{\partial x} \right) \right] \tag{2.2}
\]

and

\[
- \frac{\partial P_a}{\partial r} + \frac{1}{r} \frac{\partial}{\partial x} \left[ r \mu \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_r}{\partial r} \right) \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ r \mu \left( 2 \frac{\partial u_r}{\partial r} - \frac{2}{3} (\nabla \cdot \bar{u}) \right) \right] = \frac{1}{r} \frac{\partial}{\partial x} \left[ \nu \frac{\partial u_x}{\partial x} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ \nu \frac{\partial u_r}{\partial r} \right] - \frac{2 \mu u_r}{r^2} + \frac{2 \mu}{3} (\nabla \cdot \bar{u}) + \frac{\rho u_{\theta}^2}{r} \tag{2.3}
\]

The tangential momentum is given by:

\[
- \frac{\partial P_a}{\partial x} + \frac{1}{r} \frac{\partial}{\partial x} \left[ r \mu \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_r}{\partial r} \right) \right] = \frac{1}{r} \frac{\partial}{\partial x} \left[ r \mu \left( \frac{\partial u_x}{\partial x} \right) \right] + \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^3 \mu \frac{\partial u_{\theta}}{\partial r} \right] - \frac{\rho u_r u_{\theta}}{r} \tag{2.4}
\]

where

\[
(\nabla \cdot \bar{u}) = \frac{\partial u_x}{\partial x} + \frac{\partial u_r}{\partial r} + \frac{u_r}{r} \tag{2.5}
\]

in which \(u_{\theta}\) is the swirl (azimuthal) velocity. In the simulations the effect of rotation of the wall was taken into account by assigning a radial pressure gradient as shown in Eq. 2.6

\[
\frac{\partial P_a}{\partial r} = \frac{\rho \Omega^2}{r} \tag{2.6}
\]

As the distribution of angular momentum in non-ideal vortex evolves, the radial pressure gradient changes, driving radial and axial flows.
• **Scalar transport equation**

Since in this investigation the concentrations of both tracers and microbes were assumed to be sufficiently small so that all the physical properties of the carrying fluid remained constant, a generalized scalar transport equation (Eq. 2.7) was employed and involved in the transport dynamics:

\[
\frac{\partial \rho \phi}{\partial t} + \sum_{i} \left( \rho u_i \phi - \Gamma \frac{\partial \phi}{\partial x_i} \right) = S_{\phi}
\]  

(2.7)

where \( \Gamma \) and \( S_{\phi} \) are the diffusion coefficient and source term for the scalar equation respectively. The source term \( S_{\phi} \) for passive, reactive and microbial inactivation is given in Table 2.2.

**Table 2.2: Source terms used in the CFD model**

<table>
<thead>
<tr>
<th>Description</th>
<th>( S_{\phi} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microbial Inactivation ((N))</td>
<td>(-kIN)</td>
</tr>
<tr>
<td>Absorbed Energy (AE) – Reactive</td>
<td>(A_{\lambda}I)</td>
</tr>
<tr>
<td>Tracer concentration – Passive</td>
<td>0</td>
</tr>
</tbody>
</table>

• **Radiative transport equation**

In this study, fluence rate distribution for all three media involved (air, quartz and water) was described using the radiative transfer equation (RTE) for non-scattering media:

\[
\frac{dI(\vec{r}, \vec{s})}{ds} + A_{\lambda}I(\vec{r}, \vec{s}) = 0
\]

(2.8)

where \( A_{\lambda} \) is the absorption coefficient of each media (air, quartz, water) and \( I \) the fluence rate distribution which depends on position and direction vectors (\( \vec{r}, \vec{s} \)). Appropriate refractive indexes were set for all three media involved to account...
from light refraction. Given the high absorbing nature of the fluids involved, reflection was not considered. The discrete ordinates (DO) radiation model was used to solve the RTE for a finite number of discrete solid angles associated with a vector direction $\vec{s}$.

- **Inactivation kinetics**

  It is well documented that many pathogens, irradiated by UV light, follow a first order inactivation model (Hijnen et al., 2006; Ye et al., 2007; Mounaouer and Abdennaceur, 2012). Therefore, this study assumed that the inactivation rate changes linearly with respect to pathogen concentration, $N$, and fluence rate, $I$, such that:

  $$\frac{dN}{dt} = -kIN$$  \hspace{1cm} (2.9)

  where $k$ (or $k^{-1}$, e.g. the $D_{10}$ that is the dose required for one log inactivation of a given microbe) is the first order inactivation rate constant. After integration, the following expression can be obtained:

  $$\frac{N}{N_0} = e^{-kD}$$  \hspace{1cm} (2.10)

  where $D$ represents the UV dose (the dose for a given organism population is the integration of fluence rate and time). In an ideal apparatus suitable for kinetic studies, either the fluence rate distribution is carefully controlled such that it is uniform across the entire fluid domain or enough mixing must be provided to overcome fluence rate gradients. In the latter case, the delivered dose can be replaced with average dose ($AD$).

  **2.2.4 Grid independence study**

  Grid independence studies were carried out to determine the minimum number of elements needed to accurately solve the flow field. Simulations were carried out for a
Taylor number ($T_a$) of 46,534 corresponding to the angular velocity of 40 rpm used during the experiment. It is defined as:

$$T_a = \frac{\delta^3 R_i \Omega^2}{\nu^2}$$

where $\delta$ is the annulus width between the inner and outer cylinder, $R_i$ the inner radius of the annulus, $\nu$ is the kinematic viscosity of the treating fluid and $\Omega$ the angular velocity of the rotating cylinder. As shown by Eq. 2.11, $T_a$ is function of the reactor geometry (inner radius $R_i$ and annulus $\delta$) and the angular velocity of the inner cylinder, but it is independent of reactor flowrate which is taken into account by axial Reynolds number (Eq. 2.13).

Figure 2.2 shows the normalized velocity profiles along radial direction at different grid resolution (5x100, 10x200, 20x400, and 30x600). The first and the second number refer to the number of elements placed in the annulus and along the direction parallel to the vertical axis of the cylinder, respectively. In all cases, the aspect ratio was kept constant as 1:1. As shown in Figure 2.2, a 20x400 grid returns grid independent results (as the error compared with the solution obtained with a 30x600 grid is less than 1%).
2.2.5 Tracer studies

Two types of tracer studies using passive and UV photo-reactive fluids were conducted in order to macroscopically validate the flow field and its convolution with the fluence rate distribution within the annulus. The first type consisted of applying, at the TC-CB inlet, a step injection of a conservative, light-inert tracer (methylene blue) in order to determine the axial dispersion and the hydraulic behavior of the system (Levenspiel, 1998). The second type of tracer tests were conducted at steady state using a modified protocol of the potassium iodate actinometer (Rahn et al., 2003). It consisted of a 1:20 diluted mixture of 0.6 M of potassium iodide (KI, Sigma-Aldrich, USA) and 0.1 M of potassium iodate.
(KIO₃, Sigma-Aldrich, USA) in 0.01 M sodium tetraborate hydrate (Na₂B₄O₇·10 H₂O, Sigma-Aldrich, USA) buffer solution at pH 9.2, which was injected at the TC-CB inlet to generate a photoproduct (tri-iodide I₃⁻), the concentration of which increases as a function of the total absorbed energy accumulated during the exposure paths in the irradiated annulus. As such, its response is representative of both the fluence rate field and the flow field established in the annulus.

In both cases, the TC-CB apparatus was first brought to pseudo steady-state conditions by feeding it with deionized water contained in the 40 L reservoir (Figure 2.1) at the desired volumetric flow (Table 2.3) and waiting for more than three times the average residence time of the entire system; then, the inner quartz cylinder was put in rotation at 40 rpm to give a Taylor number of 46,534 (greater than the critical Taylor number of 2,900).

<table>
<thead>
<tr>
<th>Flowrate [mL min⁻¹]</th>
<th>Average residence time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>116</td>
<td>176.6</td>
</tr>
<tr>
<td>285</td>
<td>71.9</td>
</tr>
<tr>
<td>405</td>
<td>50.6</td>
</tr>
<tr>
<td>445</td>
<td>46.1</td>
</tr>
<tr>
<td>517</td>
<td>39.7</td>
</tr>
<tr>
<td>594</td>
<td>34.5</td>
</tr>
</tbody>
</table>

After reaching steady state, the suction pipe of the peristaltic pump was switched to a smaller reservoir containing the tracer in order to generate the desired step function. Immediately after switching, consecutive aliquots of 15 mL each were collected from the
reactor outlet for absorbance measurements (conducted using a Cary50 UV-Vis spectrophotometer).

Similarly to the procedure followed in biodosimetry studies (U.S.EPA, 2006), two parallel experiments were conducted in order to predict the steady-state conversion of the TC-CB apparatus continuously fed with the reactive tracer. The first step entailed the quantification of the tracer response using a standard collimated beam apparatus. Samples of 3, 6, 10 mL of 1:20 diluted actinometer were irradiated at different exposure times (0-2-4-6-8-10 min), and the 352 nm absorbance of the irradiated solution was measured with a Cary50 UV-Vis spectrophotometer. Those measurements were plotted against absorbed UV energy, which was calculated using the optical properties of the reactive tracer (4.832 cm$^{-1}$, base-e) as well as the incident radiation measured with an ILT1700 radiometer (International Light Technologies, USA), and the resulting curve fitted with a polynomial function relating the change in absorbance at 352 nm (i.e., proportional to the formation of the photoproduct) to the photon energy absorbed by the fluid. The resulting relationship was also used in the CFD model as source term of the scalar transport equation.

Once the response curve for the actinometric solution had been established, the second step entailed challenging the TC-CB with a pre-made 20 L solution of diluted actinometer. The actinometric solution, continuously mixed with a submersible pump, was injected, after lamp warm up, into the TC-CB annulus at various flowrates while keeping the angular velocity of the quartz rotor constant at 40 rpm. A doped quartz sleeve having 2% transmittance at 253.7 nm was used to reduce the incident radiation in order to avoid actinometer saturation. Samples were collected continuously at the outlet and the absorbance at 352 nm was measured. Utilizing the response curve established separately, the UV dose delivered by TC-CB at each test point could be calculated.

2.2.6 Numerics

The CFD model was solved in steps. In the first step, the Navier-Stokes equations were solved to obtain the flow field. In the second step, the radiative transport equation was solved using the discrete ordinate model (Crapulli et al., 2010) to determine the fluence
rate distribution in the annulus (taking into account the light transport phenomena occurring in all three media, namely air, quartz and water). Finally, using the appropriate source terms, additional scalar transport equations were solved to predict either the tracer test response or the microbial inactivation at the reactor outlet.

The properties of the simulated fluid were considered to be similar to those of water, specifically with a density and viscosity of 1000 kg m\(^{-3}\) and 0.001 kg m\(^{-1}\) s\(^{-1}\), respectively, and the refractive index at 253.7 nm was assumed constant and equal to 1.37. The absorption coefficient was either set to the experimentally measured value (for the case of tracer tests) or varied in the range of 10.5 m\(^{-1}\) (UVT\(_{253.7}\) = 90% cm\(^{-1}\)) to 1151.3 m\(^{-1}\) (UVT\(_{253.7}\) = 0.001% cm\(^{-1}\)) to investigate the response of the TC-CB for fluids at different opacity. The absorption and the refractive index at 253.7 nm of the inner rotor, made by natural quartz, were set to 39.3 m\(^{-1}\) and 1.505, respectively (Kitamura et al., 2007). The DO model, adopted for solving the RTE, was discretized using 8x8 theta and phi divisions and 4x4 as pixilation. The lamp was considered as an emitting surface with a cosine emitting behavior. A second order upwind scheme was used as the solution method for the DO radiation model.

The no-slip condition was applied at all reactor walls. Two different sets of simulations were carried out, one for each rotational speed of the rotor: 0 and 40 rpm.

As a result of the applied flowrates ranging from 116 mL min\(^{-1}\) to 594 mL min\(^{-1}\), the axial and the radial Reynolds numbers explored varied between 0 to 1018.7 and 4.09 to 20.91 (Eq. 2.12 and 2.13), respectively, thus justifying the choice of a laminar model.

\[
\text{Re}_{\text{radial}} = \frac{\delta R_i \Omega}{\nu} \quad (2.12)
\]

\[
\text{Re}_{\text{axial}} = \frac{\delta u_x}{\nu} \quad (2.13)
\]

A segregated implicit solver method was used for solving the momentum equation using a second order accurate upwind scheme (Patankar, 1980). For the pressure equation, the
standard scheme was used which is already available in FLUENT (Ansys Fluent 12.0 2009).

The power law scheme was used to solve the user defined scalars and, after full convergence, a mass-flow-weighted average calculation was applied in order to estimate the scalar concentration at the reactor outlet.

All the simulations were conducted achieving a value of residuals at least below $10^{-4}$.

### 2.3 Results and Discussion

#### 2.3.1 Model verification

Although CFD modeling of Taylor-Couette reactors were successfully used by several authors (Marchisio and Barresi, 2003; Vedantam et al., 2006; Dong, 2008), the first step in this study was to compare the predictions obtained using our CFD model against previously published information to verify their accuracy. First, it was verified whether the velocity field prediction obtained using the 2-dimentional axi-symmetric approach undertaken in this study was equivalent to ones obtained in a 3-dimensional framework of analysis. As shown in Figure 2.3 it was confirmed that both 2D and 3D frameworks yielded similar results. Second, CFD results were compared against the analytical solution available for subcritical Taylor numbers (Caton et al., 2000). In particular, the radial velocity distribution for stable flow with $T_a = 116$ was compared against Equation 2.14 and 2.15.

$$u_x = 0 ; u_r = Ar + \frac{B}{r} ; u_\theta = 0$$

(2.14)

where

$$A = -\Omega \frac{(\frac{R_i}{R_o})^2}{1 - (\frac{R_i}{R_o})^2} \text{ and } B = \Omega \frac{R_i^2}{1 - (\frac{R_i}{R_o})^2}$$

(2.15)
Third, the predicted radial velocity distribution for unstable flow at $T_a = 46,534$ (for which an analytical solution does not exist) was compared against data reported by Moser et al. (1983). As Figure 2.4 suggests, a very good agreement exists for both Taylor regimes, which verifies the accuracy of the governing equation and numerical schemes used in this work in describing the flow physics associated with the Taylor-Couette flow.
Finally, it was also verified that the Taylor number ($T_a$) selected for our experimental work was well above the critical Taylor value for which fluid instabilities are generated. The critical threshold was identified by running a series of CFD simulations at increasing values of $T_a$. Results are reported in Figure 2.5 and indicated that the critical Taylor number for the proposed TC-CB geometry would occur for $T_a = 2,908$. The critical $T_a$ is only function of geometrical properties of the TC-CB apparatus, the kinematic viscosity of the fluid, and the rotational speed of the rotor. The axial flow can affect the shape of the axial-symmetric counter-rotating vortices. In particular, for large axial Reynolds numbers, the flow becomes wavy vortex flow (Wereley and Lueptow, 1999).
2.3.2 Model calibration

After verifying the CFD model, a number of experiments were conducted to calibrate the irradiance field produced by the UV lamp located in the center axis of the TC-CB apparatus. Specifically, all the major phenomena involved in the radiation transport such as refraction and reflection through multiple media and absorption of different materials were considered and modeled. The UV lamp emission was considered to follow a Lambertian emission model. The overall UV output assigned to the lamp as a boundary condition was changed in order to have a match between numerical irradiance and radiometric measurements to ensure that the appropriate photon flux was used in the CFD simulations. As shown in Figure 2.6, an excellent agreement exists between the irradiance predicted by the CFD model and the measurements. When the doped sleeve
was used to reduce the UV output, a ~98% decrease in irradiance was observed, which is consistent with the quartz transmittance information obtained by the manufacturer.

Figure 2.6: Measured and calculated irradiance profiles at the quartz/fluid interface (with and without doped sleeve quartz)

2.3.3 Model validation

Experiments were designed to validate the different subroutines associated with the integrated CFD model. Specifically, the flow and scalar transport submodels, and their convoluted behaviour, were validated using passive and reactive tracer tests. Passive tracer tests were conducted using methylene blue dye. As Figure 2.7 shows, the virtual breakthrough curve predicted by CFD agrees well with experimental data collected for $T_a = 46,534$.

To ensure that the sensitivity of this measurement was sufficient to characterize the flow behaviour in the presence of vortices, the experimental breakthrough curve was also
compared with both the theoretical response of a plug flow reactor (dotted line) and the case of $T_a = 0$ (rotor with angular velocity equal to zero). From the simulated curves, it may be seen that the tracer response is strongly affected by the fluid instability induced by the inner quartz rotation, being markedly different for the two Taylor regimes. This confirms that the CFD model is able to represent some effects of the fluid instability, particularly the macroscopic transport phenomena associated with the TC-CB apparatus in unstable regime.

\[ \text{Figure 2.7: Breakthrough curve with passive tracer} \]

It should be noted, however, that, while radial mixing is an absolute requirement for kinetic studies in nearly opaque fluids, the presence of a strong axial dispersion as measured in this test is not an ideal attribute for a laboratory UV device. This is because the distribution of retention time may lead to a non-uniform UV dose distribution which, if not controlled properly, may lead to the quantification of apparent instead of intrinsic
UV kinetics. The presence of axial dispersion is also confirmed by the transient CFD simulations conducted for the passive tracer for both $T_a = 46,534$ and $T_a = 0$ (Figure 2.8).

![Normalized transient tracer concentration](image)

**Figure 2.8: Normalized transient tracer concentration $T_a = 46,534$ (left) and $T_a = 0$ (right).**

After validating the flow and radiation transport phenomena individually, the capability of the CFD model to predict their convoluted behaviour was tested experimentally using a light-sensitive, reactive tracer. The use of a reactive tracer enables the validation of the interplay of mass transport and reaction phenomena involved in the TC-CB apparatus. Steady-state absorbance measurements indicating the concentration of photoproduct formed were made at different flowrates for $T_a = 46,534$, and then compared with simulations obtained for the same conditions. In order to precisely model the change in absorbance occurring in the TC-CB apparatus, the response of the diluted actinometer was first characterized in a standard collimated beam (using various fluid volumes and exposure times) and then incorporated, using a user-defined function and a polynomial source term, into the CFD model (Figure 2.9).
A user-defined function is a function that can be dynamically loaded with the FLUENT solver, programmed in C language, which allows the user to introduce additional terms to the governing equations. As shown in Figure 2.10, the CFD model was capable of predicting fairly well the steady state absorbance measured at the TC-CB outlet, although some deviation could be observed for low flow conditions.
2.3.4 CFD analysis

The validated CFD model was used to locally analyze the main transport phenomena involved in the TC-CB reactor, as well as to guide the proper application of such a device for kinetic studies in low transmittance and nearly opaque fluids. Figure 2.11 shows local radial velocity and fluence rate distributions (for two different UVT$_{253.7}$) for $T_a = 46,534$ (corresponding to a steady state angular velocity of 40 rpm) together with the main features of the TC-CB apparatus used in this study (the two concentric cylinders, the UV lamp and doped quartz sleeve). The radial velocity contour (on the left) clearly shows the characteristic Taylor-Couette flow behaviour (Taylor, 1923) for which the simultaneous presence of quasi-stagnant and high radial velocity regions ranging from -2.5 cm s$^{-1}$ to 2.5 cm s$^{-1}$ can be observed. On the right side, the fluence rate distributions for a nearly
clear (UVT$_{253.7} = 90\%$ cm$^{-1}$) and a nearly opaque fluid (UVT$_{253.7} = 0.1\%$ cm$^{-1}$) are displayed. As expected, a strong fluence rate gradient is observed for the case of UVT$_{253.7} = 0.1\%$ cm$^{-1}$ which, if not properly counterbalanced by radial mixing, may induce a departure from a kinetically-controlled disinfection regime and, consequently, lead to the quantification of apparent (rather than intrinsic) inactivation rate constants due to dose distribution effects.

Moreover, a sensitivity study was conducted using the validated CFD model to determine under which conditions the TC-CB inactivation performance were kinetically controlled hence determining a quantitative criterion for the use of such apparatus in inactivation kinetic studies. CFD simulations were conducted at various flowrates (range: 116 - 594 mL min$^{-1}$), UVT$_{253.7}$ values (range: 0.001% cm$^{-1}$ - 90% cm$^{-1}$), and UV sensitivities (inactivation rate constants). For the $D_{10}$, also known as the UV dose required for 1 log$_{10}$ inactivation (or its reciprocal value, i.e. the first order microbial inactivation rate constants.

**Figure 2.11: TC-CB apparatus with radial velocity (left) and incident radiation contours (right)**
constant), a range of 5 - 40 mJ cm\(^{-2}\) was investigated. Lamp power was set to 30% of its nominal value.

All TC-CB simulated disinfection data, quantified as log\(_{10}\) of ratio between the inlet and the mass-flow weighted outlet values of the microbial concentrations predicted by the inactivation scalar transport equation, were plotted against their ideal inactivation, that is, the one which one would be obtained by dividing the average dose by the \(D_{10}\) (or, in order words, the log\(_{10}\) inactivation when the average dose is used in the first order kinetic equation for each specific microbe). Under such circumstances, an apparatus ideal for kinetic studies would return a 45 degree straight line.

To investigate the role of mixing, two sets of simulations were carried out for \(T_a = 46,534\) (vortex regime) and \(T_a = 0\) (no mixing). As may be seen in Figure 2.12-a, for \(T_a = 46,534\) the simulated inactivation, when plotted against the normalized average dose (\(\text{AD}/D_{10}\)), follows a single curve, irrespective of \(\text{UVT}_{253.7}\). Deviations from the 45 degree line are not affected by \(\text{UVT}_{253.7}\), suggesting that the shortcomings in this system are not associated with radial mixing, but rather with residence time distribution (that is invariant with optical properties).

This study attempts to identify the range and the conditions of applicability for UV kinetic studies in nearly opaque fluids. In Figure 2.12-a, the \(D_{10}\) value (as well as the \(\text{UVT}_{253.7}\) and the applied flowrate) was varied by nearly one order of magnitude. For \(\text{AD}/D_{10} > 3\), a noticeable departure is observed suggesting that the underlying dose distribution is affecting the disinfection performance of the TC-CB apparatus and hence the estimation of the microbial inactivation rate constants. It can be concluded that, in order to ensure that inactivation data were dominated by the intrinsic kinetics in this system, the reduction in organism titre should be kept below 3 log\(_{10}\) (or \(\text{AD}/D_{10} < 3\)).

For the case without mixing induced by fluid instabilities (e.g., a simple annular flow in absence of any radial mixing), the departure from the ideal 45 degree line happens at a very early stage (\(\text{AD}/D_{10} > 0.5\)) and increases as a function of log reduction (Figure 2.12-b). Furthermore, the simulated inactivation data do not describe a single law when plotted against \(\text{AD}/D_{10}\), but rather appear to be grouped by \(\text{UVT}_{253.7}\), suggesting that the radial,
or radiation-oriented, mixing in this configuration is not sufficient to yield uniform dose delivery even for relatively clear fluids.

![Figure 2.12: CFD predicted pathogen inactivation vs. AD/D_{10} for a) \( \text{Ta} = 46,534 \) and b) \( \text{Ta} = 0 \)](image)

2.4 Conclusions

Under appropriate operating conditions, the TC-CB is able to induce a vortex “chain” that mixes fluid within the irradiated zone. This fluid behavior occurs when the Taylor number exceeds 2,908. The resulting mixing can overcome the strong intensity gradients that exist in fluids with high UV absorbance, potentially making the TC-CB a suitable reactor for kinetic studies in strongly absorbing fluids. When operated with a Taylor number of 46,534 and an axial flowrate of 116 - 594 mL min\(^{-1}\), the TC-CB was able to provide accurate data for kinetic studies for UVT\(_{253.7}\) values as low as 0.001% cm\(^{-1}\). The \( \log_{10} \) reduction value, rather than the UV sensitivity of the organism, was found to be the controlling parameter of such irradiation device. Compared with an ideal apparatus, a criterion for accurate intrinsic kinetic studies was identified via CFD analysis, suggesting that the applied average dose (AD) should not be higher than 3 times the dose required for one \( \log_{10} \) removal (\( D_{10} \)). Inactivation data produced by the TC-CB apparatus displaying greater than 3 \( \log_{10} \) removals should be disregarded due to the axial transport
and dose distribution effects induced by the flow instability associated with the Taylor-Couette flow characteristics.

2.5 References


Chapter 3

3 MECHANISTIC MODELING OF VACUUM UV ADVANCED OXIDATION PROCESS IN AN ANNULAR PHOTOREACTOR

3.1 Introduction

Non-biodegradable organic micropollutants constitute a major threat to water quality, as their fate and transport can follow complex routes, and toxicologically significant concentrations can be found far from the point of discharge (Oller et al., 2011). These compounds are recalcitrant to conventional treatments but may be degraded using advanced oxidation processes (AOPs). To date, various combinations of oxidants, alone and with light and catalysts, were proposed as AOPs including $\text{O}_3$, $\text{O}_3/\text{H}_2\text{O}_2$, UV/$\text{H}_2\text{O}_2$, UV/$\text{O}_3$, UV/TiO$_2$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2+\text{hv}$, and vacuum UV (VUV) light. All these processes have as their main objective the generation of highly reactive species such as hydroxyl radicals ($\text{HO}^+$) which are then able, through a series of reactions, to achieve the oxidation or degradation of recalcitrant micropollutants present in water (Glaze et al., 1987).

Compared to hydrogen peroxide ($\text{H}_2\text{O}_2$) photolysis by 253.7 nm light, generation of $\text{HO}^+$ by water photolysis using VUV radiation emitted from xenon (Xe) excimer lamps (Oppenländer, 2003; Oppenländer, 2007) is potentially more efficient, as the rate of $\text{HO}^+$ formation induced by direct VUV photolysis of the water molecule is more than two orders of magnitude higher than that of $\text{H}_2\text{O}_2$ photolysis at 253.7 nm, mostly due to the higher molarity of water (55.5 mol L$^{-1}$).

This VUV process was studied extensively in laboratory conditions for a variety of applications ranging from the degradation of natural organic matter (NOM) to the removal of total organic carbon (TOC) for industrial applications requiring ultrapure water (Afzal et al., 2010; Giri et al., 2011; Gonzalez et al., 1994).

The common aspect associated with the studies involving the 172 nm wavelength in AOP is the use of a lab-scale annular photoreactor operating in recirculation mode and having
a water layer much greater than the ~18-36 µm photon penetration layer, which corresponds to ~90-99% of photon absorption. As a result, only a small fraction of the photoreactor annulus was actually illuminated and subjected to treatment and the observed photoreactor efficiency was far from a kinetically-controlled regime (but instead limited by mass transfer).

It should be noted that the optical thickness of water (defined as the distance where the fluence rate attenuation is equal to 1 log) at wavelengths lower than 180 nm is less than a millimeter such that the irradiated fluid behaves as nearly opaque.

Absorption coefficient spectra for pure water (Barrett and Baxendale, 1960; Barrett and Mansell, 1960; Halmann and Platzner, 1965; Querry et al., 1978; Segelstein, 1981; Weeks et al., 1963) exhibit discrepancies in particular at 185 nm which may have a considerable impact on photoreactor performance and design given the already very limited light penetration into water. Moreover, inconsistencies also exists regarding the elementary reactions (and their rate constants) that are important for the vacuum UV advanced oxidation processes initiated by water photolysis.

Extending the model to continuous flow photoreactors where the HO* formation induced by VUV water photolysis and the associated AOP chemistry is mechanistically described is a challenging task (Santoro et al., 2010) for a number of reasons: 1) multiple species with reaction time scales differing by many orders of magnitude are involved, 2) some of the species are formed in situ as a result of light-dependent reactions while others are formed by subsequent light-independent reactions and 3) some species are short lived and are characterized by extremely high reaction rate constants. Additional complexity is also caused by the severe water absorption which, for the 172 nm wavelength, can be as high as 500-600 cm⁻¹ (Weeks et al., 1963) resulting in 90-99% of photons being absorbed within a ~18-36 µm distance from the emission source. Less severe but no less challenging is the case of water photolysis initiated by the 185 nm wavelength for which the water absorption coefficient is approximately 1.8 cm⁻¹ (Weeks et al., 1963) and the 1-log photon penetration layer is 5.6 mm. In contrast, AOP photoreactors based on the
253.7 nm wavelength are not as limited by photon penetration but require the addition of an exogenous oxidant such as H$_2$O$_2$ to promote HO* formation.

In this chapter, a mechanistic model of vacuum UV advanced oxidation process in an annular photoreactor based on the use of 172 nm and 185 nm (in combination with 253.7 nm, with and without exogenous H$_2$O$_2$) is presented and discussed. This is the first time where a generalized kinetic model bridging two different mechanisms of HO* formation (by both H$_2$O and H$_2$O$_2$ photolysis) is presented and compared against a wide range of experimental conditions and data obtained from previously published studies. After verification and validation, the model was used to gain new insights into the behavior of vacuum UV advanced oxidation, revealing important features with potentially significant implications in terms of process understanding and efficient photoreactor design.

It should also be mentioned that, once sufficiently validated, the comprehensive model presented in this chapter could be used as a benchmark to determine the extent of simplification needed when more computationally-intensive three-dimensional analyses are required. Moreover, the validated model could play an important role for photoreactor optimization, where multiple designs and AOP processes could be analyzed and compared inexpensively. In the context of VUV applications, the model can offer insight in understanding the trade-off between kinetics and photoreactor hydraulics, due to the very limited light penetration in the water. It should also be emphasized that the use of the model, in its current version, should be limited to AOP applications with low scavenging potential (such as the one of ultrapure water), as the competing scavenging reactions associated with the organic and inorganic water matrix are not taken into account.

### 3.2 Materials and Methods

#### 3.2.1 Experimental set-up

Simulations were compared against data obtained by Robl et al. (2012) using 172 nm wavelength water photolysis as AOP. Those investigators carried out their advanced oxidation experiments in a recirculating annular photoreactor equipped with a custom-
built 100 W Xe-excimer lamp, where the radiant VUV power entering into the medium was determined actinometrically and found to be equal to 6.0 ± 0.7 W. The length of the photoreactor used in the experiments was 130 mm with an outer radius of 20 mm. The water layer defined by the two concentric cylinders (i.e., the annular gap) was 5 mm. Their system was configured and operated in semi-batch mode by recirculating the water continuously between a completely mixed reservoir and the photoreactor (Figure 3.1). The total volume of the system occupied by pure water was 3.7 L. Experiments were conducted under air- and oxygen-saturated conditions with a constant flowrate equal to 4.8 L min$^{-1}$, corresponding to a Re = 1,450. During both sets of experiments, the time-varying concentrations of pH, O$_2$ and H$_2$O$_2$ were measured using an online probe situated in the reservoir. Further details of the experiments conducted by Robl et al. (2012) can be found in the referenced manuscript.

![Figure 3.1: Experimental set-up modeled in the present chapter](image)

Similarly, the data presented by Imoberdorf and Mohseni (2011) were used to validate the performance of the generalized AOP model at the 185/253.7 nm and 253.7 nm
wavelengths (in combination with exogenous H$_2$O$_2$). In their work, experiments were performed using an annular photoreactor operated in semi-batch mode, equipped with either an axially mounted low-pressure VUV-Hg lamp (Light Sources Inc. G10T51-2-VH) with VUV output equal to 0.23 and 1.70 W emitted at the 185 and 253.7 nm wavelengths respectively, or a low-pressure UV-Hg lamp (Light Sources Inc. G10T5-1/2L) which emitted radiation at 253.7 nm with UV output (after the quartz sleeve) equal to 2.24 W. The lamps were inserted into a synthetic quartz sleeve with an outer radius of 75 mm and length of 275 mm.

As in Robl et al. (2012), the water layer dictated by the photoreactor annulus was 5 mm, while the total volume of water was 1 L. A solution consisting of deionized water with or without an initial concentration of formic acid (FA) were prepared for the experiments and placed in the reservoir maintained at 25 ºC. FA and H$_2$O$_2$ concentration profiles were collected under conditions with a constant O$_2$ concentration (maintained by injecting air bubbles into the recirculation tank) and a constant flowrate of 3 L min$^{-1}$ corresponding to a Re = 1,587 over a maximum recirculation time of 60 min, both in the presence and absence of initial H$_2$O$_2$ at a concentration of 0.5 mmol L$^{-1}$. Additional experimental details may be found in Imoberdorf and Mohseni (2011).

### 3.2.2 The kinetic model

The formulation of the generalized kinetic model involved two steps: (1) a comprehensive list of elementary reactions (and their rate constants) was compiled from literature; and (2) the kinetic model was implemented into MATLAB (MathWorks, Massachusetts) as a set of ordinary differential equations. The NIST database (http://kinetics.nist.gov/kinetics/index.jsp) was consulted in order to identify additional reactions (and rate constants) involving participating species not included in previous studies. The light-dependent reactions considered in the model were the ones associated with water and H$_2$O$_2$ photolysis by the 172, 185 and 253.7 nm wavelengths and, whenever present, the direct photolysis of the model organic compound.

Consistently with the water quality used in the experiments, deionized water was assumed during the simulations. The model assumed that the water was in equilibrium with atmospheric carbon dioxide, and carbonates/bicarbonates equilibrium equations
were also considered in order to take into account the important role played by these species in controlling pH. For the experiments involving FA, additional reactions were included to predict the oxidation pathways of the organic carbon in the system. The resulting generalized kinetic model, describing the VUV-driven water photolysis, the eventual direct photolysis of the model organic compound, and the UV-driven H₂O₂ photolysis, involved a total of 108 total elementary reactions and 24 different species: 4 radicals (HO⁺, H⁺, HO₂⁺, HCOO⁺), 5 radical ions (O⁺, O₂⁺, O₃⁺, CO₂⁺, CO₃⁺), 7 ions (H⁺, eaq⁻, OH⁻, HO₂⁻, HCO₂⁻, HCOO⁻, CO₃²⁻) and 8 molecules (H₂O, H₂O₂, H₂, O₂, CO₂, CO, HCOOH, O₃).

It should be mentioned that, unlike previous studies where certain specific reactions were a priori excluded, our approach was to first include all the documented reactions and then, based on a sensitivity analysis and in case of lack of computational resources, exclude the unnecessary reactions from the model. As such, the generalized kinetic model was mathematically formulated by including all the elementary reactions available in the literature, including the backward and forward reactions associated with the main equilibria affecting the system (Appendix A). Specifically, for each species involved in the process, differential mass-balance equations were set where both light-independent and light-dependent rate terms for a generic \( aA + bB \rightarrow cC + dD \) reaction were taken into account and mathematically formulated as shown in Eq. 3.1:

\[
R_d = -\frac{1}{a} \frac{dC_A}{dt} = -\frac{1}{b} \frac{dC_B}{dt} = \frac{1}{c} \frac{dC_C}{dt} = \frac{1}{d} \frac{dC_D}{dt} = k_x C_A^a C_B^b
\] (3.1)

where A, B, C and D represent generic species involved in the reaction with \( a, b, c \) and \( d \) their stoichiometric coefficients, \( k_x \) the second order kinetic rate constant, and \( C_A, C_B, C_C \) and \( C_D \) the concentrations of the species A, B, C and D, respectively. Using the same symbolism, the rate of the light-dependent reactions in the generic form of \( aA (+ \text{ light}) \rightarrow bB + cC + dD \) was formulated for each UV-initiated reaction, \( l \), giving a rate \( R_l \) as in Eq. 3.2 (Oppenländer, 2003):

\[
R_l = -\frac{1}{a} \frac{dC_A}{dt} = \frac{1}{b} \frac{dC_B}{dt} = \frac{1}{c} \frac{dC_C}{dt} = \frac{1}{d} \frac{dC_D}{dt} = \Phi_l \cdot \frac{P_{abs}}{h \nu \lambda} \cdot \frac{1}{N_A} \cdot \sum_{i=1}^{p} \frac{\epsilon_{A,A} C_A}{C_i^{l}}
\] (3.2)
where $A$, $B$, $C$ and $D$ are the generic species with $a, b, c$ and $d$ their stoichiometric coefficients, $\Phi_l$ represents the specific quantum yield, $P_{abs}$ represents the UV power absorbed by the solution, $V_{uv}$ the irradiated sub-volume of the photoreactor identified by its depth of photoactive layer $\delta_r$, $\lambda$ the wavelength, $h$ the Planck’s constant, $c_L$ the speed of light, $N_A$ the Avogadro’s number and the last term represents the fraction of light absorbed by the species $A$. The absorbed UV power ($P_{abs}$) was estimated using a radial lamp emission model (Liu et al., 2004) since, given the high absorption coefficient of water in the VUV region, there was no expected difference in terms of UV power absorbed when using a radial light model or a more sophisticated version like a cosine-corrected Lambertian emission model. Therefore, the fluence rate distribution in the photoactive layer of the photoreactor was described as in Eq. 3.3:

$$I = \frac{P_{uv}}{2\pi r L} \cdot 10^{-(A_1 (r-R_s))} \quad r \geq R_s$$ (3.3)

where $R_s$ is the quartz sleeve radius, $P_{uv}$ the UV power emitted from the sleeve, $L$ the arc length of lamp and $A_1$ the absorption coefficient of the solution at a given wavelength defined as following

$$A_{172} = (\varepsilon_{H_2O,172} \cdot [H_2O]) + (\varepsilon_{H_2O_2,172} \cdot [H_2O_2])$$ (3.4)

$$A_{185} = (\varepsilon_{H_2O,185} \cdot [H_2O]) + (\varepsilon_{H_2O_2,185} \cdot [H_2O_2]) + (\varepsilon_{HCOOH,185} \cdot [HCOOH]) + (\varepsilon_{HCOO^-,185} \cdot [HCOO^-])$$ (3.5)

$$A_{253.7} = (\varepsilon_{H_2O_2,253.7} \cdot [H_2O_2])$$ (3.6)

where $\varepsilon$ represents the molar absorption coefficient of the species at a specific wavelength. In particular, the values of $\varepsilon$ equal to 1.0, $3.24 \cdot 10^{-3}$ and $0 \text{ m}^3 \text{mol}^{-1} \text{m}^{-1}$ (base 10) were considered for water at the wavelengths of 172, 185 and 253.7 nm, respectively; for $H_2O_2$, the values of $\varepsilon$ equal to 100, 28.9 and 1.84 $\text{m}^3 \text{mol}^{-1} \text{m}^{-1}$ (base 10) were chosen for the wavelengths at 172, 185 and 253.7 nm, respectively (Oppenländer, 2003; Sosnin et al., 2006; Weeks et al., 1963). For FA and its ionic form the values of $\varepsilon$ equal to 4 and 0.18 $\text{m}^3 \text{mol}^{-1} \text{m}^{-1}$ were used respectively in the model for the wavelength of 185 nm.
(Weeks et al., 1963), while photon absorption at 253.7 nm is considered negligible (Imoberdorf and Mohseni, 2011). The absorption of the hydroperoxide ion (HO$_2^-$) was neglected since the pKa of the H$_2$O$_2$/HO$_2^-$ equilibrium is 11.6 (Baxendale and Wilson, 1957), which implies that at pH 5.5 (typical of the investigated conditions) the predominant species present is H$_2$O$_2$ (>99% at pH=9.6). Finally, the overall rate of change in concentration of each species included in the model was calculated as the sum of terms of all light-independent and light-dependent reactions. It should also be mentioned that radiation absorption, reflection and refraction at the quartz-water interface were not considered in this model, as the VUV output provided in the referenced studies was estimated experimentally by means of chemical actinometry, which would therefore already take into account the radiation losses caused by absorption and reflection. Moreover, for highly absorbing media such as water in the VUV wavelength range, the radiation is distributed mainly near the lamp wall where the displacement of UV rate due to refraction is minimal and can be ignored.

3.2.3 Sensitivity analysis of the kinetic model

A sensitivity analysis was conducted to determine, for the investigated conditions, the impact of rate constants (corresponding to each elementary reaction) on the model simulations. In case of disagreement among published values, an average rate constant was used in the sensitivity study. The relative importance of a given elementary reaction $k_x$ was estimated by quantifying the change in the time-dependent concentration profile $\Delta C_{A,k_x}$ of a generic species A (e.g., H$_2$O$_2$, HO*) obtained when all elementary reactions $k_1+k_2+\ldots+k_n$ were considered versus the case when all elementary reactions minus the one of concern $k_x$ were used in the species simulations (Eq. 3.7).

$$\Delta C_{A,k_x} = \frac{\sum_{i=1}^{N} [C_A]_{i,k_1+k_2+\ldots+k_n} - [C_A]_{i,k_1+k_2+\ldots+k_n-k_x}}{N}$$

(3.7)

It should be mentioned that the proposed approach (in which elementary reactions are eliminated from, instead of added to, the comprehensive kinetic model) was deemed necessary since a minimum number of reactions is needed in order to obtain a relevant steady-state solution in HO* concentration.
3.2.4 The semi-batch model

To fully describe the recirculating system used in Robl et al. (2012) and Imoberdorf and Mohseni (2011), a mathematical semi-batch recirculation model was developed in MATLAB consisting of the hydraulic and photochemical submodels. The two submodels describing the behavior of the recirculating reservoir and the annular photoreactor were linked in a transient fashion so that the integrated model was able to predict the evolution of the photo-reactive AOP system as tested.

In case of a single species A and two reactor components (the photoreactor and the reservoir) connected in recirculation mode and each hydraulically described by a single CFSTR, the resulting system of ordinary differential equations is given in Eq. 3.8:

\[
\begin{align*}
V_{uv} \frac{dC_{A,uv}}{dt} &= QC_{A,res} - QC_{A,uv} \pm R_t \pm R_d \\
V_{res} \frac{dC_{A,res}}{dt} &= QC_{A,uv} - QC_{A,res} \pm R_d
\end{align*}
\] (3.8)

where \( Q \) is the flowrate, \( V_{uv} \) and \( V_{res} \) are the volume of the photoreactor and the reservoir, respectively, and \( C_{A,uv} \) and \( C_{A,res} \) the species concentrations. The formalism shown in Eq. 3.8, was extended to all the species and the hydraulic components of the recirculating systems used during the experiments. Additional information about the model can be found in Appendix B.

In accordance with the flow regime employed during the experiments and due to the relatively small hydraulic diameter of the annular photoreactor, all MATLAB simulations were conducted assuming a radial velocity distribution typical of the laminar regime as described in Eq. 3.9 (Munson et al., 2002).

\[
u_r = \frac{1}{4\mu} \left( \frac{8\mu Q}{\pi (R_{uv}^2 - R_S^2)} \right) \left( \frac{1}{(R_{uv}^2 + R_S^2) - \frac{R_{uv}^2 - R_S^2}{\ln \left( \frac{R_{uv}}{R_S} \right)}} \right) \left[ \ln \left( \frac{R}{R_S} \right) \right]^{-1} \left[ \frac{1}{\ln \left( \frac{R_{uv}}{R_S} \right)} \right] (R_{uv}^2 - R_S^2) - (r^2 - R_S^2)
\] (3.9)
where $R_w$ represents the radial distance of the photoreactor wall and $\mu$ the dynamic viscosity of the solution.

The limited light penetration in the photoreactor annulus at 172 nm was mathematically addressed using the concept of depth of photoactive water layer $\delta_r$ and hydraulic bypass ($R_w - \delta_r$), which identifies the extent of the chemically-active water layer near the radiation source in which treatment occurs. It should be clarified that presence of such layer can be justified on phenomenological basis by comparing the extremely short penetration of VUV radiation in water at 172 nm (18-36 µm) and the relatively high physical dimension of the annulus used during the experiments (5 mm). Moreover, it was verified with preliminary simulations that the use of an average fluence rate value (estimated using the entire annulus) was inadequate to capture the trends observed in the experimental data leading to underestimate the production of $\text{H}_2\text{O}_2$ (Figure 3.2).

![Figure 3.2: H$_2$O$_2$ concentration produced in VUV process in air saturated. The solid line represents the modeling result including the hydraulic bypass while the dashed line is obtained excluding the hydraulic bypass](image-url)
For a radial distance greater than $\delta_r$, it was assumed that the effect of light-dependent reactions were negligible. Due to the recirculating nature of the experimental apparatus promoting random mixing between passes, the fluence rate in the photoactive water layer was assumed to be equal to the average fluence rate in $\delta_r$. The average fluence rate in the photoactive layer was obtained by calculating a radial average between $R_s \leq r \leq R_s + \delta_r$ of the fluence rate profile obtained using the radial radiation model shown in Eq. 3.3. The conceptual representation of the integrated model is provided by Figure 3.3.

![Figure 3.3: Schematic representation of hydraulic bypass $[(1-f)\cdot Q]$ in the photoreactor](image)

For an arbitrary depth of photoactive water layer $\delta_r$, it was possible to estimate the fraction, $f$, of the total flow entering the photoactive water layer as opposed to the remaining amount $(1-f)$ that was by-passed without receiving treatment and as such recirculated directly to the reservoir. This approach is justified by considering the limited radial mass-transfer occurring in the photoreactor due to the fully laminar regime at which the system was operated ($Re=1,450-1,587$) as well as the extremely short life time of hydroxyl radicals (on the order of a fraction of a second) leading to negligible convective and diffusive mass transport effects. This was also verified by means of additional CFD simulations (Figure 3.4). As illustrated in Figure 3.4, several simulations...
were conducted varying the flow rate and the diffusivity of the species by one order of magnitude observing that the penetration of HO* in the fluid was not affected by diffuse or convective transport phenomena.

Figure 3.4: Comparison between normalized concentration profile of HO* for several values of the diffusivity, $\Gamma_c$, of all the species and of the flow rate, $Q$ ($\lambda = 172$ nm)

Both the annular photoreactor and the reservoir were treated as arbitrary flow reactors. Specifically, the MATLAB model was implemented to accommodate an arbitrary number $n$ and $m$ of ideal CFSTR-in-series for each of the two system components (Figure 3.5). The use of a laminar velocity profile to estimate the extent of hydraulic by-pass is not in contradiction with the subsequent hypothesis of photoreactor hydraulics described
by CFSTR in-series as the latter is meant to represent overall mixing behavior of the system, including the fully mixed recirculating tank.

A symbolic representation of the entire recirculating system is given in Eq. 3.10:

Figure 3.5: Schematic representation of recirculating system decomposed into CFSTR-in-series

A symbolic representation of the entire recirculating system is given in Eq. 3.10:
In order to determine the appropriate number of CFSTRs to be used in the final simulations, a sensitivity study was conducted using a two level factorial scheme (1 and 5 reactors in series for both the annular photoreactor and the reservoir) and assuming, as a response variable, the concentration profile of H$_2$O$_2$ caused by one or five CFSTR-in-series. These two levels were chosen because they are representative of the extreme cases of fully-mixed and plug flow reactors (Levenspiel, 1998). The system of ordinary differential equations (ODEs) obtained was solved using the stiff MATLAB solver ODE15s with relative and absolute error tolerances set to $10^{-10}$ and $10^{-30}$, respectively.

Simulations representing different AOP processes (172, 185 and 253.7 with exogenous H$_2$O$_2$) were conducted by prescribing as initial conditions the specific geometrical, optical and chemical parameters included in the referenced manuscripts.

### 3.2.5 CFD model: governing equations and boundary conditions

To better understand the spatial distribution of the species involved in the advanced oxidation process, as well as to confirm the results obtained with the MATLAB simulations, a CFD model of the central region of the annular photoreactors used in the experiments was developed. It should be noted that the goal of the CFD simulations presented in this chapter was to generate additional supporting information for the observation made through the use of the comprehensive MATLAB model, with the intent of trying to elucidate the spatial distribution and the radial penetration of hydroxyl radicals within the photoreactor annulus. Due to the axial-symmetric nature of the photoreactors used in the experimental work as well as the well-developed laminar flow regime induced by the small hydraulic diameter of the system, a 2-dimensional
axisymmetric framework with a fully-developed laminar velocity profile was used for the CFD analysis. Steady state governing equations for continuity, momentum (axial and radial direction) and scalar transport (Eq. 3.11 – 3.14) were used in the model to predict the spatial distribution of the chemical species involved in the AOP.

\[
\frac{1}{r} \frac{\partial}{\partial r} (ru_r) + \frac{\partial}{\partial x} (u_x) = 0
\]  
(3.11)

\[
u_r \frac{\partial u_r}{\partial r} + u_x \frac{\partial u_r}{\partial x} = -\frac{1}{\rho} \frac{\partial P_A}{\partial r} + \mu \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_r}{\partial r} \right) + \frac{\partial^2 u_r}{\partial x^2} \right] + \frac{u_r}{r^2}
\]

\[
u_r \frac{\partial u_x}{\partial r} + u_x \frac{\partial u_x}{\partial x} = -\frac{1}{\rho} \frac{\partial P_A}{\partial x} + \mu \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_x}{\partial r} \right) + \frac{\partial^2 u_x}{\partial x^2} \right]
\]

\[
u_r \frac{\partial C_A}{\partial r} + u_x \frac{\partial C_A}{\partial x} = \Gamma_{C_A} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) + \frac{\partial^2 C_A}{\partial x^2} \right] + S_{C_A}
\]

\[
\Gamma_{C_A} = \frac{(2.4 \cdot 10^{-8})}{MW_A^{0.71}}
\]

(3.15)

The term \(C_A\) is the concentration of the species A, \(\Gamma_{C_A}\) is the species diffusivity estimated using the expression provided in Schwarzenbach et al. (2003), \(S_{C_A}\) and \(MW_A\) are the source term (obtained from the kinetic model) and the molecular weight of each of the transported species included in the CFD model.

The ANSYS Gambit v.2.4.6 software (Canonsburg, USA) was used to generate the computational grid for the CFD analysis of a small portion of the annular photoreactor used in Robl et al. (2012) and Imoberdorf et al. (2011). Special attention was paid to ensure a good quality of the mesh in the radial direction where the strongest gradients were expected due to the very limited light penetration in the photoreactor annulus. Mesh sensitivity analysis indicated that a 10,880-element mesh was sufficient to obtain grid independent results (Figure 3.6).
Figure 3.6: Grid independence tests on normalized fluence rate, HO*, H$_2$O$_2$ and O$_2$ species (log scale)

The photoreactor walls were described using a no-slip boundary condition. A user-defined function (UDF) was created to assign a radial fluence rate distribution profile as mathematically described in Eq. 3.3. At the photoreactor inlet, a parabolic velocity profile was specified using a UDF (according to Eq. 3.9) to mimic fully developed flow conditions. For both 172 and 185/253.7 nm cases, the simulated flowrate and lamp power were kept consistent and equal to 8•10$^{-2}$ L s$^{-1}$ and 6 W, respectively.
The ANSYS Fluent software 12.1 (Ansys Inc., USA) was used to perform the steady-state CFD simulations using the segregated solver. The SIMPLE algorithm (Patankar, 1980) was chosen for pressure-velocity coupling, with standard and second order upwind schemes for pressure and momentum equations, respectively. All scalar equations describing the transported species were solved using a third-order MUSCL scheme (van Leer, 1979). The convergence was achieved when all residuals were reduced to less than $10^{-4}$.

### 3.3 Results and discussion

A first attempt was made to interpret the experimental data from Robl et al. (2012) using Levenspiel’s recirculation theory. According to Levenspiel, a semi-batch system approaches the kinetically controlled regime when the recirculation flowrate is increased thus resulting into a minimal conversion per pass (Levenspiel, 1998). However, when such an approach was tested in this study for predicting the $\text{H}_2\text{O}_2$ profile obtained by Robl et al. (2012), the comparison between simulated and observed data showed very poor agreement (Figure 3.7).
We hypothesized that this discrepancy is due to the very limited photon penetration into water which is confined to a few microns. As described in paragraph 3.3.4, in order to take this into account, a photoactive water layer $\delta_r$ and a hydraulic bypass ($R_{W-\delta_r}$) was introduced into the Levenspiel model. Since $\delta_r$ cannot be measured directly, it was inferred in this study by minimizing the error between simulated and observed $\text{H}_2\text{O}_2$ data for both air- and oxygen-saturated conditions. To determine the robustness of the inferred quantities, we evaluated the sensitivity of the $\text{H}_2\text{O}_2$ profile against the number of CFSTRs (1 versus 5, corresponding the two extreme cases of ideal CFSTR and plug flow reactor with dispersion) used to describe the photoreactor or reservoir, concluding that such
choice had no influence on the numerical solutions (Figure 3.8). This observation suggests that the photolysis and the chemistry involved in the investigated process, not the hydraulics, are the dominant mechanisms.

Figure 3.8: \( \text{H}_2\text{O}_2 \) profile, changing the number of photoreactors and reservoirs in series

As Figure 3.9 shows the excellent agreement between the experimentally measured profile of \( \text{H}_2\text{O}_2 \) concentration and that obtained by the numerical model was obtained. The inferred depth of photoactive layer \( \delta \), ranged from 230 to 390 \( \mu \text{m} \) (depending on operating conditions, i.e. oxygen- or air-saturated respectively), with an average error of \( 1.3 \times 10^{-3} \text{ mmol L}^{-1} \) (4.1%) and \( 2.9 \times 10^{-3} \text{ mmol L}^{-1} \) (2.8%), respectively. The value of
photoactive layer was determined numerically, it is function of the initial boundary conditions, and it is difficult to predict experimentally. It should be recalled that, for the 172 nm case, the only fitted parameter used in the model is the depth of photoactive layer (while the other parameters were obtained from either the literature or from the papers where the experiments were described). Remarkably, such inferred depth was found to be an order of magnitude greater than the 1-log photon penetration layer (~18 µm), indicating the presence of hydroxyl radicals well beyond the optical layer dictated by the absorption coefficient of pure water. This can be explained, on a phenomenological basis, by the complex network of reactions and competing pathways typical of the advanced oxidation process induced by VUV wavelengths heading a rate of production of hydroxyl radicals more than two order of magnitude greater than the corresponding one associated with the photolysis of 10 mg L\(^{-1}\) of hydrogen peroxide photolysis by the 253.7 nm radiation.

Figure 3.9: H\(_2\)O\(_2\) concentration produced in VUV process (172 nm) in air saturated (○) and oxygen saturated conditions (△). The solid and dashed lines represent
modeling results for the case of n.1 CFSTR (n=1), in semi-batch mode, with hydraulic bypass

Notably, such apparent greater radial penetration of hydroxyl radicals is not caused by convective or diffusive transport phenomena affecting this species (as shown in Figure 3.4), but simply induced by a non-linear response of steady-state HO* concentration in fluence rate. Moreover, the model predicted well the initial production of the H₂O₂, with slope equal to 1.4×10⁻⁵ mmol L⁻¹ s⁻¹ as well as the asymptote of the targeted species.

The production of H₂O₂ was mostly affected by the scavenging reaction between O₂ by H* (governed by the reaction with kinetic constant k₁₂), as also suggested by Robl et al. (2012). Additional light-independent reactions playing a major role in the kinetic model were: H₂O₂ and HO*, H₂O₂ and eₐ𝑞⁻, the recombination of HO* to give H₂O₂, and, for the case of air-saturated conditions, the equilibrium reaction in water between CO₂ and HCO₃⁻ (Figure 3.10).
Figure 3.10: Kinetic constants ordered from most significant to least significant according to $\Delta_{C_A}k_x$ for the case of air-saturated condition at 172 nm irradiation with no organic pollutant in water.
To further check the general validity of the simulations presented in this work under different experimental conditions, model predictions obtained for the 185 nm case were compared against experimental data presented in Imoberdorf and Mohseni (2011). Since the 1-log penetration layer depth at 185 nm (5.6 mm) exceeds the photoreactor annulus (5.0 mm), the depth of photoactive layer $\delta_r$ was set in our model to be equal to the entire photoreactor annulus. The model was able to accurately predict the time-dependent $\text{H}_2\text{O}_2$ concentration formed during 185 nm irradiation with a relative error of $1.9\times10^{-2}$ and $2.8\times10^{-2}$ mmol L$^{-1}$ (21.4% and 3.9%) for the case of no initial $\text{H}_2\text{O}_2$ and 0.5 mmol L$^{-1}$ of $\text{H}_2\text{O}_2$, respectively (Figure 3.11).
Figure 3.11: $\text{H}_2\text{O}_2$ concentration in VUV/UV process (185/253.7 nm) with no (O) and 0.5 mmol L$^{-1}$ (□) initial concentration of $\text{H}_2\text{O}_2$. $\text{H}_2\text{O}_2$ concentration in UV process (253.7 nm) with 0.5 mmol L$^{-1}$ initial concentration (Δ). The lines represent modeling results from this work using the CFSTR, semi-batch new mechanistic photoreactor model.

It should be noted that, since the experiments were performed in presence of FA (a scavenger of HO*), the concentration of $\text{H}_2\text{O}_2$ exhibited a maximum caused by less favored scavenging reaction between HO* and $\text{H}_2\text{O}_2$ in the presence of an additional scavenger like FA. As a result of this, the $\text{H}_2\text{O}_2$ reached a maximum at 30 minutes, and then started decreasing when the FA was completely mineralized. Moreover, the model predicted very well the trend in degradation of FA and the impact of different initial concentration of FA with respect to the change in $\text{H}_2\text{O}_2$ formation. (Figure 3.12).
Figure 3.12: Comparison between FA and H$_2$O$_2$ profiles at different initial concentrations of the micropollutant ($\lambda = 185/253.7$ nm)
Finally, the model was also evaluated against the case of H₂O₂ photolysis (0.5 mmol L⁻¹) caused by the 253.7 nm wavelength alone. As shown in Figure 3.11, the agreement between model and experiments is excellent with an error as small as 7.4•10⁻³ mmol L⁻¹ (1.6%).

Under the same experimental conditions, the model predicted the degradation of FA with an error of 1.0•10⁻² (6.4%) and 3.5•10⁻² mmol L⁻¹ (24.5%) at 185/253.7 nm with and without an initial concentration of H₂O₂ respectively. We note that, even when the model predictions show a small deviation from the experiment, the overall trend is well captured in all cases. Also, in this case at 253.7 nm, the model predicted very well the oxidation of the organic pollutant over time with an error of 1.9•10⁻² mmol L⁻¹ (6.3%), showing an apparent zero-order decay at the investigated initial concentration and treatment time due to the limited extent of photolysis of hydrogen peroxide (Figure 3.13).
Figure 3.13: FA degradation in VUV/UV process (185/253.7 nm) with no (O) and 0.5 mmol L\(^{-1}\) (□) initial concentration of \(\text{H}_2\text{O}_2\). FA degradation in UV process (253.7 nm) with 0.5 mmol L\(^{-1}\) initial concentration of \(\text{H}_2\text{O}_2\) (∆). The lines represent modeling results from this work.

The absorption caused by \(\text{HO}_2^-\) was not included in the model as the simulated results were insensitive such contribution due to the acidic pH range at which experiments were conducted, resulting in very low \(\text{HO}_2^-\) concentrations (Figure 3.14).
Figure 3.14: Comparison of formic acid concentration profiles at 253.7 nm with (squares) and without (diamonds) absorption contribution of hydroperoxide ion

The robustness of the model in predicting the photoreactor behavior under a variety of operating conditions indirectly provided additional support regarding the role played by the photoactive water layer which, based on our estimates, exceeded by far the optical thickness of the fluid. In order to further investigate this potentially important result, a 2D axi-symmetric CFD model was set up to numerically explore the role played by diffusion and convection transport phenomena in the annular photoreactor.

Figure 3.15 shows the distributions of fluence rate (reported for both the 172 and 185 nm wavelengths), H$_2$O$_2$ and HO* scaled and normalized between their maximum and minimum values. As expected, the fluence rate distribution was more uniform for the 185 nm than the 172 nm case due to the difference in the absorption coefficient of water at
these two wavelengths. Remarkably, the 172 nm case confirmed our earlier observation made using the in-series CSTRs model with bypass: despite the fact that the photon penetration layer is confined to a layer of ~18 µm, the distribution of HO*, and particularly of H₂O₂, significantly exceeded the 18 µm radial threshold. Such an observation is further supported by Heit and Braun (1997) who founded experimentally that the O₂ concentration in the annulus showed a depletion gradient very different from the one of 172 nm fluence rate light.

Figure 3.15: Fluence rate, H₂O₂ and HO* normalized distributions at two conditions: 172 nm (left column) and 185/253.7 nm (right column)
Additional axial-symmetric CFD simulations were performed in order to compare whether the distribution of HO* was sensitive to the length of the photoreactor included in the model. As shown in Figure 3.16, the radial distribution of HO* was independent of the photoreactor length and residence time used in the CFD simulations.

Figure 3.16: Velocity and HO* distribution in Robl's reactor (130x5 mm, left - a) and a small part (5x5 mm, right - b) ($\lambda = 172$ nm)

To better elucidate the reasons behind a greater than expected presence of HO* beyond the 1-log photon penetration layer, a new set of CFD simulations was performed. By artificially changing the value of diffusion and convection (both the diffusion coefficient
and the flowrate increased by an order of magnitude), we determined that neither of those two mechanisms were responsible for transporting HO* outside the 1-log photon penetration layer (Figure 3.4). At this point, attention was paid to the kinetic behavior caused by the nested network and the rate of elementary reactions involved in the VUV process. Using the kinetic model presented in Table 3.1, kinetic simulations for different fluence rates (1 – 10 – 100 W m⁻²) were conducted and the steady-state HO* concentration quantified for each of the three AOPs considered in this study (172, 185/253.7 and 253.7 nm with initial 10 ppm of H₂O₂). As shown in Figure 3.17 (and confirmed by subsequent Figure 3.18 and Figure 3.19), for the cases at 172 and 185/253.7 nm it was possible to observe that a given change in fluence rate did not result in the same change in HO* concentration as indicated by the departure from the 1:1 proportionality line.

Figure 3.17: Concentration of the radical species (HO*) versus fluence rate in pure water at different conditions: 172 nm (O), 185/253.7 nm (∆) and 253.7 nm with
initial 10 ppm of H₂O₂ (□). The bold line represents the 1:1 direct proportionality curve between concentration and fluence rate.

This suggests that the HO* distribution was not dictated only by the local photon availability but instead affected by a more complex reaction mechanism. On the other hand, the 253.7 nm + H₂O₂ AOP did follow the perfect proportionality line, suggesting that the behavior of the AOPs initiated by short wavelengths via water photolysis were qualitatively distinct from those initiated by longer wavelengths via H₂O₂ photolysis. The deviation from the 1:1 proportionality line was dictated by the different value of the rate of photolysis: 17.6 mol m⁻³ s⁻¹ at 172 nm, 4.9*10⁻² mol m⁻³ s⁻¹ at 185 nm, and 3*10⁻⁴ mol m⁻³ s⁻¹ at 253.7 nm. This unique kinetic behavior also supported the higher penetration of HO* into the photoreactor annulus thus providing the appropriate theoretical framework and justification for the inferred photoactive depth being found to be an order of magnitude greater the 1-log photon penetration of the 172 nm wavelength in water.
Figure 3.18: Concentration of species (HO\(^*\) and H\(_2\)O\(_2\)) versus fluence in pure water at different conditions: 172 nm (first row), 185/253.7 nm (second row) and 253.7 nm with initial 10 ppm of H\(_2\)O\(_2\) (third row)
Figure 3.19: Concentration of the radical species versus fluence in pure water at 172 nm. The bold line represents the 1:1 proportionality curve between concentration and fluence rate

3.4 Conclusions

A novel mechanistic advanced oxidation model able to predict the H$_2$O$_2$ profiles for three different wavelengths (172 nm, 185 nm and 253.7 nm) was successfully developed and validated against a variety of different operating conditions. An additional model parameter, the hydraulic bypass, was introduced in order to take into account the limited penetration of UV radiation in water at the 172 nm wavelength.
The model revealed a new distinctive feature of AOPs initiated by the 172 wavelength. In this case, the depth of the photoactive water layer was an order of magnitude greater than the 1-log photon penetration as also confirmed by CFD simulations.

Parametric CFD analysis suggested that neither diffusion nor convection were responsible for HO* transport outside the 1-log photon penetration layer. Instead, the apparent greater penetration of HO* was due to a non-linear response at steady-state between fluence rate and HO* concentration caused by the complex AOP chemistry associated with the network of elementary reactions involved in the process. This is an important design consideration that must be taken into account when short-wavelength AOPs are engineered using annular photoreactors.

3.5 References


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the Intensity of Vacuum UV Radiation of a Xe2 Excilamp. Instruments and Experimental Techniques 49 (1), 101-105.


Chapter 4

AOPs FOR TOC REMOVAL FROM ULTRAPURE WATERS BY SHORT UV WAVELENGTHS: EXPERIMENTAL AND NUMERICAL STUDIES

4.1 Introduction

In this chapter, a series of experiments, conducted on a single-pass thin-film photoreactor with annular gap (i.e. the water layer defined by the two concentric cylinders) of 1 mm, is presented and discussed. In particular, experiments were carried out under a variety of conditions: (a) 185/253.7 nm irradiation with lamp enclosed in synthetic quartz sleeve; (b) 185/253.7 nm irradiation with lamp enclosed in natural quartz sleeve; (c) 253.7 nm irradiation with lamp enclosed in natural quartz sleeve. The main difference between synthetic and natural quartz sleeves was that the first contains lower concentrations of impurities (e.g. alkali- and metal ions in ppb) resulting in higher transmittance at short UV wavelengths (i.e. 90%/2mm at both 185 nm and 253.7 nm) than the second type of sleeve (i.e. 65%/2mm at 185 nm and 85%/2mm at 253.7 nm). Degradation of two target model pollutants in deionized water (DI) were investigated namely 4-chlorobenzoic acid (pCBA) and methylene blue (MB). Experiments were executed following a statistical Box-Behnken design with three central points and three variables: flowrate, initial concentration of model pollutant, and electrical power of the lamp. To compare the performance of the 185/253.7 nm process with an alternative VUV advance oxidation process (AOP) employing the 172 nm wavelength, a new set of single-pass experiments were conducted adopting thin-film photoreactors at different annular gaps (1.0, 2.5 and 5.0 mm) with a 172 nm Xenon (Xe) excimer lamp. The same water quality and model pollutants were taken into account. The percentage of degradation of the targeted species was quantified as well as the electrical energy per order (EEO) in order to compare the investigated AOPs.

Subsequently, modeling studies were conducted. The 2D longitudinal section of the investigated photoreactor was reproduced and simulated using MATLAB and Fluent. To closely mimic the chemistry involved in the water photolysis at short wavelengths,
additional reactions (i.e. degradation pathway of pCBA) were added into the previously validated mechanistic model reported and discussed in Chapter 3.

Finally, the CFD model was used to optimize the photoreactor by exploring different annular configurations in order to evaluate the efficiency in degradation of pCBA in DI water as well as to determine possible correlations among the fluence at 185 and 253.7 nm, and HO* doses.

4.2 Materials and Methods

4.2.1 The 185/253.7 nm photoreactors set-up

The investigated single-pass system is schematically represented in Figure 4.1. It consisted of two thin-film annular photoreactors made of stainless steel connected in series through a flexible teflon tube (Aquafine, Valencia CA). Each reactor was approximately 1,700 mm long and 50 mm in diameter.

![Figure 4.1: Schematic representation of the single-pass experiment at 185/253.7 nm](image-url)
A supply tank (Ace Roto-Mold VT00025SWSN) with capacity of approximately 25 gallons (94.63 liters) equipped with centrifugal pump (AMT ME01C0C0J0000100734 model 370B-98) was used as a feeding reservoir for the first thin-film annular photoreactor.

Each annular thin-film photoreactor, as illustrated in Figure 4.2, housed a low pressure-Hg lamp emitting 185/253.7 nm radiation with electrical lamp power equal to 240 W, and arc length equal to 1,461 mm (model 794109 GA64T6NIQ) enclosed in a quartz sleeve having internal and external diameters equal to 25 mm and 30 mm respectively. The total length was 1,657 mm. Two types of quartz sleeves were used in the experiments, namely synthetic (Suprasil 310) and natural fused quartz (Hearaeus Quartz America LLC, USA). According to the information provided by the manufacturer, the transmittance for 2 mm of Suprasil 310 at both 253.7 and 185 nm was 90% while for natural fused quartz the transmittance was 85% at 253.7 nm and 65% at 185 nm indicating the higher absorption at shorter wavelengths, and hence reduced amount of VUV radiation delivered to the fluid.

![Fig 4.2: Schematic representation of the single annular thin-film reactor](longitudinal section, not on scale)
The radial distance between the external surface of the quartz sleeve and the inner surface of the reactor, where the fluid resides, was 1 mm (water layer).

Additional control experiments were executed adopting a monochromatic 253.7 nm low pressure Hg lamp (model 794447) to quantify the contribution of direct photolysis of the target pollutants due to UV light irradiation.

4.2.2 The 172 nm photoreactor set-up

Additional thin-film annular photoreactors with different annular gaps were built at Trojan Technologies (London, Canada) to house the 172 nm lamp. Specifically, three reactors with internal diameter equal to 55, 58 and 63 mm were welded onto aluminum supports. Each cylinder (Figure 4.3) presented a hole at the bottom which consists of an inlet (diameter 6.4 mm) and two outlets at the top, in diametrical opposite direction. The cylinder can host a VUV lamp (Xeradex excimer L40/120/SB-S46/85) emitting a quasi-monochromatic light at 172 nm. It was connected through an Osram DBD-20-110/240 power supply. The single ended lamp exhibited 20 W electrical power and was mounted from the top side of the cylinder. The VUV lamp was enclosed in a special domed synthetic quartz sleeve allowing high transmittance of the 172 nm radiation into the fluid, having an external diameter equal to 53 mm therefore the investigated annular gaps were 1.0, 2.5, and 5.0 mm.

A 2L glass beaker with a magnetic stirrer, acting as fully mixed reservoir, was connected through a flexible rubber hose to a peristaltic pump (MasterFlex L/S, Cole-Parmer USA) and from it to the bottom of the photoreactor. The initial solution consisted of Milli-Q water with different initial concentration of target pollutant. The treated fluid was collected into 25 mL sterile vials (Figure 4.3).
4.2.3 Experimental procedure and analytical methods

Before conducting the irradiation of the fluid, 25 gallons of solution were prepared with different initial concentrations of the investigated organic pollutant in de-ionized (DI) water. Two organic species were studied: 4-chlorobenzoic acid (pCBA) (Sigma-Aldrich, 99% purity) and methylene blue (Sigma-Aldrich). For pCBA, the acid was dissolved in a stirred beaker with 2L of distilled water adjusting the pH to 7-8 by addition of sodium hydroxide (NaOH). After preparing this stock solution, it was added into the reservoir in order to achieve the desired initial pCBA concentration. The measured pH in the reservoir at average concentrations of pCBA and methylene blue was 4.5. For the latter chemical species, specific amount of the stock powder was added directly into the 25 gallon tank, and the centrifugal pump was used to mix and homogenize the solution.

PCBA samples were analyzed using a HPLC device (Waters, Mississauga Canada) consisting of an autosampler (Waters™ 717), a system controller (Waters™ 600-MS), a photodiode array detector (Waters™ 996) and outfitted with a Supelcosil™ column (LC-18 25cm x 4.6 mm x 5 µm). A solution consisting of 0.05% of phosphoric acid (H₃PO₄) and acetonitrile was used for elution in 52:48 ratio, with a 1.5 mL min⁻¹ flowrate. Helium was used at a flowrate of 7 mL min⁻¹ as the sparging gas in order to remove air bubbles.
from the capillary tubes. Quantification of pCBA used a detection wavelength of 238 nm and the retention time at these operating conditions of 4 min.

Methylene blue concentrations were analyzed by measuring the absorbance in a 1 cm quartz cuvette at 664 nm wavelength using a Varian Cary 50Bio spectrophotometer (Agilent Technologies Inc., USA).

4.2.4 The Box-Behnken design

A statistical Box-Behnken design (BBD) was chosen for the experiments on 185/253.7 nm irradiation. The BBD is an efficient option in which the experimental points are located on the midpoints of the edges of a cube, if three factors are considered, and at the center (central points). The following Figure 4.4 shows the graphical representation of BBD in two forms: (a) the cube with the relative position of the experiments and (b) a figure of three interlocking $2^3$ factorial designs and central point.

![Figure 4.4: The cube for BBD (a) and three interlocking $2^3$ factorial designs (b)](image)

In a system involving three independent variables $x_1$, $x_2$ and $x_3$, the response of the Box-Behnken design can be expressed by the following quadratic polynomial equation
\begin{equation}
Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2
\end{equation}

where \( Y \) is the response, \( \beta_0 \) is a constant term, and \( \beta_1 \) - \( \beta_{33} \) are the regression coefficients. One of the main advantages of the BBD design is that it takes into account quadratic terms, therefore it is suitable for design optimization. The number of experimental points can be determined by the following expression

\begin{equation}
N = 2K(K - 1) + C_p
\end{equation}

where \( K \) represents the number of parameters and \( C_p \) the number of center points.

In this study \( K \) and \( C_p \) were set at 3, therefore, 15 experiments were conducted with the possibility of estimating the mean and standard deviation at the center point. Three factors were investigated: initial concentration of target organic pollutant (\( C_0 \)), electrical power of the lamp (\( P \)), and flowrate (\( Q \)). The experimental design is illustrated in the following Table 4.1 in coded values and in standard order.

**Table 4.1: Coded factors level for a Box-Behnken design of a three variable system**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>x₁ or C₀</th>
<th>x₂ or P</th>
<th>x₃ or Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>7</td>
<td>-1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
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<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
where -1, 0, and +1 represent the lowest, middle, and highest range respectively. Low, middle and high range for initial concentrations of pCBA were chosen as 2.6 - 5.2 - 7.8 mg L\(^{-1}\) and for methylene blue as 5 - 10 - 15 mg L\(^{-1}\). In all DOE experiments the low, middle and high range for electrical power efficiency and flowrate were selected as 60% - 80% - 100% and 2.5 - 4.5 - 6.5 L min\(^{-1}\), respectively. The experiments were executed in random order to reduce the bias by equalizing other factors that were not explicitly accounted for in the experimental design.

The BBD was chosen because, if compared with other response surface designs, it was demonstrated to be more efficient than the central composite design and much more efficient than the three level full factorial design where the efficiency of one experimental design is defined as the number of coefficients in the estimated model divided by the number of experiments (Ferreira et al., 2007).

### 4.2.5 Additional reactions

The following Table reports the additional elementary reactions which were added into the MATLAB mechanistic model as well as coded in C language and added into Fluent as user-defined scalars (UDS).

<table>
<thead>
<tr>
<th>Symbol and Units</th>
<th>Elementary Reaction</th>
<th>Value and Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Phi_{11}) ([\text{mol einstein}^{-1}])</td>
<td>(\text{pCBA} + h\nu_{253.7\text{nm}} \rightarrow \text{products})</td>
<td>0.013 [Bagheri and Mohseni, 2014]</td>
</tr>
<tr>
<td>(\Phi_{12}) ([\text{mol einstein}^{-1}])</td>
<td>(\text{pCBA} + h\nu_{185\text{nm}} \rightarrow \text{products})</td>
<td>0.013 [Bagheri and Mohseni, 2014]</td>
</tr>
<tr>
<td>(k_{111}) ([\text{m}^3\text{mol}^{-1}\text{s}^{-1}])</td>
<td>(\text{pCBA} + \text{HO}^+ \rightarrow 3\text{OHpCBA})</td>
<td>(4.42\times10^6) [Mezyk et al., 2009]</td>
</tr>
<tr>
<td>(k_{112}) ([\text{m}^3\text{mol}^{-1}\text{s}^{-1}])</td>
<td>(\text{pCBA} + \text{HO}^+ \rightarrow 2\text{OHpCBA})</td>
<td>(4.42\times10^6) [Mezyk et al., 2009]</td>
</tr>
<tr>
<td>(k_{113}) ([\text{m}^3\text{mol}^{-1}\text{s}^{-1}])</td>
<td>(\text{pCBA} + e^-_{\text{aq}} \rightarrow \text{products})</td>
<td>(9.03\times10^6) [Mezyk et al., 2009]</td>
</tr>
<tr>
<td>(1.5\times10^6) [Manion et al. - NIST Database]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{114}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>pCBA + H$^+$ → products</td>
<td>1.1$\times$10$^6$ [Mezyk et al., 2009]</td>
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<td>------------------------</td>
<td>--------------------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.85$\times$10$^6$ [Manion et al. - NIST Database]</td>
</tr>
<tr>
<td>$k_{115}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>3OHpCBA + HO$^+$ → products</td>
<td>8.54$\times$10$^6$ [Mezyk et al., 2009]</td>
</tr>
<tr>
<td>$k_{116}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>3OHpCBA + e$_{aq}^-$ → products</td>
<td>7.13$\times$10$^6$ [Mezyk et al., 2009]</td>
</tr>
<tr>
<td>$k_{117}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>2OHpCBA + HO$^+$ → products</td>
<td>6.95$\times$10$^6$ [Mezyk et al., 2009]</td>
</tr>
<tr>
<td>$k_{118}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>2OHpCBA + e$_{aq}^-$ → products</td>
<td>7.66$\times$10$^6$ [Mezyk et al., 2009]</td>
</tr>
<tr>
<td>$k_{119}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>pCBA + HO$^+$ → 4ClBzA</td>
<td>2.21$\times$10$^6$ [Zona et al., 2010]</td>
</tr>
<tr>
<td>$k_{120}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>pCBA + HO$^+$ → 4HydroBzA</td>
<td>4.42$\times$10$^6$ [Zona et al., 2010]</td>
</tr>
<tr>
<td>$k_{121}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>4ClBzA + HO$^+$ → products</td>
<td>5.3$\times$10$^6$ [He et al., 2011]</td>
</tr>
<tr>
<td>$k_{122}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>4HydroBzA + HO$^+$ → products</td>
<td>2.7$\times$10$^7$ [Manion et al. - NIST Database]</td>
</tr>
</tbody>
</table>

Para-chlorobenzoic acid can be oxidized by direct photolysis at both 185 and 253.7 nm wavelengths (Bagheri and Mohseni, 2014) and the degradation process can be expressed as a sequence of reactions as shown in the following degradation pathway scheme (Figure 4.5).
Figure 4.5: Schematic illustration of the proposed degradation pathway of pCBA
(He et al., 2011; Mezyk et al., 2008; Mezyk et al., 2009; Zona et al., 2010; Manion et al. - NIST database)

It can be observed that pCBA can react with HO* to produce 4-chloro-3-hydroxybenzoic acid (3OHpCBA) or 4-chloro-2-hydroxybenzoic acid (2OHpCBA) by addition of OH group (OH-adduct) to the ring in position 3 or 2 respectively. Moreover, the HO* species can substitute the carboxylic group forming 4-chloro-phenol (4ClBzA) or the HO* species can react with pCBA producing 4-hydroxybenzoic acid (4HydroBzA) by chloride abstraction. PCBA can also react with hydrogen radical (H*) as well as hydrated electron (e$_{aq}$) to produce secondary products.

A sensitivity study against the number of reactions involved in the pCBA degradation and product formation was conducted. Results, reported in Appendix C, confirmed that simulations are basically unaffected whether or not the less probable reactions (formation of 4HydroBzA and 4ClBzA) were included in the model.
4.2.6 The modified MATLAB mechanistic model

To analyze the experiments conducted under 185/253.7 irradiation, a mathematical 2-dimensional single-pass mechanistic model was developed in MATLAB consisting of the hydraulic, optical, and photochemical submodels.

All MATLAB simulations were conducted assuming a radial velocity distribution typical of the fully-developed laminar flow regime. The annular gap was divided into 200 equidistant nodes and for each of them the analytical equation of laminar flow (already described by Eq. 3.9) at its specific radial distance was implemented.

Due to the good penetration of VUV/UV radiation in water at 185/253.7 nm and the relatively short physical dimension of the annulus used in the experiments (1 mm), the concept of the hydraulic bypass, illustrated in Figure 3.3 and discussed in the paragraph 3.2.4, was not considered in these simulations. The absorbed UV power at each node of the annular gap was estimated assuming a radial lamp emission model. The fluence rate distribution was described as in Eq. 3.3 where \( P_{uv} \) represented the UV power emitted from the sleeve obtained by multiplying the electrical power of the lamp (240 W) by a calibrated factor which took into account the UV output, the energy absorbed by air and quartz sleeve and the energy lost due to reflection across the interfaces air/quartz and quartz/water. The absorption coefficients \( A_{\lambda} \) of solution at the investigated wavelengths were defined as following

\[
A_{185} = (\varepsilon_{H_2O,185} \cdot [H_2O]) + (\varepsilon_{H_2O_2,185} \cdot [H_2O_2]) + (\varepsilon_{pCBA,185} \cdot [pCBA]) \tag{4.3}
\]

\[
A_{253.7} = (\varepsilon_{H_2O_2,253.7} \cdot [H_2O_2]) + (\varepsilon_{pCBA,253.7} \cdot [pCBA]) \tag{4.4}
\]

where \( \varepsilon_{\lambda} \) represents the molar absorption coefficient of the species at a specific wavelength. In particular, the values of \( \varepsilon \) equal to 3.24 • 10^{-3} \text{ m}^3 \text{ mol}^{-1} \text{ m}^{-1} \) (base 10) were considered for water at the wavelengths of 185 nm; for \( H_2O_2 \), the values of \( \varepsilon \) equal to 28.9 and 1.84 \text{ m}^3 \text{ mol}^{-1} \text{ m}^{-1} \) (base 10) were chosen for the wavelengths of 185 and 253.7 nm, respectively. For pCBA the values of \( \varepsilon \) equal to 2138 and 245 \text{ m}^3 \text{ mol}^{-1} \text{ m}^{-1} \) were used in the model for the wavelengths at 185 and 253.7 nm, respectively (Bagheri and Mohseni, 2014). Moreover, due to the relatively high radiation transmittance of the
solution, reflection of VUV/UV light at photoreactor wall ($R_w$) was taken into account. According to laboratory measurements, values of 24% and 20% of reflection were adopted for the stainless steel at 253.7 and 185 nm respectively (courtesy of Dr. Gord Knight, Trojan Technologies).

The system of ordinary differential equations (ODEs) was solved simultaneously in each node of the annular gap as a series of parallel kinetic models, adopting the stiff MATLAB solver ODE15s. The residence time of the solution at each node was defined as ratio between the lamp arc length and the local velocity. This residence time was applied to solve the system of kinetic reactions. The final concentration of the target pollutant was calculated as mass weighted average at each node of the outlet annular gap.

Details of the MATLAB code adopted in the numerical simulations are reported in Appendix D and E of this thesis.

4.2.7 CFD model of annular photoreactor: governing equations and boundary conditions

To validate the experimental data collected under 185/253.7 nm irradiation, a 2-dimensional axisymmetric model of an annular photoreactor was developed also using CFD.

The software ANSYS Gambit v.2.4.6 (Canonsburg, USA) was used to generate the computational grid for the CFD analysis. Two domains were reproduced: water and air. The quartz sleeve was modeled as semi-transparent wall to take into account the refraction of radiation due to the different media, according to the Snell’s law. The geometrical properties of the photoreactor reproduced in Gambit are illustrated in the following Figure 4.6.
Figure 4.6: Schematic representation of the 2-dimensional axisymmetric geometry defined in Gambit

A pre-inlet and post-outlet of length 100 mm were added to guarantee the fully developed flow and to avoid back-flow. To ensure accurate results of hydraulics, radiation, and transported species, a radial division of 20 and 6 uniform elements in water and air domains, respectively, were applied. The axial direction was discretized into a uniform distribution of nodes with interval 1.5 mm achieving an aspect ratio of about 1:7. The geometry was discretized compressively into 103,200 structural quad elements. Mesh dependency studies indicated that the computational grid was fine enough to give grid independent results. All the domains were scaled and translated in ANSYS Fluent to match the geometrical properties of the annular photoreactor investigated in the 185/253.7 nm experiments.

Due to the range of $Re$ number explored in the experimental campaign ($Re$ ranging from 940 to 2,300), laminar and turbulent models were considered in the numerical simulations. The steady state governing equations for continuity, momentum and scalar transport in laminar regime were described already in the previous chapter (Eq. 3.11 - 3.14). In addition, in case of turbulent regime, the realizable $\kappa-\varepsilon$ model was adopted (Shih et al., 1995). In this turbulent model the Boussinesq and the eddy viscosity approximations were combined to obtain an expression for the Reynolds stresses in an incompressible mean flow.

The modeled steady-state transport equations for $\kappa$ and $\varepsilon$ in the realizable $\kappa-\varepsilon$ model in cylindrical coordinates are:
\[
\frac{1}{r} \frac{\partial}{\partial r} (r \kappa u_r) + \frac{\partial}{\partial x} (\kappa u_x) = \left[ \frac{1}{r} \frac{\partial}{\partial r} \left[ (v + \frac{v_t}{\sigma_k}) r \frac{\partial \kappa}{\partial r} \right] + \frac{\partial}{\partial x} \left[ (v + \frac{v_t}{\sigma_\varepsilon}) \frac{\partial \kappa}{\partial x} \right] \right] + \frac{G_k}{\rho - \varepsilon} \quad (4.5)
\]
\[
\frac{1}{r} \frac{\partial}{\partial r} (r \varepsilon u_r) + \frac{\partial}{\partial x} (\varepsilon u_x) =
\]
\[
= \left[ \frac{1}{r} \frac{\partial}{\partial r} \left[ (v + \frac{v_t}{\sigma_\varepsilon}) \frac{\partial \varepsilon}{\partial r} \right] + \frac{\partial}{\partial x} \left[ (v + \frac{v_t}{\sigma_\varepsilon}) \frac{\partial \varepsilon}{\partial x} \right] \right] + C_1 \varepsilon S - C_2 \frac{\varepsilon^2}{\kappa + \sqrt{\nu \varepsilon}} \quad (4.6)
\]
\[
C_1 = \max \left[ 0.43, \frac{\eta}{\eta + 5} \right], \quad \eta = S \frac{\kappa}{\varepsilon}, \quad (4.7)
\]

In the previous equations \(G_k\) represents the generation of the turbulence kinetic energy due to the mean velocity gradient, \(C_2\) is a constant, \(\sigma_\kappa\) and \(\sigma_\varepsilon\) are the turbulent Prandtl numbers for \(\kappa\) and \(\varepsilon\) respectively (Ansys User Guide). \(S\) is the strain rate which can be represented as a tensor in cylindrical coordinates as follows (source: http://web.utk.edu/~kit/443/strainrate_cyl_sph.pdf)

\[
S = \begin{bmatrix}
\frac{\partial u_r}{\partial r} & \frac{1}{2} \left( \frac{\partial u_x}{\partial r} + \frac{\partial u_r}{\partial x} \right) \\
\frac{1}{2} \left( \frac{\partial u_x}{\partial r} + \frac{\partial u_r}{\partial x} \right) & \frac{\partial u_x}{\partial x}
\end{bmatrix}
\quad (4.8)
\]

All constants appearing in Eq. 4.5 - 4.7 are given in the following Table 4.3.

**Table 4.3: Empirical constants of the realizable \(\kappa\)-\(\varepsilon\) turbulence model**

<table>
<thead>
<tr>
<th>(C_2)</th>
<th>(\sigma_\kappa)</th>
<th>(\sigma_\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>1.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The scalar transport equation for single-phase flow in cylindrical coordinates is defined as:

\[
\frac{1}{r} \frac{\partial}{\partial r} (r \rho \phi u_r) + \frac{\partial}{\partial x} (\rho \phi u_x) - \Gamma_{C_A} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) + \frac{\partial^2 \phi}{\partial x^2} \right] = S_{C_A} \quad (4.9)
\]

where \(S_{C_A}\) represents the reactive species included in the model as source terms.

The species diffusivity was defined as:

\[
\Gamma_{C_A} = \frac{(2.4 \cdot 10^{-8})}{MW_{A}^{0.71}} + \frac{\mu_\varepsilon}{Sc} \quad (4.10)
\]
where the second contribution was considered only in the case of turbulent flow. The term $Sc$ is the Schmidt number equal to 0.7 while $\mu_t$ is the turbulent dynamic viscosity.

The fluence rate distribution in air and water was described using the radiative transfer equation (RTE) for non-scattering media (Eq. 2.8). The discrete ordinate (DO) radiation model was used to solve the RTE adopting an angular discretization theta and phi equal to 8x8 and theta and phi pixelation equal to 4x4. To take into account the emission at two wavelengths of the lamp, two monochromatic bands were defined in the DO model at 253.7 and 185 nm. Also, the wall of the photoreactor was considered as a reflective surface with 0.76 and 0.2 as internal emissivity and diffuse fraction, respectively for 253.7 nm which correspond to 24% of radiation reflected, 80% diffuse and 20% specular. For the case of 185 nm, the values of 0.8 and 0.2 as internal emissivity and diffuse fraction, respectively, were considered which correspond to 20% of radiation reflected, 80% diffuse and 20% specular (courtesy of Dr. Gord Knight, Trojan Technologies). The refractive index of water was assumed equal to 1.376 at both investigated wavelengths due to the negligible variation of the value at 185 nm and 253.7 nm while for the quartz sleeve the values 1.5063 and 1.576 were considered for 253.7 and 185 nm respectively.

The ANSYS Fluent software 12.1 (Ansys Inc., USA) was used to perform steady-state simulations using the segregated solver. The SIMPLE algorithm (Patankar, 1980) was chosen for pressure-velocity coupling with standard and second order upwind schemes for pressure, momentum and turbulence equations. All scalar equations describing the transported species were solved in Eulerian framework using power law scheme.

After solving the Eulerian transport equations to predict the species concentrations in the domain, a sufficient number (~1,400) of massless particles were injected uniformly at photoreactor inlet and their path tracked in Lagrangian framework by integrating the Newton’s equation of motion to simultaneously quantify the exposure of the selected species ($\text{HO}^*$, $\text{H}^*$, fluence rate at 185 and 253.7 nm).

The C code used in FLUENT to solve the spatial distribution of the species is reported in Appendix F. The convergence was achieved when all residuals were reduced to less than $10^{-4}$. 
4.3 Results and Discussion

4.3.1 Experimental data

Table 4.4 reports the concentration of pCBA before and after treatment as well as the percentage of removal measured after the first and second photoreactor at different flowrates and UV electrical powers. Experiments were conducted under 185/253.7 nm irradiation with a synthetic quartz sleeve.

Table 4.4: Initial and final concentration of pCBA after first and second annular photoreactor (185/253.7 nm irradiation - synthetic quartz sleeve)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>(C_0) [mg L(^{-1})] (after first annular photoreactor)</th>
<th>(C) [mg L(^{-1})] (after second annular photoreactor)</th>
<th>% reduction</th>
<th>(C_0) [mg L(^{-1})] (after second annular photoreactor)</th>
<th>% reduction</th>
<th>(P) [W]</th>
<th>(Q) [L min(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.39</td>
<td>1.74</td>
<td>67.75%</td>
<td>1.74</td>
<td>0.17</td>
<td>90.18%</td>
<td>108</td>
</tr>
<tr>
<td>2</td>
<td>5.39</td>
<td>3.47</td>
<td>35.69%</td>
<td>3.47</td>
<td>1.63</td>
<td>52.99%</td>
<td>108</td>
</tr>
<tr>
<td>3</td>
<td>5.41</td>
<td>0.41</td>
<td>92.39%</td>
<td>0.41</td>
<td>Not detected</td>
<td>-</td>
<td>240</td>
</tr>
<tr>
<td>4</td>
<td>5.41</td>
<td>1.85</td>
<td>65.87%</td>
<td>1.85</td>
<td>0.25</td>
<td>86.33%</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>2.65</td>
<td>0.06</td>
<td>97.78%</td>
<td>0.06</td>
<td>Not detected</td>
<td>-</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>2.65</td>
<td>0.46</td>
<td>82.71%</td>
<td>0.46</td>
<td>0.01</td>
<td>98.46%</td>
<td>180</td>
</tr>
<tr>
<td>7</td>
<td>8.12</td>
<td>2.45</td>
<td>69.85%</td>
<td>2.45</td>
<td>0.21</td>
<td>91.44%</td>
<td>180</td>
</tr>
<tr>
<td>8</td>
<td>8.12</td>
<td>5.06</td>
<td>37.66%</td>
<td>5.06</td>
<td>2.17</td>
<td>57.17%</td>
<td>180</td>
</tr>
<tr>
<td>9</td>
<td>2.65</td>
<td>0.47</td>
<td>82.28%</td>
<td>0.47</td>
<td>0.01</td>
<td>98.87%</td>
<td>108</td>
</tr>
<tr>
<td>10</td>
<td>2.65</td>
<td>0.10</td>
<td>96.11%</td>
<td>0.10</td>
<td>Not detected</td>
<td>-</td>
<td>240</td>
</tr>
<tr>
<td>11</td>
<td>8.12</td>
<td>5.12</td>
<td>36.87%</td>
<td>5.12</td>
<td>2.18</td>
<td>57.50%</td>
<td>108</td>
</tr>
<tr>
<td>12</td>
<td>8.12</td>
<td>3.09</td>
<td>61.96%</td>
<td>3.09</td>
<td>0.49</td>
<td>84.09%</td>
<td>240</td>
</tr>
<tr>
<td>13</td>
<td>5.39</td>
<td>1.73±0.1</td>
<td>67.86%</td>
<td>1.73</td>
<td>0.18</td>
<td>89.42%</td>
<td>180</td>
</tr>
</tbody>
</table>

The energy efficiency per unit of volume of treated fluid is one of the important parameters when cost function is involved. Therefore the electrical energy per order (EEO) was estimated as following

\[
EEO = \frac{P}{Q \cdot \log \left( \frac{C_0}{C} \right)} \left[ \frac{W \cdot \text{min}}{L \cdot \text{log}} \right] \tag{4.11}
\]

A low value of EEO is preferred because this means that low energy is required to mineralize a given amount of model pollutant.
A statistical analysis was conducted on the main variables ($C_0$, $P$ and $Q$) to investigate in this study their relative impact on the EEO and log removal. Figure 4.7 illustrates the t-student test conducted for pCBA degradation after the first (a) and second (b) photoreactor. Results show, in terms of percentage of significance, how the variable $C_0$ is the most significant factor with respect to EEO and log($C_0/C$). This observation is reasonable in ultrapure waters where the organic species acts simultaneously as target pollutant and HO* scavenger. Also, it can be noted that these results are valid within the range of the selected factors. In particular, we cannot extend these conclusions to very low concentrations of pCBA (ppb level).

![Figure 4.7: Overall t-student test on EEO and log($C_0/C$) after the first (a) and second (b) photoreactor. Percentage of significance for each investigated variables is](image)
reported (degradation of pCBA with 185/253.7 nm lamp and synthetic quartz sleeve)

Table 4.5 reports the concentration of pCBA before and after treatment as well as the percentage of removal obtained after the first and second photoreactor at different flowrates and UV electrical powers. Experiments were conducted at 185/253.7 nm irradiation with natural quartz sleeve, and therefore less 185 nm radiation reaching the fluid.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>(C_0) [mg L(^{-1})] (after first annular photoreactor)</th>
<th>(C) [mg L(^{-1})] (after second annular photoreactor)</th>
<th>% Reduction</th>
<th>(C_0) [mg L(^{-1})] (after first annular photoreactor)</th>
<th>(C) [mg L(^{-1})] (after second annular photoreactor)</th>
<th>% reduction</th>
<th>P [W]</th>
<th>(Q) [L min(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.74</td>
<td>3.63</td>
<td>36.71%</td>
<td>3.63</td>
<td>0.89</td>
<td>75.39%</td>
<td>108</td>
<td>2.606</td>
</tr>
<tr>
<td>2</td>
<td>5.74</td>
<td>4.58</td>
<td>20.15%</td>
<td>4.58</td>
<td>3.26</td>
<td>28.92%</td>
<td>108</td>
<td>6.741</td>
</tr>
<tr>
<td>3</td>
<td>5.96</td>
<td>2.22</td>
<td>62.72%</td>
<td>2.22</td>
<td>0.12</td>
<td>94.42%</td>
<td>240</td>
<td>2.317</td>
</tr>
<tr>
<td>4</td>
<td>5.96</td>
<td>4.13</td>
<td>30.70%</td>
<td>4.13</td>
<td>0.37</td>
<td>91.09%</td>
<td>240</td>
<td>6.723</td>
</tr>
<tr>
<td>5</td>
<td>2.84</td>
<td>0.68</td>
<td>76.13%</td>
<td>0.68</td>
<td>Not detected</td>
<td>-</td>
<td>180</td>
<td>2.737</td>
</tr>
<tr>
<td>6</td>
<td>2.84</td>
<td>1.59</td>
<td>44.11%</td>
<td>1.59</td>
<td>0.39</td>
<td>75.40%</td>
<td>180</td>
<td>6.723</td>
</tr>
<tr>
<td>7</td>
<td>8.54</td>
<td>5.31</td>
<td>37.78%</td>
<td>5.31</td>
<td>1.57</td>
<td>70.45%</td>
<td>180</td>
<td>2.503</td>
</tr>
<tr>
<td>8</td>
<td>8.54</td>
<td>7.15</td>
<td>16.31%</td>
<td>7.15</td>
<td>4.52</td>
<td>36.73%</td>
<td>180</td>
<td>6.741</td>
</tr>
<tr>
<td>9</td>
<td>2.84</td>
<td>1.60</td>
<td>43.81%</td>
<td>1.60</td>
<td>0.31</td>
<td>80.45%</td>
<td>108</td>
<td>4.387</td>
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<tr>
<td>10</td>
<td>2.84</td>
<td>0.91</td>
<td>67.97%</td>
<td>0.91</td>
<td>0.04</td>
<td>95.41%</td>
<td>240</td>
<td>4.301</td>
</tr>
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<td>11</td>
<td>8.54</td>
<td>6.74</td>
<td>21.01%</td>
<td>6.74</td>
<td>4.31</td>
<td>36.06%</td>
<td>108</td>
<td>4.061</td>
</tr>
<tr>
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<td>8.54</td>
<td>5.52</td>
<td>35.31%</td>
<td>5.52</td>
<td>2.42</td>
<td>56.20%</td>
<td>240</td>
<td>4.159</td>
</tr>
<tr>
<td>13</td>
<td>5.85</td>
<td>3.64±0.13</td>
<td>37.69%</td>
<td>3.64</td>
<td>1.26</td>
<td>65.56%</td>
<td>180</td>
<td>4.316</td>
</tr>
</tbody>
</table>

Figure 4.8 shows the relative impact of the three investigated variables on EEO and log of pCBA removal under 185/253.7 nm irradiation with natural quartz sleeve. Also in this case it can be noticed that the factor \(C_0\) is the most significant factor.
Figure 4.8: Overall t-student test on EEO and log(C₀/C) after the first (a) and second (b) photoreactor. Percentage of significance for each investigated variables is reported (degradation of pCBA with 185/253.7 nm lamp and natural quartz sleeve)

Table 4.6 reports the concentration of methylene blue before and after the treatment as well as the percentage of removal obtained after the first and second photoreactor at different flowrates and UV electrical powers. Experiments were conducted under 185/253.7 nm irradiation using synthetic quartz sleeve.
Table 4.6: Initial and final concentration of methylene blue after first and second annular photoreactor (185/253.7 nm irradiation - synthetic quartz sleeve)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>$C_0$ [mg L$^{-1}$]</th>
<th>$C$ [mg L$^{-1}$] (after first annular photoreactor)</th>
<th>% reduction</th>
<th>$C_0$ [mg L$^{-1}$] (after second annular photoreactor)</th>
<th>% reduction</th>
<th>$P$ [W]</th>
<th>$Q$ [L min$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.42</td>
<td>5.25</td>
<td>44.31%</td>
<td>5.25</td>
<td>2.53</td>
<td>51.73%</td>
<td>108</td>
</tr>
<tr>
<td>2</td>
<td>9.42</td>
<td>7.01</td>
<td>25.59%</td>
<td>7.01</td>
<td>4.93</td>
<td>29.70%</td>
<td>108</td>
</tr>
<tr>
<td>3</td>
<td>9.32</td>
<td>3.62</td>
<td>61.20%</td>
<td>3.62</td>
<td>1.09</td>
<td>69.92%</td>
<td>240</td>
</tr>
<tr>
<td>4</td>
<td>9.32</td>
<td>5.75</td>
<td>38.33%</td>
<td>5.75</td>
<td>3.20</td>
<td>44.25%</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>5.16</td>
<td>1.22</td>
<td>76.26%</td>
<td>1.22</td>
<td>0.20</td>
<td>84.00%</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>5.16</td>
<td>2.35</td>
<td>54.51%</td>
<td>2.35</td>
<td>0.92</td>
<td>60.96%</td>
<td>180</td>
</tr>
<tr>
<td>7</td>
<td>14.72</td>
<td>7.85</td>
<td>46.64%</td>
<td>7.85</td>
<td>4.22</td>
<td>46.23%</td>
<td>180</td>
</tr>
<tr>
<td>8</td>
<td>14.72</td>
<td>10.14</td>
<td>31.09%</td>
<td>10.14</td>
<td>7.33</td>
<td>27.68%</td>
<td>180</td>
</tr>
<tr>
<td>9</td>
<td>5.16</td>
<td>2.43</td>
<td>52.99%</td>
<td>2.43</td>
<td>0.97</td>
<td>60.20%</td>
<td>108</td>
</tr>
<tr>
<td>10</td>
<td>5.16</td>
<td>1.44</td>
<td>72.08%</td>
<td>1.44</td>
<td>0.29</td>
<td>79.93%</td>
<td>240</td>
</tr>
<tr>
<td>11</td>
<td>14.72</td>
<td>10.15</td>
<td>31.03%</td>
<td>10.15</td>
<td>7.27</td>
<td>28.43%</td>
<td>108</td>
</tr>
<tr>
<td>12</td>
<td>14.72</td>
<td>8.20</td>
<td>44.27%</td>
<td>8.20</td>
<td>4.63</td>
<td>43.55%</td>
<td>240</td>
</tr>
<tr>
<td>13</td>
<td>9.39</td>
<td>5.29±0.15</td>
<td>43.66%</td>
<td>5.29</td>
<td>2.66±0.09</td>
<td>49.72%</td>
<td>180</td>
</tr>
</tbody>
</table>

Analyzing the relative contribution of the three variables with respect to EEO it can be noted that the initial concentration of MB contributes 50-60% while the electrical UV power contributes 25% - 30% and the least significant is the flowrate that contributes 10% - 20%. If the response variable is the logarithm of MB degradation it can be observed that for the first annular photoreactor all factors contribute equally while for the second annular photoreactor the initial concentration contributes about 50% and the remaining contribution is almost equally divided between the power of the lamp and the flowrate.
Figure 4.9: Overall t-student test on EEO and log(C₀/C) after the first (a) and second (b) photoreactor. Percentage of significance for each investigated variables is reported (degradation of methylene blue with 185/253.7 nm lamp and synthetic quartz sleeve)

Table 4.7 reports the concentration of methylene blue before and after the treatment as well as the percentage of removal obtained after the first and second photoreactor at different flowrates and UV electrical powers. Experiments were conducted under 185/253.7 nm irradiation using natural quartz sleeve, and therefore less 185 nm radiation reaching the fluid.
**Table 4.7:** Initial and final concentration of methylene blue after first and second annular photoreactor (185/253.7 nm irradiation - natural quartz sleeve)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>$C_0$ [mg L$^{-1}$]</th>
<th>C [mg L$^{-1}$] (after first annular photoreactor)</th>
<th>% reduction</th>
<th>$C_0$ [mg L$^{-1}$] (after second annular photoreactor)</th>
<th>% reduction</th>
<th>P [W]</th>
<th>Q [L min$^{-1}$]</th>
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<td>6.67</td>
<td>27.99%</td>
<td>6.67</td>
<td>3.78</td>
<td>43.27%</td>
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<td>8.10</td>
<td>12.57%</td>
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<td>6.45</td>
<td>20.38%</td>
<td>108</td>
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<td>5.78</td>
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<td>2.63</td>
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<td>7.45</td>
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<td>7.45</td>
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<td>31.46%</td>
<td>240</td>
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<td>54.45%</td>
<td>2.37</td>
<td>0.63</td>
<td>73.27%</td>
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<td>36.95%</td>
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<td>19.00%</td>
<td>10.76</td>
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<td>33.64%</td>
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<tr>
<td>13</td>
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<td>23.80%</td>
<td>7.06</td>
<td>4.32±0.15</td>
<td>37.72%</td>
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</table>

Figure 4.10 shows the effect of the three investigated variables with respect to EEO and MB degradation considering a statistical t-student test. Similarly to the previous results, the variable $C_0$ is the most significant factor contributing 50-60% on EEO and MB degradation.
Another set of experiments was conducted using the annular photoreactors with Xe 172 nm lamp in single-pass tests as described in the paragraph 4.2.2. In the following Table 4.8 the percentage of reduction of pCBA due to 172 nm irradiation is reported at different flowrates and annular gaps.
Table 4.8: Initial and final concentration of pCBA (172 nm irradiation - synthetic quartz sleeve)

<table>
<thead>
<tr>
<th>Annular gap [mm]</th>
<th>$C_0$ [mg L$^{-1}$]</th>
<th>C [mg L$^{-1}$]</th>
<th>% reduction</th>
<th>Q [mL min$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.90</td>
<td>1.94</td>
<td>33.08%</td>
<td>274</td>
</tr>
<tr>
<td>1.0</td>
<td>2.90</td>
<td>2.08</td>
<td>28.32%</td>
<td>366</td>
</tr>
<tr>
<td>1.0</td>
<td>2.90</td>
<td>2.17</td>
<td>24.92%</td>
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</tr>
<tr>
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<td>23.97%</td>
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<tr>
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<td>5.24</td>
<td>4.20</td>
<td>19.80%</td>
<td>366</td>
</tr>
<tr>
<td>1.0</td>
<td>5.24</td>
<td>4.37</td>
<td>16.64%</td>
<td>457</td>
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<tr>
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<td>5.24</td>
<td>4.48</td>
<td>14.42%</td>
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<td>33.50%</td>
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<td>2.5</td>
<td>2.81</td>
<td>2.03</td>
<td>27.82%</td>
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<td>14.12%</td>
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<td>12.04%</td>
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<td>7.88</td>
<td>7.24</td>
<td>8.13%</td>
<td>548</td>
</tr>
</tbody>
</table>

The three investigated variables are the annular gap, initial concentration of the target pollutant and the flowrate. As observed in Figure 4.11, the factor $C_0$ is the most
significant parameter with respect to logarithm of pCBA degradation (57.0%) and EEO (73.5%). It can be noted that the gap contributes only by 11.4% with respect to log(C₀/C) and by 18% with respect to EEO, probably due the high value of water layer investigated in the 172 nm process (i.e. 1.0, 2.5, and 5.0 mm annular gap in comparison to ~18 µm which corresponds to 1-log photon penetration at 172 nm).

![Figure 4.11: Overall t-student test on log(C₀/C) (a) and EEO (b). Percentage of significance for each investigated variables is reported (degradation of pCBA with 172 nm lamp)](image)

Another set of experiments was conducted on the same apparatus using methylene blue. Results of MB degradation before and after the treatment are reported in the Table 4.9.
Table 4.9: Initial and final concentration of methylene blue (172 nm irradiation - synthetic quartz sleeve)

<table>
<thead>
<tr>
<th>Annular gap [mm]</th>
<th>C₀ [mg L⁻¹]</th>
<th>C [mg L⁻¹]</th>
<th>% reduction</th>
<th>Q [mL min⁻¹]</th>
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<tr>
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<td>14.71</td>
<td>13.87</td>
<td>5.67%</td>
<td>548</td>
</tr>
</tbody>
</table>

Similar significance levels are observed in the Figure 4.12 for methylene blue degradation as for the case of pCBA. The initial concentration is the most significant factor with respect to log(C₀/C) (53.7%) and EEO (70.8%).
Additional experiments conducted at 253.7 nm irradiation demonstrated that the contribution of direct photolysis on methylene blue and pCBA degradation, at the investigated initial concentrations, was null or negligible.

4.3.2 Comparison between VUV-AOPs (185/253.7 nm vs. 172 nm)

At this point of investigation, a figure of merit must be defined in order to compare the different advance oxidation processes in DI water and therefore the percentage of pollutant degradation versus the ratio \( P/Q \) was plotted.

Figure 4.13 shows the pCBA degradation measured in both 185/253.7 nm and 172 nm processes using synthetic quartz sleeve.
It is clearly evident that the 185/253.7 nm process is more efficient compared to the 172 nm process within the ranges of initial pCBA concentrations considered. For $P/Q$ values greater than 35, the percentage of pCBA degradation in the 185/253.7 nm process spanned a range of reduction from 36% to 98% while the efficiency of 172 nm irradiation was confined between 8% and 33%.

A confirmation that the 185/253.7 nm photolysis is an efficient process came from the case of methylene blue degradation (Figure 4.14) where the percentage reduction spanned a range from 25% to 76%, which is higher than that obtained from the 172 nm process (6%–35%).
A comparison was conducted between synthetic and natural quartz sleeve at 185/253.7 nm irradiation. Based on the BBD it was possible to fit the experimental data with a quadratic response surface where the dependent variable was the percentage of degradation of the organic pollutant and the independent variables were \( C_0 \), \( P \), and \( Q \). The polynomial coefficients of the response surface are reported in Appendix G relative to the investigated processes (i.e. pCBA degradation by 185/253.7 nm lamp enclosed in synthetic quartz, pCBA degradation by 185/253.7 nm lamp enclosed in natural quartz, methylene blue degradation by 185/253.7 nm lamp in synthetic quartz, and methylene blue degradation by 185/253.7 nm lamp enclosed in natural quartz). Parametric curves were plotted in the following Figure 4.15 and Figure 4.16 showing the predicted pollutant degradation at different initial concentrations at selected flowrates (\( Q_{\text{min}}, Q_{\text{ave}}, Q_{\text{max}} \)) and UV power (\( P_{\text{min}}, P_{\text{max}} \)).
Figure 4.15: pCBA degradation efficiency under 185/253.7 nm irradiation (synthetic and natural quartz sleeve)
From Figure 4.16 it can be noted how the parametrical curves exhibit a pronounced curvature in the direction of $C_0$. This behavior could suggest a complex mechanism of methylene blue degradation at the investigated processes. Also the parametric curves associated to the pollutant degradation using synthetic quartz (blue curves) are always above to the ones associated to the degradations with natural quartz (red curves).
indicating a better performance of the synthetic quartz sleeve. A comparison of performance between synthetic and natural quartz was evaluated by averaging the difference between pollutant degradation with synthetic quartz and pollutant degradation with natural quartz. The results are reported in the following Table 10 and Table 11.

Table 4.10: Average of difference between pCBA degradation using synthetic and natural quartz

<table>
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<th>$P_{\text{min}}$</th>
<th>$P_{\text{max}}$</th>
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</thead>
<tbody>
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<td>$Q_{\text{min}}$</td>
<td>30.0 %</td>
<td>22.7 %</td>
</tr>
<tr>
<td>$Q_{\text{ave}}$</td>
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<td>25.0 %</td>
</tr>
<tr>
<td>$Q_{\text{max}}$</td>
<td>17.4 %</td>
<td>29.4 %</td>
</tr>
</tbody>
</table>

Table 4.11: Average of difference between MB degradation using synthetic and natural quartz

<table>
<thead>
<tr>
<th></th>
<th>$P_{\text{min}}$</th>
<th>$P_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{min}}$</td>
<td>19.6 %</td>
<td>25.1 %</td>
</tr>
<tr>
<td>$Q_{\text{ave}}$</td>
<td>17.0 %</td>
<td>24.1 %</td>
</tr>
<tr>
<td>$Q_{\text{max}}$</td>
<td>14.5 %</td>
<td>21.5 %</td>
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</tbody>
</table>

The following Figure 4.17 shows the good agreement between model prediction and experimental data collected at 185/253.7 nm irradiation with synthetic and natural quartz sleeve.
4.3.3 Model calibration and validation - MATLAB

After concluding that the 185/253.7 nm process is more efficient than the 172 nm process, at the investigated conditions, a simulation tool was required to explore in depth the VUV/UV irradiation applied to ultrapure waters. In the previously described extended MATLAB mechanistic model, the only parameter requiring calibration was the fraction of 185 nm power entering in the water domain therefore a search of global minimum in MATLAB was conducted (Figure 4.18). An error function was defined as the sum of absolute differences between observed and predicted final concentrations of pCBA. The minimum was found to be at 3.25% of the electrical power of lamp with an absolute error equal to 1.16 mg L\(^{-1}\). This fraction takes into account the UV output at 185 nm, the energy absorbed in air and quartz sleeve, and the reflections along the interfaces of air/quartz and quartz/air.
Figure 4.18: Global minimum for the fraction of 185 nm power in water

The comparison between experimental and numerical data, reported in Figure 4.19, shows an excellent overall agreement.
Figure 4.19: Comparison between predicted (MATLAB) and observed (experimental) data (pCBA degradation - 185/253.7 nm)

The MATLAB model requires relative short computational time to solve the system of differential equations; however, it oversimplifies the process. For this reason a better understanding of the phenomenon can be achieved with the use of the CFD.

4.3.4 Model calibration and validation - FLUENT

The CFD model was built to take into account different features which cannot be easily implemented in MATLAB such as: 1) reflection at reactor wall, thus adding the specular and diffuse contribution; 2) a turbulent model which allows mass transfer; 3) refraction of quartz sleeve; and 4) the radiative transfer equation solved with the DO model which takes into account the cosine emission model.

As was done for the MATLAB case, the 185 nm power in CFD simulation was calibrated with the experimental data collected from the first annular photoreactor involving pCBA degradation under 185/253.7 nm irradiation with lamp enclosed in a synthetic quartz sleeve. The calibrated value was found to be 2.5% of electrical power. This value takes
into account the radiative energy absorbed by ozone gas eventually produced in the air domain as well as the energy absorbed by the quartz sleeve. Figure 4.20 shows the good agreement between CFD-generated numerical results and experimental data.

![Comparison between predicted (FLUENT) and observed (experimental) data (pCBA degradation under 185/253.7 irradiation after first annular photoreactor - synthetic quartz sleeve)](image)

**Figure 4.20: Comparison between predicted (FLUENT) and observed (experimental) data (pCBA degradation under 185/253.7 irradiation after first annular photoreactor - synthetic quartz sleeve)**

An error function was defined as the difference between the experimental and predicted data. Upon evaluating the influence of the three main variables it can be observed in Figure 4.21 that the lamp power is the most significant (61.1%) factor. This confirms the necessity of an accurate calibration of this parameter. The reason of \( P \) as most influential factor with respect to the error function could be due to the non-correct fluence rate model adopted. Another reason may be to the mismatch between the modeled and real absorption of the fluid.
The calibrated model was applied to predict the pCBA degradation through the second annular photoreactor. Figure 4.22 shows a good agreement with experimental data collected with a maximum and minimum error of 15.8% and 2.0% respectively.
Figure 4.22: Comparison between predicted (FLUENT) and experimental data (pCBA degradation under 185/253.7 irradiation after second annular photoreactor - synthetic quartz sleeve)

The fraction of VUV output at 185 nm was also calibrated by comparison of numerical with three experimental data points collected under 185/253.7 nm irradiation with lamp enclosed in a natural quartz sleeve (Figure 4.23). The percentage was found to be 1.18 % of the electrical lamp power.
Figure 4.23: Comparison between experimental and numerical data (pCBA degradation under 185/253.7 irradiation after first annular photoreactor - natural quartz sleeve)

4.3.5 CFD optimization of annular photoreactors

The validated CFD model was used to deeply explore the role of the annular gap, initial concentration of pCBA, and presence or absence of baffles in annular photoreactors with 185/253.7 nm lamp enclosed in a synthetic quartz sleeve (Figure 4.24). The optimization strategy consisted in the following steps: 1) investigation of pCBA degradation in photoreactors with different annular gaps at low and high $Re$ number; 2) investigation of reactor performance in terms of particle dose distribution of different variables; 3) investigation of the role of $C_0$ in terms of dose HO*.
The simulation reproducing the experiment #8 from Table 4.4 was considered as the reference case. The initial concentration of pCBA was set to 8.12 mg L\(^{-1}\), the flowrate 6.539 L min\(^{-1}\) and the power output was set to 56.17 and 4.83 W for 253.7 nm and 185 nm respectively. Seven baffles were added into the geometry, equally spaced, each of them exhibiting a length equal to half size of the annular gap.

An initial investigation focused on comparison the pCBA degradation and pressure drop in a photoreactor considering different annular gaps (Re ranging from 1,500 to 2,200), with and without baffles. In all photoreactor simulations the external sleeve diameter was kept constant (i.e. 30 mm). Results, reported in Figure 4.25 and Figure 4.26, show how the presence of baffles improved the mixing therefore the pCBA degradation up to 72%. The annular gap equal to 10 mm with baffles was the best configuration in terms of pressure drops (122.7 Pa) and efficiency in pCBA degradation (68%) while 5 mm was the best for an annular photoreactor without baffles (pressure drops = 180 Pa, pCBA degradation = 47%).
Figure 4.25: pCBA degradation vs. annular gap - with and without baffles at low $Re$ number and constant flowrate

Figure 4.26: Pressure drop vs. annular gap – with and without baffles at low $Re$ number
The selected best photoreactor configurations were confirmed from another set of simulations assuming 0.812 mg L\(^{-1}\) as initial pCBA concentration (10 times smaller than the previous case), and flowrate equal to 84 L min\(^{-1}\) corresponding to higher Re number (Re ranging from 17,000 to 28,000).

At this point of the investigation, attention was focused on two annular photoreactors namely 10 mm with baffles and 1 mm without baffles. The first one was chosen as the best in terms of high pCBA reduction and low pressure drops while the second was chosen because it represented the experimentally tested photoreactor. The initial concentration of pCBA was set to 1 mg L\(^{-1}\) and the flowrate to 84 L min\(^{-1}\). After solving the velocity, fluence rate and species distributions in the water domain using Eulerian framework, a sufficient number (i.e. ~1,400) of neutrally buoyant particles were injected uniformly distributed at the inlet in order to evaluate simultaneously doses per particle of different species in a Lagrangian framework. Figure 4.27 shows the dose distribution of 253.7 nm radiation for the two investigated photoreactors. It can be noted that, for the case of 10 mm annular gap, the distribution is wide due to the mixing enhanced by the baffles. The dose distribution spanned a range between 600 and 1000 J m\(^{-2}\). For the case of 1 mm annular gap, the dose distribution is narrower but much lower, spanning a range between 80 and 90 J m\(^{-2}\). This photoreactor exhibits dose 253.7 nm per particle about ten times smaller than the case of 10 mm annular gap.
Figure 4.27: Dose 253.7 nm per particle distribution

Figure 4.28 shows the dose 185 nm distribution obtained from the two investigated photoreactors. The narrow dose for 1 mm annular gap (range 3-4 J m$^{-2}$) is within the range spanned by the other photoreactor (range 2-20 J m$^{-2}$).
Figure 4.29 shows the dose HO\(^*\) distribution for the two investigated photoreactors. Even in this case, for the 1 mm annular gap, the dose HO\(^*\) (range \(1.7 \times 10^{-8} - 2.4 \times 10^{-8}\) mol s m\(^{-3}\)) is within the range spanned by the 10 mm baffled photoreactor (range \(1.6 \times 10^{-8} - 1.2 \times 10^{-7}\) mol s m\(^{-3}\)). The photoreactor with 10 mm baffled annular gap, at this investigated condition, produces higher dose HO\(^*\) than the 1 mm without baffles leading to a better degradation of the organic pollutant. It may also be seen that the 185 nm dose distribution and the HO\(^*\) dose distribution are qualitatively similar. This observation will be explored further in a later section.
Figure 4.29: Dose HO* per particle distribution

In order to gain better understanding of the performance efficiency of the VUV/UV process, the average dose HO* at different initial concentrations of target pollutant was analyzed. Two annular gaps were taken into account: 10 mm with seven baffles equally spaced and 1 mm without baffles. The flowrate was set at 84 L min\(^{-1}\) corresponding to a turbulent regime. Due to the fact that \(C_0\) was the most important factor in the analyzed processes, a total of nine different pCBA concentrations were considered in the investigation to cover the typical amounts encountered in various waters: industrial wastewater (1-100 mg L\(^{-1}\)), municipal wastewater (0.1-1 mg L\(^{-1}\)) and surface water (0.001-0.1 mg L\(^{-1}\)). Results, illustrated in Figure 4.30 in a bi-logarithmic plot, show that the average dose HO* followed a negative linear trend as the concentration of pCBA increased, with a plateau of HO* encountered as the concentration of the pollutant fell below 50 ppb. This result highlights the role of pCBA as the main scavenger for HO* species.
Figure 4.30: Average dose HO* vs. pCBA initial concentration – turbulent regime

Figure 4.30 also indicates the beneficial role of the baffles at any \( C_0 \): if the initial concentration of pCBA was lower than 50 ppb, the average dose HO* was higher by 1 order of magnitude than the case of 1 mm annular gap without baffles. This better efficiency tended to decrease at higher pCBA concentrations due to the smaller penetration of light caused by the higher absorption of the treated solution.

4.3.6 Lagrangian dose series of AOP-participating species

Lagrangian actinometry is usually employed to determine the UV dose distribution in reactors. It is a common practice in water disinfection to quantify the 253.7 nm fluence distribution for proper reactor sizing. But, in case of AOPs where degradation of pollutants are caused by reaction with radicals generated by exogenous hydrogen peroxide or water photolysis at short wavelengths such as 185 or 172 nm, the quantification of fluence rate and HO* species becomes an experimentally challenging task due to the limited penetration of radiation into the fluid. From the results reported in the previous paragraph it is not possible to find a common scaling factor among the
investigated dose distributions (253.7 nm, 185 nm, and HO*). Therefore there is the necessity to define a tool or method able to quantify these dose distributions in a photoreactor for a proper design or scale-up. In the hypothesis that the quantification of 185 nm and HO* doses is paramount in an AOP initiated by short wavelengths, a question is raised if any type of correlation exists between various species and the 253.7 nm dose distribution, which is easier to experimentally quantify. Numerical experiments were conducted on the 10 mm baffled annular gap photoreactor and 1 mm annular gap without baffles at different \( C_0 \) (i.e. 0.1 and 1.0 mg L\(^{-1}\)) and flowrates (i.e. 42, 84, and 126 L min\(^{-1}\)) exploring possible correlations among 253.7 nm, 185 nm, and HO* dose distributions. The following Figure 4.31 illustrates an example of uncorrelated (left) and perfectly correlated (right) distributions of variable A and B.

![Figure 4.31: Example of uncorrelated (left) and perfectly correlated (right) distributions of variable A and B](image)

The attention was focused on the baffled 10 mm annular gap photoreactor because it was found to be an optimal reactor in terms of pCBA degradation and pressure drops. More detailed correlations between dose distributions are reported in Appendix H-S of this thesis. It can be noted, from the following Figure 4.32, that the 185 nm and 253.7 nm dose distributions are uncorrelated therefore it is not possible to determine one from the other.
The non-correlation and an unclear pattern between the 253.7 nm and 185 nm dose per particle distributions suggest the relevant influence of the hydraulics and the local photon absorption of species in the process. Similarly it can be noted in the following Figure 4.33 that the 253.7 nm and HO* dose distributions at different flowrates and initial concentrations of pCBA are largely uncorrelated.
The following Figure 4.34 illustrates a better correlation between 185 nm and HO* dose distributions. In particular, if the concentration of pollutant is low (e.g. 0.1 mg L\(^{-1}\)) it can be observed a moderate correlation. A possible explanation could be related to the scavenging effect of organic pollutant on the HO* species: if the pollutant is present at low concentration in ultrapure water, the scavenging effect on HO* is limited, and therefore the radical species, due to the complex net of reactions involved, propagates outside the 1-log photon penetration layer, as already noticed in the numerical investigations described in Chapter 3. If the concentration of the organic pollutant is high (e.g. 1.0 mg L\(^{-1}\)), the scavenging effect limits the propagation of HO* species within the photoactive layer.
4.4 Conclusions

In this study, the degradation of para-chlorobenzoic acid and methylene blue in distilled (ultrapure) water was investigated using annular photoreactors with varying annular gaps. The water spiked with the model pollutant was irradiated by a low pressure Hg 185/253.7 nm lamp as well as a Xe excimer 172 nm lamp leading to the production, due to water photolysis, of HO* species responsible for pollutant degradation. A statistical analysis of experimental data collected revealed that the variable $C_0$ was the most significant factor with respect to EEO and log$(C_0/C)$. A figure of merit defined in terms of percentage of pollutant degradation revealed that, at the investigated experimental conditions, the
185/253.7 nm process was more efficient (three times in case of pCBA, twice in case of methylene blue) than the 172 nm process.

After extending the validated mechanistic model with additional elementary reactions, the tested annular photoreactor with 185/253.7 nm lamp was geometrically reproduced in MATLAB and ANSYS Fluent. After a careful calibration of the 185 nm power, predicted data revealed a good agreement with experimental results.

The validated numerical model was tested at different annular photoreactor gap sizes and initial pCBA concentrations to determine the dose of HO*. Simulations revealed the benefit in adopting an annular photoreactor with 10 mm baffled annular gap compared to 1 mm without baffles. The increment in dose of HO* between 10 mm baffled annular gap and 1 mm without baffles ranged from 7.8%, at $C_0 = 100$ mg L$^{-1}$, to 81%, at $C_0 = 0.001$ mg L$^{-1}$.

Since the primary degradation mechanisms behind the VUV-AOP is associated to the 185 nm and HO* dose distributions, their quantification is of paramount importance in photoreactor design. As of today, no experimental method such as Lagrangian actinometry exists for their direct quantification. The use of numerical models such as CFD can be a valid alternative for furthering the understanding VUV/AOP photoreactor performance initiated by short wavelengths and the quantification of dose distribution of species playing a relevant role in the AOP process. Once validated, the numerical models can be also used for photoreactor design, optimization and scale-up.

4.5 References


Chapter 5

5 CONCLUSIONS AND RECOMMENDATIONS

In this last chapter the main conclusions of this study are presented. Additionally, the recommendations for future works are suggested.

5.1 Conclusions

The first part of this study focused on the limitation in treating highly absorbing fluids with ultraviolet light due to the short photon penetration in the media. This optical behavior can lead to: a) photoreactors dealing with highly absorbing fluids are likely to be energy-inefficient due to a non-ideal use of the ultraviolet light; b) the quantification of fundamental parameters such photo-chemical rate constants could be a challenging task to address due to the severe mixing-limited conditions. Therefore, new alternative methods and standard modeling approaches were described.

The first investigation focused on the Taylor-Couette apparatus as an alternative collimated beam reactor to quantify the intrinsic inactivation kinetics of microorganisms in highly absorbing fluids irradiated by 253.7 nm light. A series of passive and reactive tracer experiments were conducted to validate the Taylor-Couette collimated beam apparatus CFD model. Subsequently, a sensitivity study was performed for fluids with varying absorption coefficients and for microbes with differing inactivation rate constants to determine a generalized criterion for accepting or rejecting inactivation data for precise kinetics measurements. It can be concluded that a Taylor number of \( \sim 46,500 \) was sufficient to overcome the very short UV light penetration at \( \text{UVT}_{253.7} \sim 0.001\% \text{ cm}^{-1} \) as long as the \( \log_{10} \) reduction value was used as controlling parameter. Specifically, it was identified that, in case of first order inactivation kinetics, the applied average dose (AD) should not be higher than 3 times the dose required for one \( \log_{10} \) inactivation (also known as \( D_{10} \)) in order to generate data for accurate kinetic studies.

In subsequent studies, the attention continued to address on highly absorbing fluid irradiated by UV light, but the focus shifted to advanced oxidation processes instead of
disinfection. In particular, natural pure water when irradiated by short wavelengths ($\lambda < 200$ nm) exhibits high absorbance. The energy associated to these wavelengths is transferred to the water and causes the formation of HO* species which is responsible for degradation of organic pollutants. The focus was on developing a novel mechanistic model that describes the vacuum UV advanced oxidation process in an annular photoreactor initiated by 172 nm and 185 nm (in combination with 253.7 nm, with and without exogenous H$_2$O$_2$). The model was developed from first principles by incorporating the vacuum UV-AOP kinetics into the theoretical framework of in-series continuous flow stirred tank reactors. After conducting a sensitivity analysis, model predictions were compared against experiments conducted under a variety of conditions: (a) photo-induced formation of hydrogen peroxide by water photolysis at 172 nm (for both air- and oxygen-saturated conditions); (b) photo-induced formation of hydrogen peroxide by water photolysis at 185/253.7 nm (in the presence of formic acid, with and without the initial addition of hydrogen peroxide); (c) direct photolysis of hydrogen peroxide by 253.7 nm; (d) degradation of formic acid by 185/253.7 nm (with and without initial addition of hydrogen peroxide); and (e) degradation of formic acid by 253.7 nm (with the addition of exogenous hydrogen peroxide). In all cases, the model was able to accurately predict the time-dependent profiles of hydrogen peroxide and formic acid concentrations. Two newly recognized aspects associated with water photolysis were identified through the use of the validated model. Firstly, unlike the 185 nm and 253.7 nm cases, water photolysis by the 172 nm wavelength revealed a depth of photoactive water layer that is an order of magnitude greater (~230-390 $\mu$m, depending on the specific operating conditions) than the 1-log photon penetration layer (~18 $\mu$m). To further investigate this potentially very important finding, a computational fluid dynamics model was set up to assess the role of transport mechanisms and species distributions within the photoreactor annulus. The model confirmed that short-lived hydroxyl radicals were present at a radial distance far beyond the ~18 $\mu$m photon penetration layer. Secondly, kinetic simulations showed that the higher penetration depth of hydroxyl radicals was not caused by diffusive or convective transport phenomena but rather the effect of non-linear behavior of the complex reaction kinetics involved in the process.
Experimental study were conducted on thin-film annular photoreactors with lamps emitting 185/253.7 nm and 172 nm wavelengths. Methylene blue and para-chlorobenzoic acid were selected as target organic pollutant added into distilled water in certain quantities, according to a Box-Behnken design, avoiding undetectable concentrations at the outlet. A comparison between these advanced oxidation processes was discussed. Results revealed that, in terms of percentage of pCBA degradation, at the explored conditions, the 185/253.7 nm process was more efficient by three times than the 172 nm process. Subsequently, the mechanistic model was extended with additional elementary reactions including the mechanism of degradation of pCBA due to radical species reaction. The annular photoreactor, adopted in the experiments, was modeled in MATLAB and ANSYS Fluent. The numerical model was validated with experimental data observing an overall good agreement and, subsequently, the model was used to explore different photoreactor configurations to identify optimal geometrical parameters. The final analysis between (a) an annular photoreactor with 10 mm water gap and seven equally spaced baffles with 5 mm length, and (b) an annular photoreactor with 1 mm water gap without baffles revealed that at high $Re$ number the configuration (a) was better in terms of the HO* dose leading to a higher percentage of pCBA degradation.

The 185 nm and HO* dose distributions in an AOP initiated by short wavelengths are paramount in photoreactor design. They cannot be indirectly estimated by experimental Lagrangian actinometry on 253.7 nm dose quantification due to their uncorrelation. Therefore, in absence of experimental methods for the direct measurements of HO* dose distribution, numerical models can be seen as a valid alternative for furthering the understanding VUV/AOP photoreactor performance initiated by short wavelengths. Once validated, the numerical models can be also used for photoreactor design, optimization and scale-up.

### 5.2 Recommendations for future work

From the experience acquired during the completion of this thesis, the following recommendations can be made for future work:
• The developed mechanistic model is based on elementary reactions in distilled water. To take into account a more complex water matrix, extending the model to nitrites, nitrates, chlorides, and sulphites has to be considered.

• The investigation described in the present thesis focused on different AOPs; namely, using 185/253.7 nm, 172 nm, and 253.7 nm with the exogenous hydrogen peroxide. A more comprehensive study can be achieved using the developed mechanistic model to compare other processes such as UV/O₃, and O₂/H₂O₂. Moreover the mechanistic model can be applied to lamps emitting at different wavelengths if the photolysis quantum yield, the absorption coefficient of the solution as well as the quartz sleeve, and the emission spectrum of the lamp are well known or can be measured at each investigated wavelength. A detailed analysis can be conducted on the production of dose HO* dose at different wavelengths where a trade-off may be observed due to short light penetration and high concentration of HO* species generated.

• In the present thesis annular photoreactors with their lamp parallel to the main direction of the flow were investigated. Different geometrical configurations can be explored with the use of CFD (e.g. cross-flow lamps photoreactors). Genetic algorithms can be adopted to search for optimum (e.g. the best position of the UV/VUV lamps, the number and the relative position of internal baffles to improve the mixing).

• A cost analysis has not been conducted in the present thesis and can be taken into account in future investigations. The electrical energy per order (EEO) concept could be expanded upon to be a function based on the cost of lamp, sleeve, and energy consumption. This cost function may be an important factor in an industry decision analysis.
## Appendices

### Appendix A: List of elementary reactions and rate constants (compiled from primary and secondary sources) for the 172 nm, 185 nm and 253.7 nm AOP

<table>
<thead>
<tr>
<th>Symbol and Units</th>
<th>Elementary Reaction</th>
<th>Value and Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_1$ [mol einstein$^{-1}$]</td>
<td>$\text{H}<em>2\text{O} + h\nu</em>{172\text{nm}} \rightarrow \text{HO}^* + \text{H}^*$</td>
<td>0.42 [Azrague et al., 2005]</td>
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<tr>
<td></td>
<td></td>
<td>0.45 [Gonzalez and Braun, 1995]</td>
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<td></td>
<td></td>
<td>0.42 [Gonzalez et al., 2004]</td>
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<tr>
<td></td>
<td></td>
<td>0.42 [Sosnin et al., 2006]</td>
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<td></td>
<td></td>
<td>0.37 [Zvereva, 2010]</td>
</tr>
<tr>
<td>$\Phi_2$ [mol einstein$^{-1}$]</td>
<td>$\text{H}<em>2\text{O} + h\nu</em>{172\text{nm}} \rightarrow \text{HO}^* + \text{H}^* + e^-_{\text{aq}}$</td>
<td>0.05 [Gonzalez and Braun, 1995]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.045 [Gonzalez et al., 2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 [Sosnin et al., 2006]</td>
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<tr>
<td></td>
<td></td>
<td>0.05 [Zvereva, 2010]</td>
</tr>
<tr>
<td>$\Phi_3$ [mol einstein$^{-1}$]</td>
<td>$\text{H}_2\text{O}<em>2 + h\nu</em>{172\text{nm}} \rightarrow \text{HO}^* + \text{HO}^*$</td>
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<td>$k_4$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<tr>
<td></td>
<td></td>
<td>$2.2 \times 10^7$ [Gonzalez et al., 2004]</td>
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<tr>
<td></td>
<td></td>
<td>$2.3 \times 10^7$ [Imoberdorf and Mohseni, 2011]</td>
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<td>$k_6$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<td>$k_6$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$k_7$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<td>$6.0 \cdot 10^4$ [Imoberdorf and Mohseni, 2011]</td>
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<td>$k_5$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$k_6$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<td>$6.0 \cdot 10^4$ [Gonzalez et al., 2004]</td>
<td>$6.0 \cdot 10^4$ [Imoberdorf and Mohseni, 2011]</td>
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<td>$k_{11}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$k_{12}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<tr>
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<tr>
<td>$k_{13}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$e^-_{\text{aq}} + H^+ + (+H_2O) \rightarrow H_2 + OH^-$</td>
<td>(2.5 \times 10^7) [Gonzalez and Braun, 1995] (2.5 \times 10^7) [Gonzalez et al., 2004] (2.5 \times 10^7) [Imoberdorf and Mohseni, 2011] (2.5 \times 10^7) [Zvereva, 2010] (2.8 \times 10^7) [Manion et al. - NIST Database]</td>
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<td>$k_{14}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$H^+ + OH^- \rightarrow e^-_{\text{aq}} + H_2O$</td>
<td>(1.5 \times 10^4) [Gonzalez and Braun, 1995] (2.2 \times 10^4) [Zvereva, 2010] (2.3 \times 10^4) [Manion et al. - NIST Database]</td>
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<td>$H^+ + H_2O_2 \rightarrow HO^+ + H_2O$</td>
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<td>$H^+ + O^{2-} \rightarrow HO^+$</td>
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<td>$3.5 \times 10^6$ [Imoberdorf and Mohseni, 2011]</td>
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<td>$\text{HO}^+ + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O}$</td>
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<th>$\text{HO}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^+ + \text{H}_2\text{O}$</th>
<th>$5.0\times10^4$ [Gonzalez and Braun, 1995]</th>
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<th>$\text{e}^-_{\text{aq}} + \text{HO}^+ \rightarrow \text{OH}^-$</th>
<th>$3.0\times10^7$ [Gonzalez and Braun, 1995]</th>
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<th>$k_{26}$ $[\text{m}^3\text{ mol}^{-1}\text{ s}^{-1}]$</th>
<th>$\text{HO}^+ + \text{HO}_2^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}$</th>
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<td>$O_2^{<em>-} + HO^</em> \rightarrow OH^- + O_2$</td>
<td>$6.6 \times 10^6$ [Imoberdorf and Mohseni, 2011]</td>
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<td>$HO^* + HO_2^- \rightarrow OH^- + HO_2^+$</td>
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<td>$k_{29}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<td>$e_{aq}^- + e_{aq}^- (+2H_2O) \rightarrow H_2 + 2OH^-$</td>
<td>$6.0 \times 10^6$ [Gonzalez and Braun, 1995]</td>
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<td>$k_{32} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
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<td>$2.0 \times 10^7$ [Gonzalez and Braun, 1995]</td>
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<td>$k_{33} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
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<td>$2.0 \times 10^7$ [Zvereva, 2010]</td>
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<td>$k_{34} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
<td>$e_{aq}^- + O_2^{2-} (+H_2O) \rightarrow OH^- + HO_2^-$</td>
<td>$1.3 \times 10^7$ [Zvereva, 2010]</td>
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<td>$k_{35} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
<td>$e_{aq}^- + HO_2^- \rightarrow OH^- + O^{*\ast}$</td>
<td>$3.5 \times 10^6$ [Zvereva, 2010]</td>
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<td>$k_{36} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
<td>$O^{*\ast} + O_2^{2-} (+H_2O) \rightarrow 2OH^- + O_2$</td>
<td>$6.0 \times 10^5$ [Zvereva, 2010]</td>
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<td>$k_{37} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
<td>$HO_2^- + O_3^{2-} \rightarrow OH^- + O_2 + O_2^{2-}$</td>
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<td>$k_{38} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
<td>$2O^{*\ast} (+H_2O) \rightarrow OH^- + HO_2^-$</td>
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<td>$k_{39} [\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$</td>
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<td>$k_{41}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{OH}^- + \text{HO}_2^\cdot \rightarrow \text{O}_2^\cdot^- + \text{H}_2\text{O}$</td>
<td>$1.0\times10^7$ [Zvereva, 2010]</td>
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<td>$k_{42}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2 + \text{H}_2\text{O}$</td>
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<td>$k_{43}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$</td>
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<td>$k_{44}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{O}^\cdot^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^\cdot^- + \text{H}_2\text{O}$</td>
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<td>$k_{45}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{O}^\cdot^- + \text{O}_2 \rightarrow \text{O}_3^\cdot$</td>
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<td>$k_{46}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{O}^\cdot^- + \text{O}_3^\cdot \rightarrow 2\text{O}_2^\cdot$</td>
<td>$7.0\times10^6$ [Zvereva, 2010] $7.0\times10^5$ [Manion et al. - NIST Database]</td>
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<td>$k_{47}$ [s$^{-1}$]</td>
<td>$\text{HO}_2^\cdot \rightarrow \text{H}^+ + \text{O}^\cdot^- \text{H}_2\text{O}_2$</td>
<td>$1.0\times10^6$ [Gonzalez and Braun, 1995]</td>
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<td>$k_{48}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{O}_2^\cdot^- + \text{H}^+ \rightarrow \text{HO}_2^\cdot$</td>
<td>$3.0\times10^7$ [Gonzalez and Braun, 1995] $5.1\times10^7$ [Zvereva, 2010] $5.7\times10^7$ [Manion et al. - NIST Database]</td>
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<td>$k_{49}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<td>$k_{51}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$H_2O_2 + O_3^- \rightarrow O_2 + O_2^- + H_2O$</td>
<td>1.6$\cdot 10^3$ [Zvereva, 2010]</td>
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<td>5.3$\cdot 10^{-1}$ [Gonzalez and Braun, 1995]</td>
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<td>$O_2^- + H_2O_2 \rightarrow OH^- + O_2 + HO^*$</td>
<td>1.6$\cdot 10^{-2}$ [Gonzalez and Braun, 1995]</td>
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<td>( k_{56} ) ([s^{-1}])</td>
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<td>$k_{66}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<td>$2.7\cdot10^1$ [Schulz et al., 2006]</td>
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<td>$k_{67}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$</td>
<td>$2.2\cdot10^0$ [Schulz et al., 2006]</td>
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<td>$k_{68}$ [s$^{-1}$]</td>
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<td>$9.7\cdot10^{-5}$ [Schulz et al., 2006]</td>
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<td>$k_{69}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$</td>
<td>$5.0\cdot10^7$ [Schulz et al., 2006]</td>
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<td>$k_{70}$ [s$^{-1}$]</td>
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<td>$6.0\cdot10^6$ [Schulz et al., 2006]</td>
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<td>$k_{72}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
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<td>$3.1\cdot10^5$ [Schulz et al., 2006]</td>
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<td>$k_{73}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{e}^-_{\text{aq}} + \text{CO}_3^{2-} \rightarrow \text{products}$</td>
<td>$3.9\cdot10^2$ [Basfar et al., 2005]</td>
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<td>$3.9\cdot10^2$ [Mak et al., 1997]</td>
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<td>$3.9\cdot10^2$ [Nickelsen et al., 2002]</td>
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<td>$3.9\cdot10^2$ [Buxton et al., 1988]</td>
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<td>$k_{74}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{CO}_3^{2-} + \text{HO}^- \rightarrow \text{CO}_3^{2-} + \text{OH}^-$</td>
<td>$3.9\cdot10^5$ [Basfar et al., 2005]</td>
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<td>$k_{75}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{e}^-_{\text{aq}} + \text{HCO}_3^- \rightarrow \text{products}$</td>
<td>$1.0\cdot10^3$ [Basfar et al., 2005]</td>
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</tbody>
</table>
| $k_{76}$ $[\text{m}^3\text{mol}^{-1}\text{s}^{-1}]$ | $\text{HCO}_3^- + \text{HO}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_3^-\text{H}$ | $1.0\times10^3$ [Mak et al., 1997]  
$1.0\times10^3$ [Nickelsen et al., 2002]  
$1.0\times10^3$ [Buxton et al., 1988] |
| $k_{77}$ $[\text{m}^3\text{mol}^{-1}\text{s}^{-1}]$ | $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{products}$ | $8.5\times10^3$ [Basfar et al., 2005]  
$8.5\times10^3$ [Mak et al., 1997]  
$8.5\times10^3$ [Nickelsen et al., 2002]  
$9.2\times10^3$ [Buxton et al., 1988] |
| $k_{78}$ $[\text{m}^3\text{mol}^{-1}\text{s}^{-1}]$ | $\text{CO}_3^- + \text{HO}^+ \rightarrow \text{products}$ | $4.4\times10^1$ [Basfar et al., 2005]  
$4.4\times10^1$ [Mak et al., 1997]  
$4.4\times10^1$ [Nickelsen et al., 2002]  
$4.4\times10^1$ [Buxton et al., 1988] |
| $k_{79}$ $[\text{m}^3\text{mol}^{-1}\text{s}^{-1}]$ | $\text{CO}_3^- + \text{HO}_2^- \rightarrow \text{HCO}_3^- + \text{O}_2^-\text{H}$ | $3.0\times10^6$ [Basfar et al., 2005]  
$3.0\times10^6$ [Mak et al., 1997]  
$3.0\times10^6$ [Buxton et al., 1988] |
| $k_{79}$ $[\text{m}^3\text{mol}^{-1}\text{s}^{-1}]$ | $\text{CO}_3^- + \text{HO}_2^- \rightarrow \text{HCO}_3^- + \text{O}_2^-\text{H}$ | $5.6\times10^4$ [Basfar et al., 2005]  
$3.2\times10^4$ [Buxton et al., 1988] |
<table>
<thead>
<tr>
<th>$k_{80}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</th>
<th>$\text{CO}_3^{2-} + \text{O}_2^{2-} \rightarrow \text{O}_2 + \text{CO}_3^{2-}$</th>
<th>$6.5 \times 10^5$ [Basfar et al., 2005]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{81}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{CO}_3^{2-} + \text{O}_3^{2-} \rightarrow \text{O}_3 + \text{CO}_3^{2-}$</td>
<td>$5.0 \times 10^5$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{82}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{HCO}_2^- + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^- + \text{CO}_2^-\text{C}$</td>
<td>$6.0 \times 10^4$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{83}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{CO}_3^{2-} + \text{CO}_2^- \rightarrow \text{CO}_3^2^- + \text{CO}_2$</td>
<td>$5.0 \times 10^4$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{84}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{e}_{\text{aq}}^- + \text{CO}_2^{2-} (+\text{H}_2\text{O}) \rightarrow \text{HCO}_2^- + \text{OH}^-$</td>
<td>$9.0 \times 10^6$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{85}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{H}_2\text{O}_2 + \text{CO}_2^{2-} \rightarrow \text{HO}^+ + \text{OH}^- + \text{CO}_2$</td>
<td>$6.8 \times 10^5$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{86}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{HCO}_3^- + \text{CO}_2^{2-} \rightarrow \text{HCO}_2^- + \text{CO}_3^2-$</td>
<td>$2.0 \times 10^9$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{87}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{e}_{\text{aq}}^- + \text{CO}_2 \rightarrow \text{CO}_2^{2-}$</td>
<td>$7.7 \times 10^6$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{88}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{H}^+ + \text{HCO}_2^- \rightarrow \text{H}_2 + \text{CO}_2^{2-}$</td>
<td>$2.1 \times 10^5$ [Gonzalez et al., 2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.1 \times 10^5$ [Heit et al., 1998]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.1 \times 10^5$ [Imoberdorf and Mohseni, 2011]</td>
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<tr>
<td></td>
<td></td>
<td>$2.2 \times 10^5$ [Buxton et al., 1988]</td>
</tr>
<tr>
<td>$k_{89}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{HO}^+ + \text{HCO}_2^- \rightarrow \text{H}_2\text{O} + \text{CO}_2^{2-}$</td>
<td>$3.2 \times 10^6$ [Gonzalez et al., 2004]</td>
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<td></td>
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<td>$3.2 \times 10^6$ [Heit et al., 1998]</td>
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<td>$3.2 \times 10^6$ [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$k_{90}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>$\text{CO}_2^\cdot + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^\cdot$</td>
<td>$3.5 \cdot 10^6$ [Buxton et al., 1988]</td>
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</tr>
<tr>
<td>$\Phi_4$ [mol einstein$^{-1}$]</td>
<td>H$<em>2$O + hv$</em>{185\text{nm}} \rightarrow \text{HO}^\cdot + \text{H}^+$</td>
<td>0.33 [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$\Phi_5$ [mol einstein$^{-1}$]</td>
<td>H$<em>2$O + hv$</em>{185\text{nm}} \rightarrow \text{HO}^\cdot + \text{H}^+ + e^-_{\text{aq}}$</td>
<td>0.045 [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$\Phi_6$ [mol einstein$^{-1}$]</td>
<td>H$_2$O$<em>2$ + hv$</em>{185\text{nm}} \rightarrow \text{HO}^\cdot + \text{HO}^\cdot$</td>
<td>0.5 [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$\Phi_7$ [mol einstein$^{-1}$]</td>
<td>H$_2$O$<em>2$ + hv$</em>{253.7\text{nm}} \rightarrow \text{HO}^\cdot + \text{HO}^\cdot$</td>
<td>0.5 [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$k_{95}$ [s$^{-1}$]</td>
<td>HCOOH $\rightarrow$ HCOO$^\cdot$ + H$^+$</td>
<td>$1.0 \cdot 10^1$ [assumed]</td>
</tr>
<tr>
<td>$k_{96}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>HCOO$^\cdot$ + H$^+$ $\rightarrow$ HCOOH</td>
<td>$k_{95}/K_{FA}$ [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$\Phi_8$ [mol einstein$^{-1}$]</td>
<td>HCOOH + hv$_{185\text{nm}} \rightarrow \text{H}_2\text{O} + \text{CO}$</td>
<td>1.0 [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$\Phi_9$ [mol einstein$^{-1}$]</td>
<td>HCOO$^\cdot$ + hv$_{185\text{nm}} \rightarrow \text{OH}^- + \text{CO}$</td>
<td>1.0 [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$k_{99}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>HCOOH + HO$^\cdot$ $\rightarrow$ HCOO$^\cdot$ + H$_2$O</td>
<td>$1.3 \cdot 10^5$ [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$k_{100}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>HCOOH + H$^+$ $\rightarrow$ HCOO$^\cdot$ + H$_2$</td>
<td>$6.1 \cdot 10^4$ [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$k_{101}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>HCOO$^+$ + O$_2$ $\rightarrow$ CO$_2$ + HO$_2^*$</td>
<td>3.0$\times$10$^6$ [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td>$k_{102}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>HCOOH + e$_{aq}^- \rightarrow$ products</td>
<td>1.4$\times$10$^5$ [Imoberdorf and Mohseni, 2011]</td>
</tr>
<tr>
<td>$k_{103}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>O$_3$ + OH$^-$ $\rightarrow$ HO$_2^-$ + O$_2$</td>
<td>0.07 [Garoma and Gurol, 2004]</td>
</tr>
<tr>
<td>$\Phi_{10}$ [mol einstein$^{-1}$]</td>
<td>O$_3$ + (H$<em>2$O) + h$\nu</em>{253.7nm}$ $\rightarrow$ H$_2$O$_2$ + O$_2$</td>
<td>0.48 [Garoma and Gurol, 2004]</td>
</tr>
<tr>
<td>$k_{105}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>O$_3$ + H$_2$O$_2$ $\rightarrow$ HO$_2^*$ + HO$^+$ + O$_2$</td>
<td>1.0$\times$10$^{-5}$ [Garoma and Gurol, 2004]</td>
</tr>
<tr>
<td>$k_{106}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>O$_3$ + HO$_2^-$ $\rightarrow$ O$_2^{*-}$ + HO$^+$ + O$_2$</td>
<td>5.5$\times$10$^3$ [Garoma and Gurol, 2004]</td>
</tr>
<tr>
<td>$k_{107}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>O$_3$ + O$_2^{<em>-}$ $\rightarrow$ O$_3^{</em>-}$ + O$_2$</td>
<td>1.6$\times$10$^6$ [Garoma and Gurol, 2004]</td>
</tr>
<tr>
<td>$k_{108}$ [m$^3$ mol$^{-1}$ s$^{-1}$]</td>
<td>O$_3$ + HO$^+$ $\rightarrow$ HO$_2^*$ + O$_2$</td>
<td>1.1$\times$10$^5$ [Garoma and Gurol, 2004]</td>
</tr>
</tbody>
</table>
Appendix B: Derivation of semi-batch governing equations with dark and light reaction terms.

Considering a VUV reactor, modeled as a completely mixed reactor, with a volume $V_{uv}$ where a concentration $C_{A,1}$ of species $A$ enters at flowrate $Q_1$ and exits with a concentration $C_{A,2}$ (Figure A1.1-a), the macroscopic mass balance can be written as follows:

$$V_{uv} \frac{dC_{A,2}}{dt} = Q_1 C_{A,1} - Q_1 C_{A,2} \pm R_l \pm R_d \quad (A1.1)$$

where the terms on the right side of the equation represent the convective terms plus general chemical reactions involving light-induced ($l$) and dark ($d$) processes.

By analogy a reservoir tank can be assumed as a continuous stirred reactor of volume $V_{res}$ where species $A$ with concentration $C_{A,3}$ enters at flowrate $Q_2$ and due to dark chemical reactions exits with concentration $C_{A,4}$ (Figure A1.1-b). The mass balance can be written as follows:

$$V_{res} \frac{dC_{A,4}}{dt} = Q_2 C_{A,3} - Q_2 C_{A,4} \pm R_d \quad (A1.2)$$

![Figure A1.1: Schematic representation of single-pass system](image)

(a) (b)
For a completely mixed single photoreactor connected in recirculation fashion with a completely mixed single reservoir (Figure A1.2), the resulting time-dependent concentration profile can be obtained by solving the system of ordinary differential equations shown in Eq. A1.3:

\[
\begin{align*}
V_{uv} \frac{dC_{A,uv}}{dt} &= QC_{A,res} - QC_{A,uv} \pm R_l \pm R_d \\
V_{res} \frac{dC_{A,res}}{dt} &= QC_{A,uv} - QC_{A,res} \pm R_d
\end{align*}
\]  

(A1.3)

Figure A1.2: Schematic representation of semi-batch recirculation system
Appendix C: Sensitivity study on pCBA degradation including (blue curve) or excluding (green curve) 4HydroBzA and 4ClBzA reactions. Simulations were conducted at different initial pCBA concentrations and flowrates, fixing the electrical power of the lamp (108 W)
Appendix D: MATLAB code. Discretization of an annular photoreactor, radial lamp emission model (185/253.7 nm), degradation of pCBA as target pollutant.

clear all
clc

tic
L = 1.461; %m
r_in = 0.015; %m
r_ext = 0.016; %m
gap = r_ext-r_in; %m
Area = pi*(r_ext^2-r_in^2); %m^2
Q = (4.293)/60/1000; %m^3/s
mu_H2O = 0.001003; %kg/m s
rho = 1000; %kg/m^3

% Verify Re is laminar
Re = (rho*(Q/Area)*2*gap)/mu_H2O

% Meshing the radial distance in uniform nodes
divisions = 200;
r=zeros(divisions,1);

r(1)=r_in+gap/divisions;
for i=2:divisions
    r(i)=r(i-1)+gap/divisions;
end

% Velocity distribution
deltaP = ((Q*8*mu_H2O)/Area)*1/(r_ext^2+r_in^2-(r_ext^2-r_in^2)/log((r_ext/r_in)));
vel=(1/(4*mu_H2O))*deltaP.*((log(r./r_in)/log(r_ext/r_in))*(r_ext^2-r_in^2)-(r.^2-r_in^2));
velocity = 1/gap*(trapz(r,vel));

ann_area=zeros(divisions,1);
ann_area(1,1)=pi*(r(1)^2-r_in^2);

% Flow distribution
for i=2:divisions
    ann_area(i,1)=pi*(r(i)^2-r(i-1)^2);
end
q=vel.*ann_area;
time=L./vel;
time(divisions)=time(divisions-1);
% Intensity distribution based on radial model
P = 240; %W lamp electrical power used in thin-film reactor

fraction_185 = 0.75*0.0325;
fraction_254 = 0.75*0.30;

P_185 = fraction_185*P; %W UV output at 185nm
P_254 = fraction_254*P; %W UV output at 254nm

% AOP 185/254nm MODULE

pH = 4.5; % measured values DI water + pCBA at average conc
pOH = 14-pH;

H2O = 55555.55; % mol/m3
OHstar = 0; % mol/m3
Hstar = 0; % mol/m3
Hplus = (10^(-pH))*1000; % mol/m3
electr = 0; % mol/m3
H2O2 = 0/34; % mol/m3
H2 = 0; % mol/m3
Ostar_ = 0; % mol/m3
O3star_ = 0; % mol/m3
O2 = 0.25; % mol/m3
OH_ = (10^(-pOH))*1000; % mol/m3
HO2star = 0; % mol/m3
O2star_ = 0; % mol/m3
HO2_ = 0; % mol/m3

CO2 = (1.18*10^-5)*1000; % mol/m3
CO2star_ = 0; % mol/m3
CO3star_ = 0; % mol/m3
HCO3_ = (2.23*10^-6)*1000; % mol/m3
CO32_ = (5.60*10^-11)*1000; % mol/m3
HCOOstar = 0; % mol/m3
O3 = 0/48; % mol/m3

OH3pCBA = 0; % mol/m3
OH2pCBA = 0; % mol/m3
ClBzA = 0; % mol/m3
HydroBzA = 0; % mol/m3

eps_H2O_185 = 3.24*10^(-3); % m3/mole 1/m at 185nm base 10
eps_H2O_254 = 10^-20; % m3/mole 1/m at 254nm base 10
eps_H2O2_cm_185 = 289; % 1/M 1/cm (base 10)
eps_H2O2_185 = eps_H2O2_cm_185*100*10^-3; % m3/mole 1/m at 185nm (base 10)
eps_H2O2_cm_254 = 18.4; % 1/M 1/cm (base 10)
eps_H2O2_254 = eps_H2O2_cm_254*100*10^-3; % m3/mole 1/m at 254nm (base 10)
eps_HCOOH_185 = 4; % m3/mole 1/m base 10
eps_HCOOH_185 = 0.18; % m3/mole 1/m base 10
eps_O3_185 = 175; % m3/mol 1/m base 10
eps_O3_254 = 306.3; % m3/mol 1/m base 10
eps_pCBA_185 = 2138; % m3/mol 1/m (Bagheri and Mohseni, 2014)
eps_pCBA_254 = 245; % m3/mol 1/m (Bagheri and Mohseni, 2014)

Abs185 = (eps_H2O_185*H2O+eps_H2O2_185*H2O2+eps_HCOOH_185*HCOOH+eps_HCOO__185*HCOO+eps_O3_185*O3+eps_pCBA_185*pCBA)*log(10); % 1/m Absorption solution at 185nm base e
Abs254 = (eps_H2O_254*H2O+eps_H2O2_254*H2O2+eps_O3_254*O3+eps_pCBA_254*pCBA)*log(10); % 1/m Absorption solution at 254nm base e

I_185 = (P_185./(2*pi.*r*L)).*exp(-Abs185.*(r-r_in)); %W/m2
I_254 = (P_254./(2*pi.*r*L)).*exp(-Abs254.*(r-r_in)); %W/m2
R_factor_185 = 0.2;
I_185_wall=R_factor_185*I_185_wall;
I_185_refl = I_185_wall*R_factor_185;

I_254 = (P_254./(2*pi.*r*L)).*exp(-Abs254.*(r-r_in)); %W/m2
R_factor_254 = 0.24;
I_254_wall=R_factor_254*I_254_wall;
I_254_refl = I_254_wall*R_factor_254;

%%%%%%%%%%%%%%%%%%%%
% Photochemical calculations
hPlank = 6.626*10^-34 ; % J s (Plank constant)
c = 299790000 ; % m/s (light speed in void)
lambda_185 = 185*10^-9 ; % m
lambda_254 = 254*10^-9 ; % m
Energy_185 = (hPlank*c)/lambda_185; % J (energy associated with 1 photon)
Energy_254 = (hPlank*c)/lambda_254; % J (energy associated with 1 photon)
NA = 6.0221412927*10^23 ; % Avogadro Number (molecules/mol)

%%%%%%%%%%%%%%%%%%%%

% Reactions
%H2O + hv --> OH* + H*
QY1_H2O_185 = 0.33; % mole of OH* formed per einstein absorbed
QY1_H2O_254 = 0; % mole of OH* formed per einstein absorbed

%2- H2O + hv  --> OH* + H+ + e-
QY2_H2O_185 = 0.045; % mole of OH* formed per einstein absorbed
QY2_H2O_254 = 0; % mole of OH* formed per einstein absorbed

%3- H2O2 + hv --> OH* + OH*
QY_H2O2_185 = 0.5; % mole of OH* formed per einstein absorbed
QY_H2O2_254 = 0.5; % mole of OH* formed per einstein absorbed

%4- e-  + H+ --> H* 3.80*10^(-11) cm3/(molecules s)
k4 = 22456800; % (m3/mol 1/s) (Zvereva)

% OMISSIS %
%
% pCBA + hv(254) --> products (Bagheri and Mohseni, 2014)
QY_pCBA_254 = 0.013;

% pCBA + hv(185) --> products (Bagheri and Mohseni, 2014)
QY_pCBA_185 = 0.013;

% pCBA + OH* --> 3OHpCBA (Mezyk, Rosario-Ortiz, Vanderford)
k107 = (4.42*10^9)/1000; % m3/mol 1/s

% OMISSIS %
%
pCBA_fin=zeros(divisions,1);

step=10;

%ODE MODULE
for i=1:divisions
    tsmin=0:(time(i)/step):time(i);
    I_ode_185 = I_185(i)+I_185_refl(i);
    I_ode_254 = I_254(i)+I_254_refl(i);
    Photon_rate_ode_185 = I_ode_185/Energy_185; % Number of photons per second per m2
    einstein_ode_185 = Photon_rate_ode_185/NA; % Mole of photons per seconds per m2
    Photon_rate_ode_254 = I_ode_254/Energy_254; % Number of photons per second per m2
    einstein_ode_254 = Photon_rate_ode_254/NA; % Mole of photons per seconds per m3

    pCBA_fin = zeros(divisions,1);
\[ k_{1H2O\_185} = (QY_{1H2O\_185} \cdot \text{einstein\_ode\_185} \cdot \text{eps\_H2O\_185}) \cdot \log(10) \cdot \log(10); \quad \text{mol OH\* per m3 per second} \]

\[ k_{1H2O\_254} = (QY_{1H2O\_254} \cdot \text{einstein\_ode\_254} \cdot \text{eps\_H2O\_254}) \cdot \log(10) \cdot \log(10); \quad \text{mol OH\* per m3 per second} \]

\[ k_{105} = \text{eps\_pCBA\_254} \cdot \text{einstein\_ode\_254} \cdot \text{QY\_pCBA\_254} \cdot \log(10) \cdot \log(10); \]
\[ k_{106} = \text{eps\_pCBA\_185} \cdot \text{einstein\_ode\_185} \cdot \text{QY\_pCBA\_185} \cdot \log(10) \cdot \log(10); \]

\[ [t,x] = \text{ode15s}(@\text{IVP\_Kinetic\_model\_185\_254\_FA\_O3},t\text{span},[\text{H2O};\text{OHstar}; \ldots ;\text{HydroBzA}]); \]

\[ \text{OHstar\_fin} = \text{OHstar\_fin}'; \]
\[ \text{H2O2\_fin} = \text{H2O2\_fin}'; \]
\[ \text{O2\_fin} = \text{O2\_fin}'; \]
\[ \text{HCOOH\_fin} = \text{HCOOH\_fin}'; \]
\[ \text{O3\_fin} = \text{O3\_fin}'; \]
\[ \text{pCBA\_fin} = \text{pCBA\_fin}'; \]

\[ \text{pCBA\_out} = (\text{pCBA\_fin} \cdot (\text{q}/\text{sum(q)})) \cdot 156.57 \quad \text{mg/L} \]
\[ \text{pCBA\_initial} = \text{pCBA} \cdot 156.57 \quad \text{mg/L} \]
\[ \text{Flow\_rate} = Q \cdot 60 \cdot 1000 \quad \text{L/min} \]

toc

\[ C\_C0 = \text{pCBA\_out} / (\text{pCBA} \cdot 156.57) \]
Appendix E: Initial value problem (IVP) function - MATLAB.

```matlab
function dNdt=IVP_Kinetic_model_185_254_FA_03(t,x)

% Variables association

H2O = x(1);
OHstar = x(2);
Hstar = x(3);
Hplus = x(4);
electr = x(5);
H2O2 = x(6);
H2 = x(7);
Ostar_ = x(8);
%
% OMISSIS %
%
k118 = x(152);
OH3pCBA = x(153);
OH2pCBA = x(154);
ClBzA = x(155);
HydroBzA = x(156);
%
% Ordinary Differential Equations
%
% OMISSIS %
%
dpCBA = -k105*(pCBA)-k106*(pCBA)-k107*(pCBA*OHstar)-k108*(pCBA*OHstar)-k109*(pCBA*electr)-k110*(pCBA*Hstar)-k115*(pCBA*OHstar)-k116*(pCBA*OHstar);


```
dNdt =
[dH2O; dOHstar; dHstar; dHplus; delectr; dH2O2; dH2; d0star_; d03star_; d02; d0H_;
dH2Ostar; dO2star_; dHO2_; dCO2; dCO2star_; dCO3star_; ... 
dHCO3_; dC032_; dHCOO_; dHCOOH; dC0; dHCOOstar; ... 
% OMISSIS %
%

dOH3pCBA; dOH2pCBA; dClBzA; dHydroBzA];
Appendix F: C code implemented in ANSYS Fluent to calculate the spatial distribution of the species.

/* UDFs for VUV-dose and Concentration */

#include "udf.h"

/* storage Fluence rate E = DO_Irradiation */

#define C_DO_IRRAD(c,t,nb) C_STORAGE_R_XV(c,t,SV_DO_IRRAD,nb)

#define k4  22456800 /* Reaction rate, [m3/mol 1/s] */
#define k5  53567 /* Reaction rate, [m3/mol 1/s] */
#define k6  80094.0 /* Reaction rate, [m3/mol 1/s] */

/* OMITISSIS */

#define eps_PCBA_185  2138*2.302585 /* Molar absorption base e [m3/mol 1/m] */
#define eps_PCBA_254  245*2.302585 /* Molar absorption base e [m3/mol 1/m] */

/* OMITISSIS */

DEFINE_SOURCE(source_OHstar, c, t, ds, eqn) {

real source_OHstar, I_185=C_DO_IRRAD(c,t,1), I_254=C_DO_IRRAD(c,t,0),
H2O=C_UDSI(c,t,0), OHstar=C_UDSI(c,t,1), Hstar=C_UDSI(c,t,2),
Hplus=C_UDSI(c,t,3), electr=C_UDSI(c,t,4), H2O2=C_UDSI(c,t,5), H2=C_UDSI(c,t,6),
Ostar_ =C_UDSI(c,t,7), O3star_ =C_UDSI(c,t,8), O2=C_UDSI(c,t,9),
OH_ =C_UDSI(c,t,10), HO2star=C_UDSI(c,t,11), O2star_=C_UDSI(c,t,12),
HO2_ =C_UDSI(c,t,13), CO2=C_UDSI(c,t,14), CO2star_=C_UDSI(c,t,15),
CO3star_=C_UDSI(c,t,16), HC03_ =C_UDSI(c,t,17), CO32_=C_UDSI(c,t,18),
HCO0_ =C_UDSI(c,t,19), HCOOH=C_UDSI(c,t,20), CO=C_UDSI(c,t,21),
HCOOstar=C_UDSI(c,t,22), O3=C_UDSI(c,t,23), PCBA=C_UDSI(c,t,24),
OH3PCBA=C_UDSI(c,t,25), OH2PCBA=C_UDSI(c,t,26), ClBzA=C_UDSI(c,t,27),
HydroBzA=C_UDSI(c,t,28);
source_OHstar=(+(eps_H2O_185)*((I_185*2.302585)/(1.0737e-18*6.0221412927e23))*0.33*H2O+ (eps_H2O_254)*((I_254*2.302585)/(7.8205e-19*6.0221412927e23))*0*H2O+(eps_H2O_185)*((I_185*2.302585)/(1.0737e-18*6.0221412927e23))*0.045*H2O+(eps_H2O_254)*((I_254*2.302585)/(7.8205e-19*6.0221412927e23))*0.045*H2O+(eps_H2O2_185)*((I_185*2.302585)/(1.0737e-18*6.0221412927e23))*0.5*H2O2+2*(eps_H2O2_254)*((I_254*2.302585)/(7.8205e-19*6.0221412927e23))*0*H2O2+2*(eps_H2O2_185)*((I_185*2.302585)/(1.0737e-18*6.0221412927e23))*0*H2O2-k5*(OHstar*H2)+k9*(Hstar*H2O)-k11*(OHstar*Hstar)+k15*(Hstar*H2O2)+k18*(electr*H2O2)+k19*(Ostar_*H2O)+k20*(Hplus*Ostar_)+k21*(electr*HO2_)-2*k22*(OHstar*OHstar)-k23*(OHstar*OH_)-k24*(OHstar*H2O2)-k25*(electr*OHstar)-k26*(OHstar*HO2star)-k27*(O2star_*OHstar)-k28*(OHstar*HO2_)-k29*(OHstar*Ostar_)+k53*(HO2star*H2O2)+k54*(O2star_*H2O2)-k58*(OHstar*HO2_)+k59*(Hstar*HO2_)-k60*(OHstar*O3star_)+k61*(Hplus*O3star_)-k89*(OHstar*HCOO_)-k74*(CO32_*OHstar)-k76*(HCO3_*OHstar)-k78*(CO3star_*OHstar)+k85*(H2O2*CO2star_)-k95*(HCOOH*OHstar)+k101*(O3*H2O2)+k102*(O3*HO2_)-k104*(O3*OHstar)-k107*(PCBA*OHstar)-k108*(PCBA*OHstar)-k111*(OH3PCBA*OHstar)-k113*(OH2PCBA*OHstar)-k115*(PCBA*OHstar)-k116*(PCBA*OHstar)-k117*(ClBzA*OHstar)-k118*(HydroBza*OHstar)*C_R(c,t) ;

ds[eqn] = (-k5*(H2)-k11*(Hstar)-4*k22*(OHstar)-k23*(OH_)-k24*(H2O2)-k25*(electr)-k26*(HO2star)-k27*(O2star_)-k28*(HO2_)-k29*(Ostar_)-k58*(HO2_)-k60*(O3star_)-k89*(HCOO_)-k74*(CO32_)-k76*(HCO3_)-k78*(CO3star_)-k95*(HCOOH)-k104*(O3)-k107*(PCBA)-k108*(PCBA)-k111*(OH3PCBA)-k113*(OH2PCBA)-k115*(PCBA)-k116*(PCBA)-k117*(ClBzA)-k118*(HydroBza))*C_R(c,t) ;

return source_OHstar;
}

/* OMISSIS

DEFINE_GRAY_BAND_ABS_COEFF(user_gray_band_abs,c,t,nb)
{
 real H2O, H2O2, HCOOH, HCOO_, O3, PCBA;
 real abs_coeff = 0;
 real molar_abs_coeff_H2O_185 = 2.302585*0.00324;
 real molar_abs_coeff_H2O_254 = 2.302585*10e-20;

return source_OHstar;
}
real molar_abs_coeff_H2O2_185 = 2.302585*28.9;
real molar_abs_coeff_H2O2_254 = 2.302585*1.84;
real molar_abs_coeff_HCOOH_185 = 2.302585*4.0;
real molar_abs_coeff_HCOO__185 = 2.302585*0.18;
real molar_abs_coeff_O3_185 = 2.302585*175;
real molar_abs_coeff_O3_254 = 2.302585*306.3;
real molar_abs_coeff_PCBA_185 = 2.302585*2138;
real molar_abs_coeff_PCBA_254 = 2.302585*245;

H2O = C_UDSI(c,t,0);
H2O2 = C_UDSI(c,t,5);
HCOOH = C_UDSI(c,t,20);
HCOO_ = C_UDSI(c,t,19);
O3 = C_UDSI(c,t,23);
PCBA=C_UDSI(c,t,24);

switch(nb)
{
  case 0 : abs_coeff = H2O*molar_abs_coeff_H2O_254 +
            H2O2*molar_abs_coeff_H2O2_254 + O3*molar_abs_coeff_O3_254 +
            PCBA*molar_abs_coeff_PCBA_254; break;

  case 1 : abs_coeff = H2O*molar_abs_coeff_H2O_185 +
            H2O2*molar_abs_coeff_H2O2_185 + HCOO_*molar_abs_coeff_HCOO__185 +
            O3*molar_abs_coeff_O3_185 + PCBA*molar_abs_coeff_PCBA_185; break;
}

return abs_coeff;

*/ OMISSIS
DEFINE DIFFUSIVITY(Dcoeff_PCBA,c,t,i)

{
    real Db;

    real Dcoeff_PCBA;

    Db = 6.63694E-10; /* m2/s */

    Dcoeff_PCBA = Db*C_R(c,t)+C_MU_T(c,t)/0.7;

    return Dcoeff_PCBA;

}
Appendix G: Polynomial coefficient of the fitted response surfaces

| pCBA degradation by 185/253.7 nm irradiation – synthetic quartz sleeve |
|---------------------------------|-----------------|
| $\beta_0$                      | 1.323·10$^0$    |
| $\beta_1$                      | -1.166·10$^{-1}$|
| $\beta_2$                      | 1.756·10$^{-3}$ |
| $\beta_3$                      | -1.357·10$^{-1}$|
| $\beta_{12}$                   | 1.684·10$^{-4}$ |
| $\beta_{13}$                   | -8.230·10$^{-3}$|
| $\beta_{23}$                   | 1.507·10$^{-4}$ |
| $\beta_{11}$                   | 5.047·10$^{-5}$ |
| $\beta_{22}$                   | 4.518·10$^{-6}$ |
| $\beta_{33}$                   | 8.916·10$^{-3}$ |

| pCBA degradation by 185/253.7 nm irradiation – natural quartz sleeve |
|---------------------------------|-----------------|
| $\beta_0$                      | 8.531·10$^{-1}$ |
| $\beta_1$                      | -1.239·10$^{-1}$|
| $\beta_2$                      | 3.380·10$^{-3}$ |
| $\beta_3$                      | -1.167·10$^{-1}$|
| $\beta_{12}$                   | 1.684·10$^{-4}$ |
| $\beta_{13}$                   | -1.310·10$^{-4}$|
| $\beta_{23}$                   | -2.370·10$^{-4}$|
| $\beta_{11}$                   | 6.122·10$^{-3}$ |
| $\beta_{22}$                   | 4.347·10$^{-6}$ |
| $\beta_{33}$                   | 7.472·10$^{-3}$ |
### MB degradation by 185/253.7 nm irradiation – synthetic quartz sleeve

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### MB degradation by 185/253.7 nm irradiation – natural quartz sleeve

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<td>$\beta_{33}$</td>
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</table>
Appendix H: Dose per particle distributions and correlations among 185 nm, 253.7 nm, \( \text{HO}^* \), and \( \text{H}^* \) doses (10 mm annular photoreactor with baffles, \( C_0 = 0.1 \text{ mg L}^{-1} \), \( Q = 42 \text{ L min}^{-1} \))
Appendix I: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (10 mm annular photoreactor with baffles, $C_0 = 1.0 \text{ mg L}^{-1}$, $Q = 42 \text{ L min}^{-1}$)
Appendix J: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (10 mm annular photoreactor with baffles, $C_0 = 0.1 \text{ mg L}^{-1}$, $Q = 84 \text{ L min}^{-1}$)
Appendix K: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO\textsuperscript{•}, and H\textsuperscript{•} doses (10 mm annular photoreactor with baffles, C\textsubscript{0} = 1.0 mg L\textsuperscript{-1}, Q = 84 L min\textsuperscript{-1})
Appendix L: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (10 mm annular photoreactor with baffles, $C_0 = 0.1$ mg L$^{-1}$, $Q = 126$ L min$^{-1}$)
Appendix M: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (10 mm annular photoreactor with baffles, $C_0 = 1.0 \text{ mg L}^{-1}$, $Q = 126 \text{ L min}^{-1}$)
Appendix N: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO\(^*\), and H\(^*\) doses (1 mm annular photoreactor without baffles, \(C_0 = 0.1\) mg L\(^{-1}\), \(Q = 42\) L min\(^{-1}\))
Appendix O: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (1 mm annular photoreactor without baffles, $C_0 = 1.0$ mg L$^{-1}$, $Q = 42$ L min$^{-1}$)
Appendix P: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (1 mm annular photoreactor without baffles, $C_0 = 0.1 \text{ mg L}^{-1}$, $Q = 84 \text{ L min}^{-1}$)
Appendix Q: Dose per particle distributions and correlations among 185 nm, 253.7 nm, \( \text{HO}^* \), and \( \text{H}^* \) doses (1 mm annular photoreactor without baffles, \( C_0 = 1.0 \text{ mg L}^{-1} \), \( Q = 84 \text{ L min}^{-1} \))
Appendix R: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (1 mm annular photoreactor without baffles, $C_0 = 0.1 \text{ mg L}^{-1}$, $Q = 126 \text{ L min}^{-1}$)
Appendix S: Dose per particle distributions and correlations among 185 nm, 253.7 nm, HO*, and H* doses (1 mm annular photoreactor without baffles, $C_0 = 1.0 \, \text{mg L}^{-1}$, $Q = 126 \, \text{L min}^{-1}$)
Appendix T: Permission request relating the material published in Water Research Journal of Canada

Mr Ferdinando Crapulli  
PhD Candidate - Department of Chemical and Biochemical Engineering  
Faculty of Engineering  
Western University - Canada  
London, Ontario - Canada - N6A 2J4  

27 February 2015

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IWA Publishing
Curriculum Vitae

Name: Ferdinando Crapulli

Post-secondary Education and Degrees:
Polytechnic of Bari Taranto, Italy
2005 B.A. with honor

The University of Western Ontario
London, Ontario, Canada
2011-2012 Master Accelerated Program

The University of Western Ontario
London, Ontario, Canada
2013-2015 Ph.D.

Honors and Awards:
Province of Ontario Graduate Scholarship
2011-2015

MITACS - Accelerate Graduate Research Internship Program
May-Oct 2012

MITACS - Accelerate Graduate Research Internship Program
Sept-Dec 2013

Second prize at Research Bridges
Sarnia, Ontario, Canada
June 2014

MITACS - Accelerate Graduate Research Internship Program
Sept-Dec 2014

Related Work Experience
Researcher under contract for the Project 21
Polytechnic of Bari
2006

Researcher under contract "Asse III, Misura 3.12"
Apulia Region
2006-2007

Engineering consultant
Military Center for Strategic Studies (CeMiSS)
2008
Researcher under contract in SIRPAR project
Polytechnic of Bari
2009-2010

Researcher under contract "Linea 1.1 - Azione 1.1.2"
Aquasoil Srl. (Fasano, Italy)
2010

Teaching Assistant in Heat Transfer
The University of Western Ontario
2011

Teaching Assistant in Statistical Methods applied in Engineering
The University of Western Ontario
2012-2014

**Publications:**


• D.Santoro, **F.Crapulli**, M.Raisee, G.Raspa, C.N.Haas "Non-deterministic CFD Modeling of Escherichia Coli Inactivation by Peracetic Acid in Municipal Wastewater Contact Tanks", Environmental Science and Technology, 2014 (accepted).

• A.Turolla, D.Santoro, J.R. de Bruyn, **F.Crapulli**, M.Antonelli "Modelling the optical behaviour of TiO₂ suspensions and oxalic acid degradation in a photocatalytic reactor using computational fluid dynamics (CFD)", Environmental Science and Technology, 2015 (to submit).