UNIVERSITY OF SÃO PAULO
DEPARTMENT OF CHEMICAL ENGINEERING
ESCOLA POLITÉCNICA

MARÍA ADELFA ABREU ZAMORA

**Development of a computational tool for the modeling and simulation
of advanced oxidation processes**

São Paulo
2019

MARÍA ADELFA ABREU ZAMORA

**Development of a computational tool for the modeling and simulation
of advanced oxidation processes**

Thesis submitted to the Escola Politécnica of
the University of São Paulo in partial
fulfillment of the requirements for the degree
of Doctor of Science

Concentration area: Chemical Engineering

Supervisor: Prof. Dr. Galo Antonio Carrillo
Le Roux

Cosupervisor: Prof. Dr. Antonio Carlos Silva
Costa Teixeira

São Paulo

2019

Autorizo a reprodução e divulgação total ou parcial deste trabalho, por qualquer meio convencional ou eletrônico, para fins de estudo e pesquisa, desde que citada a fonte.

Este exemplar foi revisado e corrigido em relação à versão original, sob responsabilidade única do autor e com a anuência de seu orientador.

São Paulo, _____ de _____ de _____

Assinatura do autor: _____

Assinatura do orientador: _____

Catálogo-na-publicação

Abreu Zamora, María Adelfa

Development of a computational tool for the modeling and simulation of advanced oxidation processes / M. A. Abreu Zamora -- versão corr. -- São Paulo, 2019.

171 p.

Tese (Doutorado) - Escola Politécnica da Universidade de São Paulo. Departamento de Engenharia Química.

1.Advanced oxidation processes 2.Mathematical modeling 3.Parameter estimation 4.Sensitivity analysis 5.Process simulation I.Universidade de São Paulo. Escola Politécnica. Departamento de Engenharia Química II.t.

DEDICATION

To my grandmother, Norma (in memoriam)

To my parents, Adria and Carlos Alberto

ACKNOWLEDGMENTS

My special thanks go to professor Galo Carrillo Le Roux for the opportunity to conduct my Ph.D. in his research group, for supervising my work and for his friendship.

I would also like to thanks professor Antonio Carlos Silva Costa Teixeira for his co-supervision.

Thank you very much to professor Vinay Prasad for hosting me and supervise my work during my stay in the Department of Chemical and Materials Engineering at the University of Alberta in Canada.

I am very grateful to my family and, specially, to my parents for their support and comprehension during all this time far away from home.

Thanks to my husband and his family for their constant support.

Thank you very much to all my colleagues and friends at the Department of Chemical Engineering at the University of São Paulo.

Thank you so much to my Cuban friends here in São Paulo, for all the good moments shared.

I am grateful for the financial support given by the Government of Canada through the Emerging Leaders in the Americas Program (ELAP).

Finally, this study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001".

*“Discovery consists of seeing what
everybody has seen, and thinking what
nobody has thought”*

Albert Szent-Gyorgyi

RESUMO

ABREU ZAMORA, María Adelfa. **Desenvolvimento de uma ferramenta computacional para a modelagem e simulação de processos oxidativos avançados**. 2019. 171 f. Tese (Doutorado) – Departamento de Engenharia Química, Escola Politécnica, Universidade de São Paulo, São Paulo, 2019.

Palavras-chave: Processos oxidativos avançados. Modelagem matemático. Estimação de parâmetros. Análise de sensibilidade. Simulação de processo.

Neste trabalho, uma ferramenta computacional para a modelagem e estimação de parâmetros de processos oxidativos avançados (POAs) é proposta. A ferramenta, desenvolvida no Matlab®, tem quatro módulos principais: módulo da modelagem do processo (Módulo I), dois módulos dedicados à estimação de parâmetros do modelo a partir de dados experimentais disponíveis (Módulos II e III) e o módulo de simulação (Módulo IV). A ferramenta é baseada em um modelo fenomenológico geral e estruturado, sendo formulado no Módulo I. Nos Módulos II e III, a função objetivo é minimizada usando o algoritmo *trust-region-reflective* implementado na função *lsqnonlin* do Matlab® e o método do enxame de partículas, respectivamente. Quando o algoritmo *trust-region-reflective* é utilizado, as equações diferenciais do modelo e as equações de sensibilidade são integradas empregando o CVODES *solver* do SUNDIALS. As sensibilidades são usadas no cálculo da matriz Jacobiana analítica dos resíduos que é fornecida ao algoritmo de otimização. Quando o problema de otimização é resolvido usando o método do enxame de partículas, as equações do modelo são integradas por meio do *solver* ode15s do Matlab®. Finalmente, no Módulo IV, podem ser feitas simulações do processo tanto com os parâmetros estimados quanto pelos fornecidos pelo usuário. A ferramenta proposta foi aplicada à degradação do fenol pelo processo de eletro-Fenton. Simulações do processo mostraram que o modelo com os parâmetros estimados foi capaz de prever relativamente bem as concentrações experimentais de fenol e os seus intermediários aromáticos. Também foi aplicada ao tratamento de ciprofloxacina (CIP) em solução aquosa pelo processo de ozônio. Os parâmetros: coeficiente volumétrico de transferência de massa na fase líquida

($k_L a$), fração de líquido (β) e constantes cinéticas do modelo de degradação foram estimados desconsiderando e considerando a concentração de ozônio na fase gasosa na função objetivo. O modelo com os parâmetros estimados desconsiderando a concentração de ozônio na fase gasosa ajustou adequadamente as concentrações experimentais de CIP e carbono orgânico total (COT). No entanto, as concentrações preditas de ozônio na fase gasosa foram maiores que as experimentais em todos os casos. Quando a concentração de ozônio foi considerada na função objetivo um intento por ajustar essa concentração foi observado, mas os ajustes da CIP e COT pioraram. Esses comportamentos foram observados usando ambos os métodos de otimização.

ABSTRACT

ABREU ZAMORA, María Adelfa. **Development of a computational tool for the modeling and simulation of advanced oxidation processes**. 2019. 171 p. Tese (Doutorado) – Departamento de Engenharia Química, Escola Politécnica, Universidade de São Paulo, São Paulo, 2019.

Keywords: Advanced oxidation processes. Mathematical modeling. Parameter estimation. Sensitivity analysis. Process simulation.

In this work, a computational tool for the modeling and the parameter estimation of advanced oxidation processes is proposed. The tool, developed in Matlab[®], contains four main modules: process modeling module (Module I), two modules dedicated to the model parameter estimation from available experimental data (Modules II and III) and the simulation module (Module IV). It is based on a general phenomenological structured model formulated in Module I. In Modules II and III, the objective function is minimized by using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab[®] function and the particle swarm optimization method, respectively. When using the trust-region-reflective algorithm, the model differential equations and forward sensitivity equations are integrated employing the CVODES solver of SUNDIALS. The sensitivities are used to compute the analytical Jacobian matrix of the residuals that is supplied to the optimization algorithm. When the optimization problem is solved by means of particle swarm optimization method, the model equations are integrated by using the ode15s Matlab[®] solver. Finally, in Module IV, process simulations with the estimated parameters or parameters supplied by the user can be carried out. The proposed tool was applied to the phenol degradation by electro-Fenton process. Process simulations demonstrated that the model with the adjusted parameters was able to predict relatively well the experimental concentrations of phenol and its aromatic intermediates. The tool was also applied to the treatment of ciprofloxacin (CIP) in aqueous solution by ozonation process. The model parameters: volumetric mass transfer coefficient (k_La), liquid holdup (β) and kinetic constants were estimated by neglecting and considering the ozone concentration in the gas phase in the objective function. The model with the adjusted parameters

neglecting the ozone concentration in the gas phase was able to adjust adequately the experimental concentrations of CIP and total organic carbon (TOC). However, predicted concentrations of ozone in the gas phase were higher than the experimental values for all the experimental conditions. When the ozone concentration in the gas phase was accounted for in the objective function there was an attempt to adjust this concentration, nevertheless, the adjustments of CIP and TOC concentrations worsened. These behaviors were observed using both optimization methods.

LIST OF FIGURES

Figure 1 – Schematic representation of the direct and indirect reaction mechanisms in the ozonation process, S: scavengers (compounds that terminate the chain reaction), R: reaction product, M: pollutant, M_{oxid} : oxidized pollutant (modified from Gottschalk; Libra; Saupe (2000)).	31
Figure 2 – Representation of the two-film theory. c_G : bulk concentration in the gas phase, c_{Gi} : concentration at the interface in the gas phase, c_L^* : liquid concentration in equilibrium with the bulk gas concentration, c_{Li} : concentration at the interface in the liquid phase and c_L : bulk liquid concentration (modified from Gottschalk; Libra; Saupe (2000)).	35
Figure 3 – System configuration considered in the model development. V_{co} : gas-liquid contact column volume (L), V_{mt} : mixing tank volume (L), q : number of tanks representing the system, and $[c]_{G_{inlet}}$: species concentration in the gas phase at the column inlet (mol L^{-1}).	50
Figure 4 – Module I: process modeling module. ODEs: ordinary differential equations, ν : stoichiometry matrix, α : matrix of partial orders of reactions, k : vector of kinetic rate constants, q : number of tanks forming the system, Q_L and Q_G : flow rates in liquid and gas phases, V_{co} : gas-liquid contact column volume, V_{mt} : mixing tank volume, and He : dimensional Henry's law constant.	63
Figure 5 – Module II: estimation module I. OF : objective function, lb and, ub : lower and upper bounds, and θ' : vector of model parameters.	63
Figure 6 – Module III: estimation module II. lb and ub : lower and upper bounds, OF : objective function, $MaxIter$: maximum number of iterations, c_1 and c_2 : cognitive and social coefficients, $wmax$ and $wmin$: maximum and minimum values of the inertia weight, and N_p : number of particles.	64
Figure 7 – Module IV: simulation module. ν : stoichiometry matrix, α : matrix of partial orders of reactions, k : vector of kinetic rate constants, q : number of tanks forming the system, Q_L and Q_G : flow rates in liquid and gas phases, V_{co} : gas-liquid contact column volume, V_{mt} : mixing tank volume, and He : dimensional Henry's law constant.	64
Figure 8 – Experimental and predicted concentration profiles of phenol (PH) and catechol (CT) by using the set of adjusted parameters when the trust-region-reflective algorithm was employed.	76

Figure 9 – Experimental and predicted concentration profiles of hydroquinone (HQ) and resorcinol (RS) by using the set of adjusted parameters when the trust-region-reflective algorithm was employed.	76
Figure 10 – Experimental and predicted concentration profiles of phenol (PH) and catechol (CT) by using the set of adjusted parameters when the PSO method was employed.	77
Figure 11 – Experimental and predicted concentration profiles of hydroquinone (HQ) and resorcinol (RS) by using the set of adjusted parameters when the PSO method was employed.	77
Figure 12 – Schematic representation of the experimental set-up. SP: sampling point and M: mechanical stirrer (modified from Bardauil (2012)).	81
Figure 13 – Concentration profiles of ciprofloxacin (CIP) for the experiments 1 to 4. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	95
Figure 14 – Concentration profiles of ciprofloxacin (CIP) for experiments 4 to 8. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	95
Figure 15 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	96
Figure 16 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	96
Figure 17 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	97
Figure 18 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	97
Figure 19 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	98
Figure 20 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	98
Figure 21 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	99
Figure 22 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.	100

Figure 23 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	100
Figure 24 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.	101
Figure 25 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	101
Figure 26 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	102
Figure 27 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	102
Figure 28 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	103
Figure 29 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	103
Figure 30 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	104
Figure 31 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	108
Figure 32 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	109
Figure 33 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.	109
Figure 34 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	110
Figure 35 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	110
Figure 36 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	111
Figure 37 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	111

Figure 38 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	112
Figure 39 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.....	112
Figure 40 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	113
Figure 41 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	113
Figure 42 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.	114
Figure 43 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	114
Figure 44 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	115
Figure 45 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	115
Figure 46 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	116
Figure 47 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	116
Figure 48 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.....	117
Figure 49 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	121
Figure 50 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	122
Figure 51 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	122

Figure 52 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	123
Figure 53 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	123
Figure 54 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	124
Figure 55 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	124
Figure 56 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	125
Figure 57 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.	125
Figure 58 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	126
Figure 59 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	126
Figure 60 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	127
Figure 61 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	127
Figure 62 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	128
Figure 63 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	128

Figure 64 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	129
Figure 65 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	129
Figure 66 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.	130

LIST OF TABLES

Table 1 – Advanced oxidation processes (AOPs) classification in photochemical and non-photochemical processes. H_2O_2 : hydrogen peroxide, Fe^{2+} : iron, UV: ultraviolet radiation, and TiO_2 : titanium dioxide (modified from Domènech; Jardim; Litter and Mandal (2001; 2018)).	29
Table 2 – Reaction mechanism for the ozone decomposition at acidic to neutral conditions (modified from Lovato; Martín; Cassano (2009)).	32
Table 3 – Reaction mechanism for the ozone decomposition at basic conditions (modified from Lovato; Martín; Cassano (2009)).	33
Table 4 – Correlations to calculate the dimensional (He) or dimensionless (He^*) Henry's law constants.	36
Table 5 – Main characteristics of the developed model. q : number of tanks representing the system, p : number of species in the liquid phase and n : number of chemical reactions.	56
Table 6 – Reaction mechanism involved in the phenol degradation by electro-Fenton process (modified from Mousset et al. (2016)).	67
Table 7 – Numbered species according to the reaction mechanism involved in the phenol degradation by electro-Fenton process.	69
Table 8 – Main characteristics of the model when the computational tool is applied to the treatment of phenol by electro-Fenton process.	71
Table 9 – Parameter values used in the parameter estimation by using the particle swarm method.	73
Table 10 – Estimated kinetic constants for the treatment of phenol by electro-Fenton process. N_p : number of particles.	74
Table 11 – Root mean square error (RMSE) values calculated for the phenol ($\text{RMSE}_{[\text{PHI}]}$) and its aromatic intermediates: catechol ($\text{RMSE}_{[\text{CTI}]}$), hydroquinone ($\text{RMSE}_{[\text{HQI}]}$) and resorcinol ($\text{RMSE}_{[\text{RSI}]}$).	78
Table 12 – Second-order reaction rate constants for the ozone (k_{O_3}) and hydroxyl radical ($k_{\text{HO}^\bullet}$) reactions with ciprofloxacin.	80
Table 13 – Experimental conditions of the ozonation experiments (modified from Bardaui (2012)).	82
Table 14 – Ozone decomposition reactions in water for acidic to neutral and basic conditions (modified from Lovato et al., (2009)).	84

Table 15 – Second order reactions of ozone and hydroxyl radical with ciprofloxacin and its intermediate compounds until the formation of the species with four carbon atoms.	85
Table 16 – Numbered species according to the reaction mechanism.	86
Table 17 – Main characteristics of the model when the computational tool was applied to the treatment of ciprofloxacin by ozonation process considering different numbers of tanks representing the system (q).	88
Table 18 – Adjusted parameters (θ'_1) by considering experimental and predicted concentrations of CIP and TOC in the objective function (OF_1) by using the trust-region-reflective algorithm. q : number of tanks representing the system.	93
Table 19 – Adjusted parameters (θ'_1) by considering experimental and predicted concentrations of CIP, TOC and ozone in the gas phase in the objective function (OF_2) by using the trust-region-reflective algorithm. q : number of tanks representing the system.	94
Table 20 – Root mean square error values for concentrations of ciprofloxacin ($RMSE_{[CIP]}$), total organic carbon ($RMSE_{[TOC]}$) and ozone in the gas phase ($RMSE_{[O_3]_G}$).	99
Table 21 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of CIP and TOC in the objective function (OF_1) by using the trust-region-reflective algorithm. q : number of tanks representing the system.	105
Table 22 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of CIP, TOC and ozone in the gas phase in the objective function (OF_2) by using the trust-region-reflective algorithm. q : number of tanks representing the system.	106
Table 23 – Values of parameters used in the PSO implementation.	117
Table 24 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of ciprofloxacin and total organic carbon in the objective function (OF_1) using the PSO method. N_p : number of particles.	118
Table 25 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of ciprofloxacin, total organic carbon and ozone in the gas phase in the objective function (OF_2) using the PSO method. N_p : number of particles.	119

Table 26 – Lower and upper bounds established for the parameter estimation in the first case study.	160
Table 27 – Calculated initial concentrations of TOC and correction factors. ..	169
Table 28 – Lower and upper bounds established for the parameter estimation in the second case study.....	170

NOMENCLATURE

Symbol	Definition	Units
c_G	Bulk gas concentration	(mol L^{-1})
c_L	Bulk liquid concentration	(mol L^{-1})
c_L^*	Liquid concentration in equilibrium with the bulk gas concentration	(mol L^{-1})
$k_L a$	Volumetric mass transfer coefficient in the liquid phase	(s^{-1})
H_e	Dimensional Henry's law constant	$\text{atm}(\text{mole fraction})^{-1}$
H_e^*	Dimensionless Henry's law constant	Dimensionless
k_{O_3}	Second-order reaction rate of the reaction between ozone and ciprofloxacin	$(\text{mol}^{-1} \text{ L s}^{-1})$
$k_{HO^\bullet}$	Second order reaction rate of the reaction between hydroxyl radical and ciprofloxacin	$(\text{mol}^{-1} \text{ L s}^{-1})$
V_{mt}	Mixing tank volume	(L)
V_{co}	Gas-liquid contact column volume	(L)
q	Number of tanks representing the system	Dimensionless
p	Number of species in the liquid phase	Dimensionless
n	Number of chemical reactions	Dimensionless
V_L	Liquid volume of each tank that forms the column	(L)
V_G	Gas volume of each tank that forms the column	(L)
ΔV	Total volume of each tank that forms the column	(L)
β	Liquid holdup or liquid fraction in each tank that forms the column	Dimensionless
$(1 - \beta)$	Gas holdup or gas fraction in each tank that forms the column	Dimensionless
Q_G	Flow rate in the gas phase	(L/s)
Q_L	Flow rate in the liquid phase	(L/s)
k_I	Kinetic rate constant for the reaction I	$(\text{s}^{-1} \text{ for first order reactions and } \text{mol}^{-1})$

		L s ⁻¹ for second order reactions)
r_{lj}	Vector of reaction rates	(mol L ⁻¹ s ⁻¹)
	Absorption rate for the species	
N_j	concentration in the gas phase in the j th tank that forms the column	(mol L ⁻¹ s ⁻¹)
$[c_i]_{Lj}$	Concentration of species in the liquid phase in the j th tank that forms the system	(mol L ⁻¹)
$[c]_{G_{inlet}}$	Species concentration in the gas phase at the column inlet	(mol L ⁻¹)
$[c]_{Gj}$	Concentration of species in the gas phase in the j th tank that forms the column	(mol L ⁻¹)
R_{iLj}	Generation/consumption rate of species in the liquid phase in the j th tank that forms the system	(mol L ⁻¹ s ⁻¹)

LIST OF ABBREVIATIONS

Abbreviation	Meaning
CIP	Ciprofloxacin
AOPs	Advanced Oxidation Processes
SUNDIALS	SUite of Nonlinear and Differential/Algebraic Equation Solvers
PSO	Particle swarm optimization
NDFs	Numerical Differentiation Formulas
BDF	Backward Differentiation Formulas
UV	Ultraviolet
CSTRs	Continuous Stirred Tank Reactors
FSA	Forward sensitivity analysis
SA	Sensitivity analysis
TOC	Total Organic Carbon
S	Scavenger
M	Pollutant
M _{oxid}	Oxidized pollutant
ODEs	Ordinary differential equations
DAE	Differential-algebraic equation
PH	Phenol
HQ	Hydroquinone
CT	Catechol
RS	Resorcinol
ACE	Acetic acid
ACRac	Acrylic acid
DHDac	2,5-dioxo-3-hexenedioic acid
DHOac	2,5-dioxo-6-hydroxy-3-hexenoic acid
DHpBQ	2,3-dihydroxy-1,4-benzoquinone
DHsBQ	2,3-dihydroxy-semobenzoquinone
DOB	1,4-dioxo-2-butene
FOR	Formic acid
FUM	Fumaric acid
GLYOX	Glyoxylic acid
HPac	3-hydroxy-propanoic acid

KETO	Ketomalonic acid
MLE	Maleic acid
MLO	Malonic acid
MUC	Muconic acid
oBQ	Ortho-benzoquinone
oPac	3-oxo-propanoic acid
OXA	Oxalic acid
pBQ	Para-benzoquinone
PG	Pyrogallol
PROP	Propanoic acid
RS	Resorcinol
SUC	Succinic acid
TAR	Tartronic acid

TABLE OF CONTENTS

Chapter 1. Introduction	24
1.1. Motivation and objectives.....	25
1.2. Importance of the study.....	26
1.3. Thesis structure	27
Chapter 2. Literature review	28
2.1. Advanced oxidation processes.....	28
2.1.1. Ozonation.....	30
2.1.1.1. Ozone decomposition.....	30
2.1.1.2. Mass transfer	34
2.1.2. Electro-Fenton.....	37
2.2. Mathematical modeling of advanced oxidation processes	37
2.3. Partial conclusions	47
Chapter 3. Methodology.....	49
3.1. Modeling.....	49
3.1.1. Hypotheses	49
3.1.2. Model formulation.....	50
3.2. Parameter estimation.....	56
3.2.1. Parameter estimation by using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab® function.....	57
3.2.1.1. Sensitivity analysis.....	58
3.2.2. Parameter estimation by using the particle swarm optimization method	60
3.3. Process simulations.....	62
3.4. Computational tool.....	62
Chapter 4. First case study: phenol degradation by electro-Fenton process	66
4.1. Results and discussion	66
4.1.1. Modeling	66
4.2.2. Parameter estimation and process simulations.....	71
4.2. Partial conclusions	78

Chapter 5. Second case study: treatment of ciprofloxacin in aqueous solution by ozonation process.....	79
5.1. Description of the system.....	80
5.2. Available experimental data	81
5.3. Results and discussion	82
5.3.1. Modeling	82
5.3.2. Parameter estimation and process simulations.....	88
5.4. Partial conclusions	130
Chapter 6. Conclusions and recommendations for future works	132
6.1. Conclusions.....	132
6.2. Recommendations for future works	134
References	135
Appendix A. Derivatives of the right-hand side of the model differential equations with respect to the model parameters	147
Appendix B. Analytical Jacobian matrix of the model	149
Appendix C. Stoichiometry matrix for the first case study: phenol degradation by electro-Fenton process	152
Appendix D. Matrix of partial orders of reactions for the first case study: phenol degradation by electro-Fenton process	156
Appendix E. Lower and upper bounds for the parameter estimation in the first case study	160
Appendix F. Stoichiometry matrix for the second case study: treatment of ciprofloxacin in aqueous solution by ozonation process.....	162
Appendix G. Matrix of partial orders of reactions for the second case study: treatment of ciprofloxacin in aqueous solution by ozonation process	165
Appendix H. Correction of the experimental concentrations of TOC	169

Appendix I. Lower and upper bounds used in the parameter estimation for the second case study	170
--	------------

Chapter 1. Introduction

There is an increasing concern regarding water pollution with emerging organic pollutants such as pharmaceutical compounds, personal care products and pesticides (WOLS; HOFMAN-CARIS, 2012a; RIVERA-UTRILLA et al., 2013; MEIJIDE et al., 2017). These compounds are characterized for high chemical stability and/or low biodegradability (OLLER; MALATO; SÁNCHEZ-PÉREZ, 2011; POYATOS et al., 2010). Conventional methods of treatment are inefficient in the total removal of this type of compounds (POYATOS et al., 2010; RIVERA-UTRILLA et al., 2013; POZA-NOGUEIRAS et al., 2018). Therefore, they have been detected in effluents from wastewater treatment plants, from pharmaceutical manufacturing plants and hospital effluents (RIVERA-UTRILLA et al., 2013). In considering this issue, the implementation of alternative methods of treatment to reach their degradation is necessary.

The advanced oxidation processes (AOPs) constitute an effective alternative in the treatment of water contaminated with emerging pollutants (DEWIL et al., 2017; POYATOS et al., 2010; RIVERA-UTRILLA et al., 2013). These processes involve the generation and use of highly reactive species, especially hydroxyl radicals ($\text{HO}^\bullet$) (BELTRÁN, 2004; GLAZE; KANG; CHAPIN, 1987). AOPs are able to transform recalcitrant or non-biodegradable compounds into biodegradable ones that can be efficiently treated by biological process. One of the major drawbacks of AOPs, whenever compared to conventional methods of treatment, is the use of expensive reagents such as ozone (O_3) and hydrogen peroxide (H_2O_2) (DEWIL et al., 2017; ESPLUGAS et al., 2002; ANDREOZZI, 1999). In addition, in the case of photochemical processes that use artificial UV radiation sources (UV lamps) for the generation of $\text{HO}^\bullet$, the high consumption of electrical energy by these sources as well as their maintenance represent a problem (ESPLUGAS et al., 2002; PERA-TITUS et al., 2004). In general, high capital and operating costs are associated with these processes.

Many studies to evaluate the performance of AOPs treating model solutions at lab and pilot scales have been carried. Nevertheless, more work needs to be done in order to evaluate their performance when real wastewater is treated and in the process scaling-up.

The mathematical modeling of AOPs is very important for the design of water treatment plants, for doing an economic evaluation of the process and for process control purposes (DE TORRES-SOCÍAS et al., 2014; GLAZE et al., 1992). Models of varying complexity of AOPs can be developed for different study purposes, depending on either on the availability of kinetic rate constants and of a reaction mechanism (CRITTENDEN et al., 1999). By using a model, it is possible to carry out process simulations. In this way, a more detailed understanding of the system behavior can be obtained. In addition, the influence of process variables and parameters on the process performance can be studied. Besides, different experimental conditions can be tested reducing the number of experiments that need to be performed, which generally involve the use of expensive reagents or have a high energy consumption. Moreover, the process optimization shall be only performed after obtaining good parameters estimates to describe the process, aiming for a design that effectively produces a cost reduction. Mathematical models with estimated parameters are useful tools for the reactor design and process scale-up. These are two important issues related to the future implementation of AOPs (DEWIL et al., 2017).

It is important to highlight that the phenomenological mathematical modeling of AOPs is not an easy task due to the complexity of the kinetics and a large number of reactions involved in these processes.

1.1. Motivation and objectives

Mathematical models of AOPs have been reported in the literature. However, most of them are specific to a process and/or a pollutant. Besides, assumptions are made in order to simplify the model formulation or decrease the number of equations. Sometimes, these assumptions cause the loss of valuable information about the process or they bring to the development of models with a limited range of validity. In addition, the fact that the proposed models are not structured constitutes an inconvenient since slight changes in the degradation mechanism, for instance, the insertion of a new reaction or species could lead to the reformulation of the computational code.

Moreover, it is not common to carry out sensitivity analyses of the model responses with respect to the model parameters, however, these analyses are powerful tools in the development of mathematical models. The information generated by a sensitivity analysis is useful in the evaluation of optimization gradients, in the quantification of uncertainties as well as in the determination of the parameters that have a greater influence on the model responses. Another thing that needs to be highlighted is that a good part of the proposed models uses parameters reported in the literature or experimentally determined. When employing parameters reported in the literature, there exists the possibility that they were determined at different experimental conditions to those of the process that is being modeled. On the other hand, the experimental parameter determination may result in costly experiments. For all these reasons, the development of a tool that allows the modeling, parameter estimation from real process data and simulation of AOPs is important and necessary.

This work addresses the development of a computational tool for the modeling, parameter estimation and simulation of AOPs. The tool is based on a general phenomenological structured model capable to describe the system as a whole, considering as much information as possible about the process. The widely applicable model is formulated from the mole balance equations of species in gas and liquid phases and the kinetic expressions. These equations are generated from the kinetic information given by the reaction mechanism involved in the process. Besides, a sensitivity analysis using the forward method of CVODES solver of SUNDIALS is performed and the generated information is used in the task of parameter estimation from experimental data. The proposed tool is applied to the phenol degradation by electro-Fenton process and the treatment of ciprofloxacin in aqueous solution by ozonation process.

1.2. Importance of the study

The determination of the second-order kinetic constants of the reactions of organic pollutants and their intermediates, with hydroxyl radical and other oxidant species like ozone, is very important in the AOPs. The knowledge of these constants allows evaluating the feasibility of the removal of certain

compounds by given AOPs. Nevertheless, these constants are available for only some compounds. In the case of intermediate compounds, there is a lack of data since most of the time their identification is only qualitative since this involve expensive experiments and/or complex analytical techniques (JIN; PELDSZUS; HUCK, 2012). Therefore, a computational tool, based on a general phenomenological model, for the modeling and parameter estimation of AOPs, is of high relevance.

By using the proposed tool in the current work kinetic parameters, not available in the literature, important for the reactor design and the process scale-up could be estimated from real process data. Kinetic models of AOPs, with estimated parameters are useful tools since different experimental conditions can be tested and the influence of process variables on the pollutant removal can be studied. In addition, they can be used for obtaining a better understanding of the process behavior as well as to evaluate and predict the removal of a given pollutant by a specific process.

1.3. Thesis structure

This thesis is organized into six chapters, the list of literature references and nine appendixes. Chapter 1 summarizes the introduction, motivation, objectives, and importance of the done work. An overview of the AOPs as well as their mathematical modeling is provided by chapter 2. The following chapter describes in detail the methodology employed in the development of the computational tool based on phenomenological principles. Chapter 4 deals with the first case study which consists of the application of the proposed tool to the degradation of phenol by electro-Fenton process. Chapter 5 is devoted to the second case study: treatment of ciprofloxacin in aqueous solution by ozonation process. Finally, in chapter 6, conclusions and recommendations for future works are presented.

Chapter 2. Literature review

This chapter gives an overview on topics related to the developed work. First, the AOPs are defined and some theory associated with them is presented. In addition, due to the relevance for the current work, the ozonation and electro-Fenton processes are described. From the literature review, some studies focused on the mathematical modeling of AOPs are presented and analyzed.

2.1. Advanced oxidation processes

The advanced oxidation processes (AOPs) were defined by Glaze et al., (1987). These processes involve the generation of highly reactive radical species, principally the hydroxyl radical ($\text{HO}^\bullet$), in sufficient quantities to achieve the water purification. Hydroxyl radicals are non-selective strong oxidant species, with a standard redox potential equal to 2.8 V (WANG; XU, 2012a). They are capable of oxidizing the most part of the organic molecules with second-order reaction rates that vary between 10^{-2} - $10^{12} \text{ mol}^{-1} \text{ L s}^{-1}$ (ANDREOZZI, 1999; GOTTSCHALK; LIBRA; SAUPE, 2000; DOMÈNECH; JARDIM; LITTER, 2001; BELTRÁN, 2004; OPPENLÄNDER, 2003; JIN; PELDSZUS; HUCK, 2012; RIVERA-UTRILLA et al., 2013; MANDAL, 2018).

AOPs are proposed as effective and useful alternative methods in the treatment of water and wastewater contaminated with emerging pollutants such as pharmaceutical compounds, personal care products and pesticides (POYATOS et al., 2010). Based on the way that $\text{HO}^\bullet$ is generated, the AOPs can be classified in photochemical and non-photochemical processes (see Table 1). In the non-photochemical processes, the generation of the radicals involves the transformation of chemical species or the use of different energy forms (for instance, ultrasound or electrical energies) except the light radiation. On the other hand, in the photochemical processes, the hydroxyl radicals are produced by using artificial or natural UV radiation sources (UV lamps or solar radiation) (DOMÈNECH; JARDIM; LITTER, 2001; POYATOS et al., 2010; MANDAL, 2018).

Table 1 – Advanced oxidation processes (AOPs) classification in photochemical and non-photochemical processes. H₂O₂: hydrogen peroxide, Fe²⁺: iron, UV: ultraviolet radiation, and TiO₂: titanium dioxide (modified from Domènech; Jardim; Litter and Mandal (2001; 2018)).

Non-photochemical	Photochemical
Ozonation (O ₃)	O ₃ /UV
O ₃ /H ₂ O ₂	UV/H ₂ O ₂
Fenton (Fe ²⁺ /H ₂ O ₂)	Photo-Fenton
Electrochemical oxidation	Heterogeneous photocatalysis (UV/TiO ₂)
γ-Radiolysis and electron beam	UV/H ₂ O ₂
Ultrasound (US)	

AOPs can be also classified as homogeneous or heterogeneous processes (POYATOS et al., 2010). The homogeneous processes can use or not energy sources (UV, ultrasound or energy obtained from an electrochemical reaction). On the other hand, heterogeneous processes involve the use of catalysts (solid phase). Catalytic and photocatalytic ozonation and heterogeneous photocatalysis are among heterogeneous AOPs.

When using the AOPs, it is possible to achieve the complete mineralization of the organic pollutant (CO₂ and H₂O); however, it is expensive (OLLER; MALATO; SÁNCHEZ-PÉREZ, 2011; POYATOS et al., 2010). The AOPs can be used alone, combined with each other or with biological methods of treatment. Their combination with biological processes is proposed as a feasible alternative to reduce operating costs associated to the treatment (DEWIL et al., 2017; OLLER; MALATO; POYATOS et al., 2010; SÁNCHEZ-PÉREZ, 2011). AOPs can be used as pre-treatment in order to transform non-biodegradable organic compounds into biodegradable compounds that can be effectively removed by biological processes. They can be also used as post-treatment when a higher quality of the treated water is desired. The most common is to use the AOPs as pre-treatment followed by biological methods of treatment (DEWIL et al., 2017; WANG; XU, 2012).

According to the literature (POYATOS et al., 2010; DEWIL et al., 2017), conventional methods of treatment cannot be totally replaced by AOPs. From an economic feasibility point of view, the use of these processes combined with

biological processes is suggested. Besides, the use of renewable energy sources (solar radiation) in the photochemical processes is proposed as an alternative to reduce the operating costs related to the consumption of electrical energy (DEWIL et al., 2017).

Ozonation and electro-Fenton processes are explained below, due to their relevance for the current work.

2.1.1. Ozonation

Ozone is an unstable and soluble gas in water that has a high power as oxidant with a standard redox potential of 2.07 V (BELTRÁN, 2004). It is capable of oxidizing selectively organic and inorganic compounds in water and effluents. However, its use in water treatments is limited by its solubility and the kinetics of its reactions (QUERO-PASTOR et al., 2014).

2.1.1.1. Ozone decomposition

The ozone decomposition in aqueous solution plays an important role in the application of ozonation processes. Its decomposition rate is influenced by factors such as the pH, temperature, and composition of the water among others.

The pH is one of the factors that most affect the ozone decomposition. For pH values below seven, the influence is not very significant, but at higher values, it increases considerably because there are more hydroxide ions (OH^-) that act as initiators of the ozone decomposition (BELTRÁN, 2004; VON GUNTEN, 2003). In addition, to promote the ozone decomposition, H_2O_2 can be added to the solution (QUERO-PASTOR et al., 2014; WANG; WANG, 2016).

The dissolved ozone can react with organic compounds through direct and indirect reactions obtaining in each case different oxidation products (VON GUNTEN, 2003; BELTRÁN, 2004). The direct reactions are those reactions between organic compounds and molecular ozone. These reactions are selective, slow ($k = 1\text{-}10^3 \text{ mol}^{-1} \text{ L s}^{-1}$) and frequently occur at low or neutral pH values (GOTTSCALK; LIBRA; SAUPE, 2000; QUERO-PASTOR et al., 2014; VON GUNTEN, 2003). On the other hand, during the ozone decomposition in water free radical species are formed, principally hydroxyl radical ($\text{HO}^\bullet$). The

reactions between these species and compounds present in water are the indirect reactions and occur in basic media. Figure 1 shows a schematic representation of the direct and indirect reaction mechanisms.

Figure 1 – Schematic representation of the direct and indirect reaction mechanisms in the ozonation process, S: scavengers (compounds that terminate the chain reaction), R: reaction product, M: pollutant, M_{oxid} : oxidized pollutant (modified from Gottschalk; Libra; Saupe (2000)).

The indirect reaction mechanism is complex. It is divided into three parts: initiation, propagation or radical chain and termination (BELTRÁN, 2004; GOTTSCHALK; LIBRA; SAUPE, 2000). Based on a literature review, two reaction mechanisms for the ozone decomposition in water are proposed (BELTRÁN, 2004; GOTTSCHALK; LIBRA; SAUPE, 2000; LOVATO; MARTÍN; CASSANO, 2009; VON GUNTEN, 2003). One of them is valid for acidic to neutral conditions ($pH \leq 7$) and the other one for basic conditions ($pH > 7$). Tables 2 and 3 summarize these sets of reactions along with their rate constants.

Table 2 – Reaction mechanism for the ozone decomposition at acidic to neutral conditions (modified from Lovato; Martín; Cassano (2009)).

Initiation	Rate constant	Units
$O_3 + OH^- \rightarrow HO_2^- + O_2$	70	$\text{mol}^{-1} \text{L s}^{-1}$
$O_3 + HO_2^- \rightarrow HO_2^\bullet + O_3^{\bullet-}$	2.20×10^6	$\text{mol}^{-1} \text{L s}^{-1}$
Propagation		
$HO_2^\bullet \rightarrow O_2^{\bullet-} + H^+$	7.90×10^5	s^{-1}
$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet$	5.00×10^{10}	$\text{mol}^{-1} \text{L s}^{-1}$
$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$	$(1.6 \pm 0.2) \times 10^9$	$\text{mol}^{-1} \text{L s}^{-1}$
$O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet$	$(5.2 \pm 0.6) \times 10^{10}$	$\text{mol}^{-1} \text{L s}^{-1}$
$HO_3^\bullet \rightarrow O_3^{\bullet-} + H^+$	$(3.7 \pm 0.3) \times 10^4$	s^{-1}
$HO_3^\bullet \rightarrow HO^\bullet + O_2$	$(1.009 \pm 0.06) \times 10^5$	s^{-1}
$O_3 + HO^\bullet \rightarrow HO_4^\bullet$	2.00×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO_4^\bullet \rightarrow HO_2^\bullet + O_2$	$(2.8 \pm 0.3) \times 10^4$	s^{-1}
Termination		
$HO_2^- + H^+ \rightarrow H_2O_2$	5.00×10^{10}	$\text{mol}^{-1} \text{L s}^{-1}$
$H_2O_2 \rightarrow HO_2^- + H^+$	0.125 s^{-1}	s^{-1}
$HO_4^\bullet + HO_4^\bullet \rightarrow H_2O_2 + 2O_3$	5.00×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO_4^\bullet + HO_3^\bullet \rightarrow H_2O_2 + O_2 + O_3$	5.00×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$	2.70×10^7	$\text{mol}^{-1} \text{L s}^{-1}$
$HO^\bullet + HO_2^- \rightarrow HO_2^\bullet + OH^-$	7.50×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO^\bullet + HO^\bullet \rightarrow H_2O_2$	5.20×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$	8.30×10^5	$\text{mol}^{-1} \text{L s}^{-1}$

Table 3 – Reaction mechanism for the ozone decomposition at basic conditions (modified from Lovato; Martín; Cassano (2009)).

Initiation	Rate constant	Units
$O_3 + OH^- \rightarrow HO_2^- + O_2$	70	$\text{mol}^{-1} \text{ L s}^{-1}$
$O_3 + HO_2^- \rightarrow HO_2^\bullet + O_3^{\bullet-}$	2.20×10^6	$\text{mol}^{-1} \text{ L s}^{-1}$
Propagation		
$HO_2^\bullet \rightarrow O_2^{\bullet-} + H^+$	7.90×10^5	s^{-1}
$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet$	5.00×10^{10}	$\text{mol}^{-1} \text{ L s}^{-1}$
$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$	$(1.6 \pm 0.2) \times 10^9$	$\text{mol}^{-1} \text{ L s}^{-1}$
$O_3^{\bullet-} + H_2O \rightarrow HO^\bullet + O_2 + OH^-$	(20 – 30)	$\text{mol}^{-1} \text{ L s}^{-1}$
$O_3^{\bullet-} + HO^\bullet \rightarrow HO_2^\bullet + O_2^{\bullet-}$	6.00×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2$	3.00×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO_2^- + H^+ \rightarrow H_2O_2$	5.00×10^{10}	$\text{mol}^{-1} \text{ L s}^{-1}$
$H_2O_2 \rightarrow HO_2^- + H^+$	0.125	s^{-1}
Termination		
$O_3^{\bullet-} + HO^\bullet \rightarrow O_3 + OH^-$	2.50×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$	2.70×10^7	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO^\bullet + HO_2^- \rightarrow HO_2^\bullet + OH^-$	7.50×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$

In the ozonation process, there are two oxidant species, the ozone (O_3) and the hydroxyl radical ($HO^\bullet$). Therefore, the kinetics of their reactions with the dissolved organic pollutants should be considered. Direct molecular ozone and hydroxyl radical reactions with organic compounds are considered to be second order, first order with respect to the oxidant (ozone or hydroxyl radical) and first order with respect to the pollutant (M) (Reactions 1 and 2) (GOTTSCALK; LIBRA; SAUPE, 2000; VON GUNTEN, 2003).

Thereby the balances can be written as follows:

$$\frac{d[M]}{dt} = -k_{O_3}[M][O_3] \quad (3)$$

$$\frac{d[M]}{dt} = -k_{HO^\bullet}[M][HO^\bullet] \quad (4)$$

where k_{O_3} and $k_{HO^\bullet}$ ($\text{mol}^{-1} \text{ L s}^{-1}$) are the second-order rate constants for the ozone and hydroxyl radical reactions with the pollutant M, respectively. $[O_3]$, $[HO^\bullet]$ and $[M]$ (mol L^{-1}) are the ozone, hydroxyl radical and pollutant concentrations, correspondingly.

2.1.1.2. Mass transfer

Analyses on ozone absorption and kinetic studies in the ozonation processes in the liquid phase are commonly performed in bubble column reactors or continuous stirred-tank reactors. The ozone in the gas phase (mixtures of air-ozone or oxygen-ozone) is bubbled into the liquid phase. The ozone in the gas phase has to be in contact with the aqueous solution that will be ozonized. Hence, an efficient ozone mass transfer from gas to the liquid phase is necessary (BELTRÁN, 2004; BIÑ, 2004; GOTTSCHALK; LIBRA; SAUPE, 2000).

The mass transfer from gas to liquid phase can be described by the two-film theory (LEWIS; WHITMAN, 1924) (see Figure 2). According to this theory, two films are formed in the separating interface surface, one of them gas and the other one liquid. These films cause resistance to mass transfer; therefore, a linear concentration gradient in steady state in each phase is developed. This gradient constitutes the driving force for the mass transfer. Both, resistances in liquid and gas phases are composed of a diffusional resistance in the laminar film and a negligible resistance in the bulk fluid (BELTRÁN, 2004; GOTTSCHALK; LIBRA; SAUPE, 2000).

Figure 2 – Representation of the two-film theory. c_G : bulk concentration in the gas phase, c_{Gi} : concentration at the interface in the gas phase, c_L^* : liquid concentration in equilibrium with the bulk gas concentration, c_{Li} : concentration at the interface in the liquid phase and c_L : bulk liquid concentration (modified from Gottschalk; Libra; Saupe (2000)).

The ozone absorption rate N_{O_3} ($\text{mol L}^{-1} \text{s}^{-1}$), for the slow regime of ozone absorption (Equation 5), can be expressed as the product of the volumetric mass transfer coefficient in the liquid phase $k_L a$ (s^{-1}), and the gradient of concentrations (BELTRÁN, 2004; GOTTSCHALK; LIBRA; SAUPE, 2000).

$$N_{O_3} = k_L a (c_{O_{3L}}^* - c_{O_{3L}}) \quad (5)$$

$c_{O_{3L}}^*$ and $c_{O_{3L}}$ are the liquid ozone concentration in equilibrium with the bulk gas concentration ($c_{O_{3G}}$) and the ozone concentration in the liquid bulk, respectively.

The ozone solubility in water obeys the Henry's law (GOTTSCHALK; LIBRA; SAUPE, 2000). Therefore, $c_{O_{3L}}^*$ can be calculated from the dimensional (He) or dimensionless (He^*) Henry's law constants and $c_{O_{3G}}$.

In the literature, there are reported empirical correlations to calculate He or He^* . Table 4 summarizes some of these correlations along with their interval of application. S is the solubility rate and it is defined as the inverse of the dimensionless Henry's law constant.

Table 4 – Correlations to calculate the dimensional (He) or dimensionless (He^*) Henry's law constants.

Correlation	Units	System	Interval of application	Reference
$\log(He^*) = A + B/T$ $B = -1752 \pm 17.1$ $A = 6.5987 \pm 0.0591$	Dimensionless	O ₃ /H ₂ O	$0 \leq T \leq 308.2 \text{ K}$	(BIÑ, 2006)
$He = 3.84 \times 10^7 [OH^-]^{0.035} \exp(-2428/T)$	atm(mole fraction) ⁻¹	O ₃ /H ₂ O	$276.7 \leq T \leq 333.2 \text{ K}$ $0.65 \leq \text{pH} \leq 10.2$	(ROTH; SULLIVAN, 1981)
$He = \exp(18.1 - 2846/T)$	atm	O ₃ /H ₂ O	$273 \leq T \leq 333 \text{ K}$ $\text{pH} = 7$	(OUEDERNI; MORA; BES, 1987)
$\log(He) = 5.12 - 1230/T$	kPa m ³ mol ⁻¹	O ₃ /H ₂ O	$273 \leq T \leq 333 \text{ K}$	(RISCHBIETER; STEIN; SCHUMPE, 2000)
$He^* = 3.1124 \left(\frac{\text{pH}}{7} \right)^{0.0297}$	Dimensionless	O ₃ /H ₂ O	$T = 21^\circ\text{C}$ $4 \leq \text{pH} \leq 11$ $0.004 \leq U_G \leq 0.021 \text{ m/s}$	(KUOSA; LAARI; KALLAS, 2004)
$\ln(He) = 0.23\ln(\text{pH}) + 12.6$ $\ln(He) = 0.57\ln(T) + 11.7$	atm	O ₃ /H ₂ O	$5 \leq \text{pH} \leq 9$ $T = 20^\circ\text{C}$	(RHIM JUNG-A, 2004)
$He^* = 1/s$ $s = -0.0067T + 0.4474$	Dimensionless	O ₃ /H ₂ O	$T = 15, 20, 30^\circ\text{C}$ $c_G > 100 \text{ mg/L}$	(MIZUNO; TSUNO, 2010)
$\log(s) = 3.302 - 0.013T$	Dimensionless	O ₃ /H ₂ O	$0 \leq T \leq 80^\circ\text{C}$	(CARELL MORRIS, 1988)

2.1.2. Electro-Fenton

The electro-Fenton process is based on the electrochemical reactions (Liu et al., 2007; POYATOS et al., 2010). There are three key reactions involved in this process. The first one describes the H_2O_2 generation from dissolved oxygen on the cathode surface (Reaction 6). Afterward, the generated H_2O_2 in acidic medium reacts with the added Fe^{2+} or iron catalysts leading to the $HO^\bullet$ formation via Fenton's reaction (Reaction 7). The last reaction is that one the $HO^\bullet$ undergoes with the organic compound in order to reach its degradation. This process needs an optimum pH value equal to three (POZA-NOGUEIRAS et al., 2018).

2.2. Mathematical modeling of advanced oxidation processes

Many works focused on the mathematical modeling of AOPs have been developed. Some of them are here listed and discussed. The emphasis was laid on the modeled processes, main adopted hypotheses, reactor types as well as their operation modes. In addition, the generality and flexibility of the proposed models are examined. Moreover, attention is paid whether the kinetic parameters are estimated from real process data, taken from the literature or experimentally determined.

Hoigné and Bader (1978) and Staehelin and Hoigné (1985) were one of the first authors developing models of AOPs. In addition, the research groups lead by Glaze (GLAZE et al., 1992; GLAZE; KANG, 1989a, 1989b; GLAZE; LAY; KANG, 1995) and Beltrán (BELTRÁN et al., 1999a, 1995, 1998, 2000, 2002; BELTRÁN; ENCINAR; GARCÍA-ARAYA, 1995; BELTRÁN; GÓMEZ-SERRANO; DURÁN, 1992; POCOSTALES; ÁLVAREZ; BELTRÁN, 2012; POCOSTALES; ALVAREZ; BELTRÁN, 2010) have also published several papers aiming to model AOPs.

Kinetic models for the ozonation, its combination with H_2O_2 and UV/ H_2O_2

processes were developed by Glaze et al. (1992; 1989a; 1989b). They were formulated based on the mole balance equations assuming the quasi-steady state hypothesis for the hydroxyl radical formation. In addition, the ozone mass transfer from gas to liquid phase was considered.

In the work of Kallas et al., (1995) the oxidation of phenolic compounds by O_3 , O_3/UV , O_3/H_2O_2 , $O_3/H_2O_2/UV$, O_3/TiO_2 , $O_3/TiO_2/UV$ in a wetted-wall column was modeled. In the model development, the ozone mass transfer from gas to liquid phase was considered. In addition, it was assumed that chemical reactions only occur in the liquid phase. The column was represented according to the tanks-in-series model. Moreover, the reaction mechanism was simplified because only the reaction between the ozone and the organic compound was taken into account neglecting the ozone decomposition reactions. The mass balance equations in steady state were written for the organic compound and the ozone in both liquid and gas phases. The kinetic constant and the stoichiometric coefficient of the reaction of ozone with the organic compound, the mass transfer enhancement factor and the Henry's law constant were estimated from available experimental data. The objective function was formulated by considering the square of the differences between predicted and experimental concentrations of the organic compound and the ozone in the liquid phase. In the process of parameter estimation, the random search method was used. The proposed model was capable to describe the degradation of various organic compounds by evaluating each one by separated.

Beltrán et al., (1998) studied the oxidation of atrazine by O_3/H_2O_2 process. A model based on the mole balance equations applied to an agitated reactor operating in semi-batch mode was developed. Free radical and direct reactions of atrazine and its principal intermediates (DEA: deethylatrazine and DIA: deisopropylatrazine) with O_3 and hydroxyl radical were considered in the reaction mechanism. Both, gas and liquid phases were assumed to be well mixed. This hypothesis, in the liquid phase, was validated by using tracer experiments. Mole balance equations were written for O_3 in gas and liquid phases, H_2O_2 , atrazine and its intermediates. Kinetic constants for the reactions of DEA and DIA with O_3 and the mass transfer coefficient for high H_2O_2

concentrations were experimentally determined. On the other hand, kinetic constant values reported in the literature for the reactions of atrazine with O_3 and atrazine, DEA and DIA with hydroxyl radical were employed. The system of ordinary differential equations describing the process was integrated by using the Runge-Kutta method.

A model for the oxidation of two aromatic hydrocarbons was also developed (BELTRÁN et al., 1999). It was applied to the treatment of nitrobenzene and phenanthrene by O_3 , UV, O_3/H_2O_2 , O_3/UV , and UV/H_2O_2 processes. The two aromatic hydrocarbons studied have different reactivity with O_3 . The nitrobenzene reacts mainly with the hydroxyl radical and the phenanthrene only reacts with O_3 . The mole balance equations were applied to two reactors operating in semi-batch mode. The ozone mass transfer from gas to liquid phase was considered. The complete mixture in the gas phase was assumed and this hypothesis in the liquid phase was proved by using tracer experiments. In this work, the importance of considering intermediate compounds and their reactions in the reaction mechanism was discussed. In a first approach, the model was developed neglecting the intermediates. In this case, the model overestimated all the experimental concentrations. By considering the intermediates it was possible to observe improvements in the model predictions, however, the predicted ozone concentrations in the gas phase were still higher than the experimental values. An important conclusion of this work was that for the species only reacting with O_3 the model can be used neglecting the intermediates. Nevertheless, for those compounds that generally react with the hydroxyl radical, it is necessary to include the intermediates in the reaction mechanism to obtain a better agreement between the model predictions and the experimental data. The proposed model was not capable to reproduce the experimental data for the O_3/UV process.

Another two works carried out by Beltrán et al., (2000, 2002) involved the modeling of the atrazine ozonation and its combination with H_2O_2 or UV radiation and the simazine ozonation. In the first study, the experiments were performed in two continuous bubble column reactors, one of them photochemical and the other one non-photochemical. In the second work, a laboratory bubble column reactor was used. Both models took into account the

information obtained from tracer experiments in both gas and liquid phases and the kinetic information given by the reaction mechanisms composed of direct and indirect reactions. Both models were also based on the mole balance equations of species and the non-ideal flow behavior was considered. In the first case, the tanks-in-series and the dispersion models were used. In the second case, complete mixture in the liquid phase was considered and three different flow patterns for the gas phase (well-mixed flow, plug flow, and axial-dispersion flow) were assumed. Volumetric mass transfer coefficients in the liquid phase ($k_L a$) were experimentally determined and used in the models.

The ozonation process was also modeled by Carini et al., (2001) and Chu et al., (2004). Carini et al., (2001) proposed a model that described the ozonation of 3-methylpyridine in a semi-batch bubble column reactor. In the model development, the mass transfer from gas to liquid phase as well as the intermediate compounds of the pollutant degradation were considered. Chu et al., (2004) studied the ozonation of the herbicide 2,4-D in a cylindrical contact tower. It was proposed a model based on the 2,4-D mass balance considering its reactions with O_3 and hydroxyl radical. The hydroxyl radical concentration was expressed as the product of OH^- and O_3 concentrations.

Reinik et al., (2004) modeled the degradation of 2,4-xylidine by ozonation process in a wetted-wall reactor in steady-state. In the model development, the mass transfer from gas to liquid phase was considered. Moreover, plug flow regime for both phases was assumed and there were no reactions in the gas phase. Besides, the process was considered isothermal and the Henry's law was used to describe the solubility of ozone and 2,4-xylidine. The reactor was modeled by using the tanks-in-series model considering gas and liquid phases in countercurrent. The balance equations were written for the 2,4-xylidine and the ozone in gas and liquid phases neglecting the ozone decomposition in water. The mass transfer coefficient was estimated from available experimental data of experiments in pure water. Predicted and experimental concentrations of ozone in gas and liquid phases were considered in the objective function. On the other hand, the kinetic constant as well as the stoichiometric coefficient of the reaction of 2,4-xylidine with O_3 were estimated from the minimization of another objective function that related experimental and predicted

concentrations of 2,4-xylidine and ozone in the gas phase.

A kinetic model describing the degradation of diclofenac in aqueous solution by photocatalytic ozonation process was proposed by Beltrán; Aguinaco; and García-Araya (BELTRÁN; AGUINACO; GARCÍA-ARAYA, 2010). Experiments were performed in a photoreactor working in semi-batch mode. Gas and liquid phases were assumed to be perfectly mixed, ozone mass transfer was taken into account and the steady state hypothesis for the free radicals was assumed. The model formulation was based on the mole balance equations of the target pollutant, ozone in both phases, H_2O_2 , free radical species, and intermediate compounds. The total organic carbon (TOC) was treated as a state variable of the model. Some kinetic parameters were experimentally determined and others were taken from the literature.

The removal of cytostatic compounds from hospital wastewaters by ozonation process and its combination with H_2O_2 was modeled by Ferre-Aracil et al., (2016). The degradation experiments were carried out in a pilot plant mainly composed by a small bubble column reactor. In all the experiments the reactor temperature was controlled and the ozone concentration in the gas phase at the reactor inlet or outlet was measured. Complete mixture in gas and liquid phases were assumed and chemical reactions only in the liquid phase were considered. The model was based on the double film model for gas-liquid reactions. It was formulated from the mass balance equations. These equations were written for the ozone in gas and liquid phases and the organic bulk matter. As a result, the reaction rates between the ozone and the organic matter and cytostatic compounds were determined.

A kinetic model capable to describe the degradation of organic compounds by ozonation process in a bubble column reactor operating in batch mode was built by Heynderickx et al., (2016). It was based on the mass balance equations of species in gas and liquid phases. The liquid phase was assumed to be well mixed and different models such as CSTR, plug flow reactor (PFR) and PFR with back mixing were considered for the gas phase. It was also assumed that chemical reactions only occur in the liquid phase. Direct and indirect reactions were considered in the reaction mechanism. The proposed model was validated

from real process data of ciprofloxacin ozonation. In this work, concentrations of radical species were lumped into one concentration in order to reduce the number of kinetic constants to be estimated. Besides, reactions of radicals with ciprofloxacin (CIP) and desethylen ciprofloxacin (DES) were described by the same kinetic constant from the non-selectivity character of the reaction of radical species with organic compounds. Kinetic constants of the degradation model and the volumetric mass transfer coefficient in the liquid phase were estimated from experimental data. Experimental and predicted concentrations of CIP and DES at the column outlet were considered in the objective function.

Wang et al., (2017) proposed a mathematical model for the degradation of dimethyl phthalate by ozonation process in a bubble column reactor working at semi-batch mode. The ozone mass transfer from gas to the liquid phase, enhanced by chemical reactions, was considered. Direct and indirect reactions were taken into account in the reaction mechanism. The flow pattern of both gas and liquid phases was determined by tracer experiments using the ozone as a tracer. The model formulation was based on the balance equations. The volumetric mass transfer coefficient in the liquid phase, the stoichiometry as well as the rate constant of direct reaction between the ozone and dimethyl phthalate were experimentally determined.

Crittenden et al., (1999) developed a kinetic model for the UV/H₂O₂ process in a completely mixed batch reactor. It was also based on the mass balance equations of species. The main contributions of this work were not to consider the pseudo-steady state assumption for the formation of radical species and take into account the pH variation during the process. Chemical and photochemical reactions were involved in the reaction mechanism. Rate constants, rate laws, photochemical and kinetics parameters were taken from the literature. The proposed model was verified against available experimental data from the oxidation of 1,2-dibromo-3-chloropropane by UV/H₂O₂ process (GLAZE; LAY; KANG, 1995). The model differential equations were integrated by using the Gear's method. The predictions of the model proposed by Crittenden et al., (1999) were better than the predictions of the model developed by Glaze, Lay, and Kang (1995) in which it was adopted the pseudo-steady state assumption and the pH was considered constant during the process. This

work, allowed to study the effect of considering the pseudo-steady state assumption for the formation of radical species.

Besides, the phenol degradation by UV/H₂O₂ process was modeled by Edalatmanesh et al., (2008). The model was based on chemical and photochemical reactions and the assumption of pseudo-steady state for the formation of radical species was not employed. In a first approach, intermediate compounds were not considered. In a second approach, the two major intermediates of phenol degradation, catechol, and hydroquinone, were considered. The presence of other organic contaminants was negligible and the kinetic rate expressions were written for the interest species in the model development. In addition, the process was considered isothermal and the pH was assumed constant. In this study, an optimization problem was solved and the second order rate constants of the reactions of phenol intermediates were estimated. The model predictions were compared with available experimental data in the literature (ALNAIZY; AKGERMAN, 2000).

Three works focused on the mathematical modeling of the UV/H₂O₂ process were done by Hofman-Caris et al., (2011, 2012a, 2012b). The models (UVPerox, UVPerox I and UVPerox II), were a result of combining kinetic models with the approach of Computational Fluid Dynamics (CFD). The kinetic models described the direct photolysis and the organic compound degradation by hydroxyl radicals as a function of the UV doses. The UV doses were determined by using the CFD approach. The models were validated by using data of NDMA, ibuprofen and atrazine degradation in a collimated bean apparatus, a pilot UV reactor with four UV lamps and two pilot plants.

Another kinetic model describing the degradation of pharmaceutical compounds by UV/H₂O₂ process with a low-pressure lamp in a collimated bean apparatus operating in batch mode was developed by Wols et al., (2014). Photolysis, equilibrium and radical reactions were considered in the reaction mechanism. The equilibrium reactions were treated as two different reactions. In this work, the balance equations were written in a general way as the product of the stoichiometry matrix and the reaction rate vector. No pseudo-steady state assumption for the radical species was adopted. The model differential

equations were integrated by using the ode15s Matlab® solver. Afterward, in a later work (WOLS et al., 2015), the same authors applied the proposed model to the treatment of pharmaceuticals by UV/H₂O₂ process using a medium-pressure lamp by incorporating the polychromatic reactions in the reaction mechanism. Both models were validated using real process data from the degradation of pharmaceutical compounds (WOLS et al., 2013). The importance of each reaction involved in the reaction mechanism was determined by performing a sensitivity analysis.

The degradation of phenol and *p*-cresol by UV/H₂O₂ process in batch reactors with low-pressure lamps was also modeled (ALNAIZY; AKGERMAN, 2000; ZHANG et al., 2016). The first kinetic model was based on a simplified reaction mechanism and the pseudo-steady state hypothesis for the hydroxyl radical concentrations was adopted. Mass balance equations were written for a reactor operating at batch mode. On the other hand, the second model used a more complex reaction mechanism since reactions of intermediate compounds with hydroxyl radicals were considered. In addition, the pseudo-steady state hypothesis for the concentration of hydroxyl radical was not invoked. The main contribution of the second work was to show how the reactions between intermediate compounds and hydroxyl radical need to be considered in the reaction mechanism.

The benzothiazole degradation by photo-assisted Fenton process in an annular glass reactor operating at batch mode was modeled by Andreozzi et al., (ANDREOZZI; D'APUZZO; MAROTTA, 2000). The mass balance equations were written one by one for all the species assuming the steady-state hypothesis for the hydroxyl radicals. The proposed model needs all the parameters involved in its formulation to be available. Values of the kinetic constants as well as the quantum yields were taken from the literature. On the other hand, the intensities of the UV lamps and the molar extinction coefficients were directly measured. The model equations were integrated and species concentration profiles were obtained. The main differences between the experimental data and the model predictions were due to the intermediate compounds in the reaction mechanism were not considered.

Beltrán de Heredia et al., (2001) developed a kinetic model for the degradation of phenolic compounds by Fenton process in a batch reactor. Steady-state hypothesis for the hydroxyl radical was assumed and intermediate compounds were not considered. The mass balance equations for the hydroxyl radical and the organic compound were written. The model was used to calculate the kinetic constants of the Fenton reaction and the reaction between the *p*-hydroxybenzoic acid and the hydroxyl radical. Besides, reaction rates of hydroxyl radical with other 10 phenolic compounds by a competitive method were also determined.

Besides, the oxidation of phenol and monochlorophenols by Fenton process was modeled by Kang N. et al., (KANG; LEE; YOON, 2002). Intermediate compounds in the reaction mechanism were considered and their role by means of sensitivity analysis was studied.

Other two works, devoted to study the phenol degradation by Fenton process were performed by Zazo et al., (ZAZO et al., 2005, 2009). The first paper was focused on the modeling of phenol degradation in a well-mixed batch reactor assuming steady state for the hydroxyl radicals. On the other hand, in the second research, the degradation experiments were carried out in a well-mixed reactor with a continuous supply of H_2O_2 . In this latter work, two kinetic models were elaborated. One of them described the evolution of phenol, its intermediate compounds, and H_2O_2 and the other one the TOC behavior for different initial concentrations of Fe^{2+} and H_2O_2 .

Pontes et al., (2010) developed a phenomenological model for the phenol degradation by Fenton process in a semi-batch reactor. The first stage of this study consisted of developing a stoichiometric model by considering the chemical reactions that took place during the phenol oxidation. Afterward, a kinetic model based on the mole balance equations was developed. In this work, the pseudo-steady state hypothesis for the radical species was not applied. In addition, a sensitivity analysis was carried out. In a first approach, simulations of the phenol degradation by Fenton process using the proposed model with values of the kinetic parameters reported in the literature were performed. Afterward, the kinetic parameters were estimated in order to obtain

a better agreement between predicted and experimental results. The model was validated by comparing its predictions to the experimental data. The model differential equations were integrated by employing the ode23t Matlab® solver and the optimization problem was solved by using LSQCURVEFIT.

There are very few works regarding the modeling of the electro-Fenton process. Liu et al., (2007) and Regalado-Méndez et al., (2010) developed kinetic models to assess the H₂O₂ accumulation and the phenol degradation for different values of current density, the concentration of dissolved O₂ and initial concentration of Fe²⁺ in batch and stirred tank reactors, respectively. These works were based on a reaction mechanism where intermediate compounds of phenol degradation were not considered. Both models were formulated from the mass balance equations assuming the steady-state approximation for the hydroxyl radicals. In the first work, these equations were written for the phenol and H₂O₂ and the model was validated by using experimental data of the phenol degradation. In the second paper, only the phenol mass balance equation was written and the model behavior was tested by performing process simulations.

Mousset et al., (2016) modeled the phenol degradation by electro-Fenton process. The experiments were performed in a batch reactor at pH equal to three. Reactions of phenol, its aromatic intermediates and carboxylic acids with the hydroxyl radical were considered in the reaction mechanism. In this work, the quasi-steady state assumption for the hydroxyl radical was adopted. The system of ODEs describing the process was integrated by using the ode15s solver of Matlab®. An optimization problem was formulated to estimate kinetic parameters from the experimental data. It was solved by using the fminsearch Matlab® function. In addition, a sensitivity analysis to study the importance of each reaction was performed. The model with the estimated parameters was capable to fit adequately the experimental concentrations of phenol, its aromatic intermediates: catechol, hydroquinone and resorcinol and carboxylic acids.

A model for the *p*-nitrophenol mineralization by electro-Fenton process was proposed by Meijide et al., (MEIJIDE et al., 2017). The model formulation was based on the mass balance equations applied to a well-mixed reactor operating in batch mode. These equations were written for the *p*-nitrophenol, its

intermediate compounds, and by-products. Quasi-state approximation for the hydroxyl radical was assumed. The system of differential algebraic equations (DAE system) was solved by using the ode15s Matlab® solver and kinetic model parameters were estimated by employing the fmincon Matlab® function.

The cork boiling wastewater treatment by photo-Fenton process using solar radiation at pilot scale was modeled by De Torres-Socías et al., (2014). The degradation experiments using real industrial wastewater were carried out in a compound parabolic collector solar located at Plataforma Solar de Almería. The model was based on the mass balance equations of the interest species considering batch mode operation. In the process modeling, two groups of reactions: the iron photo-Fenton cycle defined for two reactions and the mineralization/oxidation reactions (four reactions) were considered. The first group is responsible for the generation of radicals and the second for their consumption.

2.3. Partial conclusions

- From the literature review it can be concluded that mathematical models of AOPs, formulated from the mole balance equations of species and the kinetic expressions, have been proposed. However, most of the developed models are usually restrictive and specific to a process and/or a pollutant. Besides, the models are not structured. This constitutes an inconvenient since slight changes in the degradation mechanism could lead to the reformulation of the computational code.
- Besides, assumptions are made to simplify the model formulation or decrease the number of equations. These assumptions can lead to the loss of important information of the process or the development of models with a limited range of validity.
- It is not very common to perform sensitivity analyses of the model responses with respect to the model parameters. When these analyses are performed, the generated information is used to determine the parameters that have a higher influence on the model outputs but is not used in the parameter estimation task.

- Most of the models uses parameters reported in the literature or experimentally determined and not estimated parameters from real process data.

Chapter 3. Methodology

This chapter details the followed methodology to develop the computational tool for the modeling and parameter estimation of AOPs. First, the system configuration considered in the model development, the adopted hypotheses, and the model formulation is presented. Besides, the parameter estimation problem is posed as an optimization problem. This problem is solved by using the trust-region-reflective algorithm implemented in the `lsqnonlin` Matlab® function and the particle swarm optimization (PSO) method. In addition, the sensitivities of the model are obtained by using the forward method. On the other hand, the process simulations with the adjusted parameters are presented. Finally, the proposed computational tool with some of its characteristics is proposed.

3.1. Modeling

3.1.1. Hypotheses

In order to develop the model, some hypotheses are assumed. The considered system configuration is shown in Figure 3. This configuration is mainly composed of a gas-liquid contact column with chemical reactions in the liquid phase and a mixing tank, common elements in systems where AOPs are implemented. In the column, the liquid flow is descendent and the gas flows in countercurrent. Therefore, the liquid phase outlet is for the bottom of the column and the gas phase outlet is for the top of the column. The mass transfer from gas to the liquid phase is considered (LEWIS; WHITMAN, 1924). In addition, complete mixture in both phases is assumed. There are no chemical reactions in the gas phase and in the mixing tank, there is no gas phase. Moreover, the non-ideal flow behavior into the column is simulated by using the tanks-in-series model (LEVENSPIEL, 1999; FOGLER, 2006). According to this model, the column is represented as a set of continuous stirred tank reactors (CSTRs) connected in series ($q-1$ tanks, where q is the number of tanks representing the system). Thus, the gas outlet stream of the first tank is the feed of the second one, the gas outlet stream of the second is the feed of the third one and so on. The liquid flows in countercurrent. Tanks 1 (R_1) and $(q-1)$ ($R_{(q-1)}$) represent the bottom and the top of the column, respectively. The mixing tank (R_q) is modeled

as a CSTR fed by the liquid outlet stream of the column. The outlet stream of the mixing tank returns to the column.

In general, the proposed kinetic model considers p chemical species ($i = 1, \dots, p$) in the liquid phase undergoing n chemical reactions ($l = 1, \dots, n$) in the same phase in each tank that constitutes the system ($j = 1, \dots, q$). In addition, it is considered one species in the gas phase in the tanks that form the column ($j = 1, \dots, (q - 1)$) since in the mixing tank there is no gas phase (see Figure 3).

Figure 3 – System configuration considered in the model development. V_{co} : gas-liquid contact column volume (L), V_{mt} : mixing tank volume (L), q : number of tanks representing the system, and $[c]_{G_{inlet}}$: species concentration in the gas phase at the column inlet (mol L^{-1}).

3.1.2. Model formulation

The proposed dynamic model is based on the phenomenological knowledge of the process and the kinetic information obtained from the reaction mechanism.

Taking into account the reaction mechanism, the species are identified and numbered. The first species in the liquid phase ($i = 1$) is the same species considered in the gas phase. Afterward, a matrix containing the species concentrations in the liquid phase in each tank of the system ($p \times q$ matrix) and a vector of species concentrations in the gas phase ($(q - 1) \times 1$ vector) are formed. Besides, the stoichiometry matrix (ν matrix), the matrix of partial orders

of reactions (α matrix) and the vector of kinetic constants (k vector) are constructed.

The stoichiometry matrix is a $p \times n$ matrix, where each row corresponds to one chemical species in the liquid phase ($i = 1, \dots, p$) and each column to a chemical reaction ($l = 1, \dots, n$). In this matrix, the reactants are represented with negative stoichiometric coefficients ($-v_{i,l}$), products with positive stoichiometric coefficients ($+v_{i,l}$), and the other positions have a 0 entry. On the other hand, the α matrix is a $n \times p$ matrix and relates the partial order of each reaction l ($l = 1, \dots, n$) with respect to each species i in the liquid phase ($i = 1, \dots, p$). Each column of this matrix corresponds to one species and each row to a chemical reaction. The k vector is a column vector that contains the kinetic constants of the reactions contemplated in the reaction mechanism ($n \times 1$ vector).

The model formulation is based on the mole balance equations for a CSTR in the non-steady state for liquid and gas phases well mixed taking into consideration the mass transfer from gas to the liquid phase, convection and chemical reactions in the liquid phase (Equations 9 and 10). The absorption rate N (mol L⁻¹ s⁻¹) is given by Equation 11 (GOTTSCALK; LIBRA; SAUPE, 2000).

$$V_L \frac{dc_L}{dt} = Q_L(c_{L0} - c_L) + V_L N - R_L V_L \quad (9)$$

$$V_G \frac{dc_G}{dt} = Q_G(c_{G0} - c_G) - V_L N \quad (10)$$

$$N = k_L a (c_L^* - c_L) \quad (11)$$

where c_{L0} and c_{G0} are the inlet concentrations in liquid and gas phases, respectively. c_L^* and c_L are the liquid concentration in equilibrium with the bulk gas concentration (c_G) and the bulk liquid concentration, respectively. V_L and V_G are the liquid and gas volumes, correspondingly. Q_L and Q_G denote the flow rates in liquid and gas phases. R_L and $k_L a$ are the generation/consumption rate of species and the volumetric mass transfer coefficient in the liquid phase, respectively. All the concentrations are in mol L⁻¹, the volumes in L, the flow

rates in L/s, the generation rate in $\text{mol L}^{-1} \text{s}^{-1}$ and the volumetric mass transfer coefficient in s^{-1} .

Equations 9 and 10 are written for each species in each tank representing the system ($j = 1, \dots, q$).

Mole balance equations in the liquid phase

In this work, it is supposed that each tank forming the column ($j = 1, \dots, (q - 1)$) has the same total volume (ΔV), the same liquid volume (V_L) and therefore the same gas volume (V_G). Hence, the volume of a single tank can be expressed by Equation 12 with respect to the total column volume (V_{co}).

$$\Delta V = \frac{V_{co}}{(q - 1)} \quad (12)$$

The liquid holdup or liquid fraction (BELTRÁN, 2004; KANTARCI; BORAK; ULGEN, 2005), β (dimensionless), relates the liquid volume of a single tank with its total volume (Equation 13). In this work, the same value of β for each tank that forms the column is considered.

$$\beta = \frac{V_L}{\Delta V} \quad (13)$$

From Equations 12 and 13, the liquid volume of a tank that represents the column is given as follows:

$$V_L = \frac{\beta V_{co}}{(q - 1)} \quad (14)$$

Substituting the expression of V_L in Equation 9, the mole balance equations for the first species ($i = 1$) and the remaining species ($i = 2, \dots, p$) in the liquid phase in the j^{th} tank that composes the column ($j = 1, \dots, (q - 1)$) are given by Equations 15 and 16, respectively. Equation 17 represents the mole balance equations for all the species in the liquid phase in the mixing tank ($j = q$).

$$\frac{d[c_1]_{L_j}}{dt} = \frac{Q_L (q - 1)}{\beta V_{co}} ([c_1]_{L_{(j+1)}} - [c_1]_{L_j}) + N_j + R_{1L_j} \quad (15)$$

$$\frac{d[c_i]_{L_j}}{dt} = \frac{Q_L (q - 1)}{\beta V_{co}} ([c_i]_{L_{(j+1)}} - [c_i]_{L_j}) + R_{i_{L_j}} \quad (16)$$

$$\frac{d[c_i]_{L_q}}{dt} = \frac{Q_L}{V_{tr}} ([c_i]_{L_1} - [c_i]_{L_q}) + R_{i_{L_q}} \quad (17)$$

$[c_i]_{L_j}$ and $R_{i_{L_j}}$ denote the concentration and the generation/consumption rate of species in the liquid phase ($i = 1, \dots, p$) in the j^{th} tank that forms the system ($j = 1, \dots, q$), respectively. N_j is the absorption rate in the tanks that form the column ($j = 1, \dots, (q - 1)$), correspondingly.

The absorption rate for the species concentration in the gas phase in the j^{th} tank (N_j) that forms the column ($j = 1, \dots, (q - 1)$) is expressed according to the following equation:

$$N_j = k_L a ([c_1]_{L_j}^* - [c_1]_{L_j}) \quad (18)$$

where $[c_1]_{L_j}^*$ and $[c_1]_{L_j}$ are the liquid concentration in equilibrium with the bulk gas concentration and the bulk liquid concentration.

The solubility of the species in the gas phase is described by Henry's law. Defining the dimensional Henry's law constant (GOTTSCALK; LIBRA; SAUPE, 2000):

$$He = \frac{P_G}{[c_1]_{L_j}^*} \quad (19)$$

$$[c_1]_{L_j}^* = \frac{P_G}{He} \quad (20)$$

where P_G (atm) and $[c_1]_{L_j}^*$ (mol L⁻¹) are the partial pressure of the gas and the liquid concentration in equilibrium with the bulk gas concentration, respectively.

The ideal gas law is used to express the pressure (Equation 21). Therefore, $[c_1]_{L_j}^*$ can be calculated from the dimensional Henry's law constant (atm L mol⁻¹) and the bulk gas concentration of species ($[c]_{G_j}$) in the j^{th} tank (Equation 22). Correlations reported in the literature are used to determine He .

$$P_G = [c]_{G_j} RT \quad (21)$$

$$[c_1]_{L_j}^* = \frac{[c]_{G_j} RT}{He} \quad (22)$$

where R (L atm K⁻¹ mol⁻¹) and T (K) are the gas constant and the absolute temperature, correspondingly.

Then, by substituting the expression of $[c_1]_{L_j}^*$ in Equation 18, N_j is given by Equation 23.

$$N_j = k_L a \left(\frac{[c]_{G_j} RT}{He} - [c_1]_{L_j} \right) \quad (23)$$

The generation rate term of species in the j^{th} tank ($p \times 1$ vector) is written as the product of the stoichiometry matrix ($p \times n$ matrix) and the vector of reaction rates r_{lj} ($n \times 1$ vector) (mol L⁻¹ s⁻¹):

$$r_{lj} = k_l \prod_{i=1}^p [c_i]_{L_j}^{\alpha_{i,l}} \quad (24)$$

k_l ($l = 1, \dots, n$) (s⁻¹ for first order reactions and mol⁻¹ L s⁻¹ for second order reactions) is the kinetic rate constant for the reaction l and $\alpha_{i,l}$ the partial order of reaction l with respect to species i .

Mole balance equations in the gas phase in each tank that forms the column

The gas holdup, $(1 - \beta)$ (dimensionless) relates the gas volume of a single tank with its total volume (Equation 25). Working in a similar way as the liquid volume, V_G can be given by Equation 26.

$$(1 - \beta) = \frac{V_G}{\Delta V} \quad (25)$$

$$V_G = \frac{(1 - \beta) V_{co}}{(q - 1)} \quad (26)$$

Substituting Equations 14 and 26 in Equation 10, the mole balance equations for the species in the gas phase in the j^{th} tank ($j = 1, \dots, (q - 1)$)

can be expressed by Equation 27. For the first reactor ($j = 1$), $[c]_{G(j-1)} = [c]_{G_{inlet}}$. In the mixing tank, there is no gas phase.

$$\frac{d[c]_{G_j}}{dt} = \frac{Q_G (q - 1)}{(1 - \beta) V_{co}} ([c]_{G(j-1)} - [c]_{G_j}) - \frac{\beta}{(1 - \beta)} N_j \quad (27)$$

As a result, a vector that summarizes the mole balances of species in both phases is defined $((q * p + (q - 1)) \times 1$ vector) (Equation 28). This vector comprises the set of ordinary differential equations (ODEs) that describe the dynamic process.

$$\frac{dc}{dt} = \begin{bmatrix} \frac{d[c_1]_{L_1}}{dt} \\ \vdots \\ \frac{d[c_p]_{L_1}}{dt} \\ \frac{d[c_1]_{L_2}}{dt} \\ \vdots \\ \frac{d[c_p]_{L_2}}{dt} \\ \vdots \\ \frac{d[c_1]_{L_q}}{dt} \\ \vdots \\ \frac{d[c_p]_{L_q}}{dt} \\ \frac{d[c]_{G_1}}{dt} \\ \vdots \\ \frac{d[c]_{G_{(q-1)}}}{dt} \end{bmatrix}_{((q*p+(q-1)) \times 1)} \quad (28)$$

The proposed model, based on a system of ODEs, is implemented in Matlab[®]. Its main characteristics are listed in Table 5. The model's state variables are the species concentrations in both, liquid and gas phases in each tank that is assumed in order to represent the system. The model parameters are the volumetric mass transfer coefficient in the liquid phase ($k_L a$), the liquid holdup (β) and the kinetic constants ($k_l, l = 1, \dots, n$) of the set of reactions considered in the reaction mechanism.

It should be highlighted that the total number of perfectly mixed tanks (q) can be modified (see Figure 3). Therefore, a parameter estimation, as well as process simulations with different values of q , can be performed.

Table 5 – Main characteristics of the developed model. q : number of tanks representing the system, p : number of species in the liquid phase and n : number of chemical reactions.

Number of ODEs: $q * p + (q - 1)$
Number of state variables: $q * p + (q - 1)$
Number of model parameters (n_p): $n + 2$

The proposed model is structured. It is not necessary to insert one by one the mole balance equations of species. These equations, in both phases, are generated from the stoichiometry matrix (ν matrix), the matrix of partial orders of reactions (α matrix) and the vector of kinetic rate constants (k vector). Changes in the reaction mechanism are translated into changes in ν and α matrices and k vector. The initial conditions are set according to the experimental conditions.

β and $k_L a$ are key parameters for the scale-up and design of columns (KANTARCI; BORAK; ULGEN, 2005). In addition, the knowledge of the second-order reaction rates of organic pollutants and their intermediate compounds with the hydroxyl radical and with other oxidant species (O_3 and H_2O_2) in the AOPs is very important for evaluating their removal. Some of these kinetic constants are not reported in the literature, therefore, their estimation from real process data is a necessary task. In the next section, the estimation of model parameters from available experimental data is discussed.

3.2. Parameter estimation

The main goal in a parameter estimation problem is to fit a model with unknown variables (model parameters) to experimental data by adjusting the parameters through the minimization of an objective function (OF) subject or not to constraints. The objective function establishes how close the model predictions and the experimental results are. Therefore, the estimated parameters guarantee model predictions as close as possible to the measured results (BARD, 1974; BEERS, 2007; BIEGLER; DAMIANO; BLAU, 1986).

In the present work, the parameter estimation problem, based on the developed model, is translated into a constrained optimization problem. The weighted least squares method is used, therefore, the sum of squares of residuals is defined as the objective function. This function, relating the differences between experimental (or measured) and predicted concentrations of species, is defined according to Equation 29. The maximum value of the experimental concentration of species j ($j = 1, \dots, n_{var}$) in the i^{th} experiment ($MV_{[c_j]_{exp_i}}$) is used as weight. Reparameterization of the kinetic constants ($\varphi_l = \ln(k_l)$, $l = 1, \dots, n$), to avoid their variation in large orders of magnitude, is used (BIEGLER; DAMIANO; BLAU, 1986). Then, the vector of model parameters $\theta' \in R^{n_p}$ ($n_p \times 1$ vector) can be expressed by Equation 30.

$$\min_{\theta'} OF(\theta') = \sum_{i=1}^{n_{exp}} \sum_{j=1}^{n_{var}} \left(\frac{[c_j]_{exp_i} - [c_j]_{pred_i}(\theta')}{MV_{[c_j]_{exp_i}}} \right)^2 \quad (29)$$

$$\text{subject to: } lb \leq \theta' \leq ub$$

$$\theta' = \begin{bmatrix} k_L a \\ \beta \\ \ln(k_l) \end{bmatrix}^T \quad l = 1, \dots, n \quad (30)$$

being ub and lb two row vectors ($1 \times n_p$ vectors) that contain the upper and lower bounds for the initial guesses of the model parameters. n_{exp} and n_{var} are the number of experiments and the number of experimental variables that are considered in the objective function.

The objective function is minimized by using the trust-region-reflective algorithm implemented in the `lsqnonlin` Matlab® function (MATHWORKS, 2018a) and the particle swarm optimization (PSO) method (EBERHART; KENNEDY, 1995; SHI; EBERHART, 1998).

3.2.1. Parameter estimation by using the trust-region-reflective algorithm implemented in the `lsqnonlin` Matlab® function

The `lsqnonlin` Matlab® function (MATHWORKS, 2018a) has implemented the least squares method. When using this function, initial guesses for the

model parameters must be supplied. The selection of good initial guesses has a great influence on the resolution of the optimization problem (BARD, 1974).

On the other hand, the trust-region-reflective algorithm (MATHEWORKS, 2018a) is a large scale optimization algorithm that can be used in the resolution of problems with bound constraints (lb and ub). Besides, this algorithm uses the information of the Jacobian matrix of the residuals ($Jac_{\theta'}R(\theta')$).

In order to obtain the analytical Jacobian matrix (Equation 31), the residuals (see Equation 29) are differentiated with respect to the model parameters θ' (Equation 30). The validity of this matrix, written as sensitivity functions, is checked by using the DerivativeCheck Matlab® function. When $Jac_{\theta'}R(\theta')$ is provided to the optimization algorithm, the solution of the optimization problem is faster and more precise (BARD, 1974).

$$Jac_{\theta'}R(\theta') = \begin{bmatrix} -MV_{[c_j]_{exp_i}}^{-1} \frac{\partial \left([c_j]_{pred_i}(\theta') \right)}{\partial \theta'} \\ \vdots \\ -MV_{[c_{nvar}]_{exp_i}}^{-1} \frac{\partial \left([c_{nvar}]_{pred_i}(\theta') \right)}{\partial \theta'} \end{bmatrix} \quad (31)$$

in which $\partial \left([c_j]_{pred_i}(\theta') \right) / \partial \theta'$ is the sensitivity matrix of the predicted concentration of species j for the i^{th} experiment.

The sensitivity matrices are obtained through the forward sensitivity analysis (FSA). In the next section, it is explained how this analysis is made.

3.2.1.1. Sensitivity analysis

Sensitivity analyses are powerful tools in the development of mathematical models. The information generated by a sensitivity analysis (SA) is useful in the evaluation of optimization gradients and in the uncertainty analysis in the task of parameter estimation (PETZOLD et al., 2006). Additionally, this type of analysis allows studying the influence of model parameters on the model predictions and in this way to determine the parameters that have a greater influence on the model responses (HAMBY, 1994; PETZOLD et al., 2006; SEFERLIS, 1996).

Besides, the analysis of the sensitivity functions generates valuable information related to the estimability of the model parameters (MCLEAN; MCAULEY, 2012).

In the present work, the SA of the model responses is carried out with respect to all the model parameters (θ' , see Equation 30). The forward method of CVODES solver (SERBAN; HINDMARSH, 2005) of SUNDIALS (Suite of Nonlinear and Differential/Algebraic Equation Solvers) (HINDMARSH et al., 2005) is used. CVODES is an ODE solver capable to deal with stiff and nonstiff problems by using the Backward Differentiation Formulas (BDF) and the Adams-Moulton method, respectively. This solver has also incorporated sensitivity analysis capabilities (HINDMARSH; SERBAN, 2009).

In a general way, an initial value problem can be represented by Equation 32 (BEERS, 2007):

$$\dot{y} = f(t, y, p), \quad y(t_0) = y_0 \quad (32)$$

where t , y ($y \in R^N$) and p ($p \in R^{n_p}$) are the independent and dependent variables and the parameters, respectively.

By deriving Equation 32 with respect to the parameters it is possible to obtain the forward sensitivity equations (HINDMARSH; SERBAN, 2009). These equations are given as follows:

$$\dot{s}_i = \frac{\partial f}{\partial y} s_i + \frac{\partial f}{\partial p_i}, \quad s_i(t_0) = \frac{\partial y_0(p)}{\partial p_i} \quad (33)$$

being f the right-hand side of the model differential equations. s_i is the vector of sensitivity with respect to the model parameter p_i and is defined as $s_i(t) = dy(t)/dp_i$. $\partial f/\partial y$ and $\partial f/\partial p_i$ represent the Jacobian matrix of the model and the derivatives of the right-hand side of the model differential equations with respect to the model parameter p_i , respectively.

The Jacobian matrix of the model (Jac_{model}) as well as the derivatives of the right-hand side of the model equations with respect to the model parameters θ' are analytically obtained and summarized in Appendixes B and A, respectively.

The analytical Jacobian matrix is validated by means of its comparison to the numerical Jacobian matrix computed by forward finite differences implemented in Matlab® ($h = 1 \times 10^{-6}$). In the comparison process, feasible values for the species concentrations and nominal values for the model parameters are used. A relative error of 1×10^{-4} between both matrices is considered as acceptable.

When doing the FSA, CVODES integrates a system of ODEs composed of the model differential equations describing the dynamic process and the forward sensitivity equations (HINDMARSH; SERBAN, 2009). Therefore, as a result, the concentration profiles of species in both liquid and gas phases in each tank of the system and its respective sensitivities with respect to the model parameters θ' are obtained. The generated information by the FSA is used in the construction of the objective function and in the evaluation of the Jacobian matrix of the residuals.

3.2.2. Parameter estimation by using the particle swarm optimization method

PSO is a heuristic optimization algorithm based on the social and collective behaviors of animals (SCHWAAB et al., 2008). It was proposed by Kennedy and Eberhart (1995) and modified by Shi and Eberhart (1998) and Clerc (1999). In this method, each particle represents a possible solution of the optimization problem. Hence, the swarm is formed by N_p particles ($j = 1, \dots, N_p$) that move along the multidimensional search space looking for the best solution. The dimension of the search space is given by the number of parameters to be estimated. While the particles are moving along the search space, they are communicating and sharing information. According to Shi and Eberhart (1998), the movement of the particles in the search space is described by Equations 34 and 35.

$$V_j(i) = wV_j(i-1) + c_1r_1[P_{best,j} - X_j(i-1)] + c_2r_2[G_{best} - X_j(i-1)] \quad (34)$$

$$X_j(i) = X_j(i-1) + V_j(i) \quad (35)$$

being $V_j(i)$ and $X_j(i)$ the velocity and position of the particle j ($j = 1, \dots, N_p$) in the i^{th} iteration ($i = 1, \dots, MaxIter$). c_1 and c_2 are the cognitive and social coefficients, respectively. These coefficients are real constant numbers and commonly take values equal to two ($c_1 = c_2 = 2$) (RAO, 2009). On the other hand, r_1 and r_2 are random numbers with uniform distributions in the range $[0, 1]$. w denotes the inertia weight, $P_{best,j}$ and G_{best} are the best position (or solution) found by the particle j and the whole swarm of particles, correspondingly. It is understood by best position, the position found by the particle j or the whole swarm with the lowest value of the objective function.

The swarm size or number of particles influences the performance of the method. According to the literature, swarms with 20 or 30 particles are commonly used (RAO, 2009; MARINI; WALCZAK, 2015).

This algorithm is of easy and simple implementation. Moreover, it does not use derivatives of the objective function and constraints. PSO has been employed in the resolution of different optimization problems with different objective functions and a large number of parameters (DA et al., 2013; LEE; PRASAD; LEE, 2011; POPLI; PRASAD, 2015; SCHWAAB et al., 2008; WANG et al., 2016).

The optimization problem is formulated according to Equations 29 and 30. PSO method is implemented in Matlab® (MATHWORKS, 2016). A maximum velocity (V_{max}) in each search direction is defined according to Equation 36. Furthermore, a linearly decreasing inertia weight calculated by Equation 37 is used (RAO, 2009). The maximum number of iterations to be performed ($MaxIter$) is used as stopping criterion.

$$V_{max} = \frac{(ub - lb)}{2} \quad (36)$$

$$w(i) = w_{max} - \left(\frac{w_{max} - w_{min}}{MaxIter} \right) i \quad (37)$$

where w_{max} and w_{min} represent the maximum and minimum values of w and take values equal to 0.9 and 0.4, respectively (RAO, 2009).

When using PSO, the system of ODEs describing the dynamic process is integrated by using the Matlab® ode15s solver (MATHWORKS, 2018b). This multistep, variable-step, variable-order solver is based on the Numerical Differentiation Formulas (NDFs) and it is appropriate for solving stiff problems and differential-algebraic equation systems (DAE systems).

3.3. Process simulations

Process simulations, using the dynamic model with the estimated parameters, can be performed. As a result, predicted concentration profiles of species in liquid and gas phases in each considered tank are obtained.

In all cases, the accuracy of the model predictions is determined by means of the root mean square error (RMSE) expressed according to the following equation:

$$RMSE = \left[\sum_{i=1}^N (\hat{y}_i - y_i)^2 / N \right]^{1/2} \quad (38)$$

where $\hat{y}_i$ and y_i are the predicted and experimental values of the variable y , respectively. N is the number of experimental points.

3.4. Computational tool

The proposed computational tool for the modeling and parameter estimation of AOPs is developed in Matlab®. It contains four main modules. Figure 4 shows the process modeling module (Module I) that is devoted to the generation of the system of ODEs that describes the dynamic process. These equations are generated from ν and α matrices and the k vector.

Figures 5 and 6 depict the schematic representation of the modules dedicated to the model parameter estimation from available experimental data (Modules II and III). In Module II the objective function (weighted least squares) is minimized by using the lsqnonlin Matlab® function with the trust-region-reflective algorithm. In Module III the optimization problem is solved by employing the PSO method.

Figure 4 – Module I: process modeling module. ODEs: ordinary differential equations, ν : stoichiometry matrix, α : matrix of partial orders of reactions, k : vector of kinetic rate constants, q : number of tanks forming the system, Q_L and Q_G : flow rates in liquid and gas phases, V_{co} : gas-liquid contact column volume, V_{mt} : mixing tank volume, and He : dimensional Henry's law constant.

Figure 5 – Module II: estimation module I. OF : objective function, lb and, ub : lower and upper bounds, and θ' : vector of model parameters.

Figure 6 – Module III: estimation module II. lb and ub : lower and upper bounds, OF : objective function, $MaxIter$: maximum number of iterations, c_1 and c_2 : cognitive and social coefficients, w_{max} and w_{min} : maximum and minimum values of the inertia weight, and N_p : number of particles.

Figure 7 displays the simulation module (Module IV). In this module, simulations using the estimated parameters are carried out. Module IV can also be used to perform process simulations with model parameters supplied by the user.

Figure 7 – Module IV: simulation module. v : stoichiometry matrix, α : matrix of partial orders of reactions, k : vector of kinetic rate constants, q : number of tanks forming the system, Q_L and Q_G : flow rates in liquid and gas phases, V_{co} : gas-liquid contact column volume, V_{mt} : mixing tank volume, and He : dimensional Henry's law constant.

Some characteristics of the proposed computational tool are listed below:

- Easy implementation of different compartment schemes (different values of q), different degradation models (different reaction mechanisms), different weights in the objective function or even different objective functions.
- It is possible to decide which model parameters will be estimated from the construction of the vector of estimated parameters.
- Process simulations with estimated model parameters or parameters supplied by the user can be performed.
- Predicted concentration profiles of all the considered species in each tank representing the system can be obtained.
- Different experimental conditions can be tested.
- Since the tool is based on a general phenomenological structured model of AOPs, it can be used to describe different AOPs.

Chapter 4. First case study: phenol degradation by electro-Fenton process

The proposed methodology in the previous section is applied to the treatment of phenol (PH) by electro-Fenton process (MOUSSET et al., 2016). The degradation experiments were carried out in a reactor operating in batch mode at constant pH equal to three.

The available experimental data consists of concentrations of PH and its aromatic intermediates: catechol (CT), hydroquinone (HQ) and resorcinol (RS). Besides, concentrations of carboxylic acids: maleic (MLE), fumaric (FUM), succinic (SUC), glyoxylic (GLYOX), oxalic (OXA) and formic (FOR) are available, but were not taken into account. It is worth to mention that in the paper of Mousset et al. (2016), the analytical procedure followed to determine the concentrations of PH and its aromatic intermediates was explained. However, there is a lack of information on how concentrations of carboxylic acids were measured. Besides, incoherencies in their experimental values were observed. Therefore, in this thesis, only the experimental concentrations of PH, CT, HQ, and RS are used.

A more detailed description of the experimental work can be found in Mousset et al., (2016).

4.1. Results and discussion

4.1.1. Modeling

The reaction mechanism considered is displayed in Table 6 (MOUSSET et al., 2016). The equilibrium reactions were treated as two reactions, one forward and the other one backward. From the reaction mechanism, the species were identified and numbered (see Table 7). There are 30 species in the liquid phase ($p = 30$) undergoing 52 chemical reactions ($n = 52$) in the same phase. In addition, ν and α matrices were constructed. These matrices are summarized in Appendixes C and D.

Table 6 – Reaction mechanism involved in the phenol degradation by electro-Fenton process (modified from Mousset et al. (2016)).

Reactions
$O_2 + 2H^+ + 2e^- \xrightarrow{k_1} H_2O_2$
$Fe^{2+} + H_2O_2 + H^+ \xrightarrow{k_2} Fe^{3+} + HO^\bullet + H_2O$
$Fe^{2+} + HO^\bullet \xrightarrow{k_3} Fe^{3+} + OH^-$
$PH + HO^\bullet + O_2 \xrightarrow{k_4} CT + HO_2^\bullet$
$PH + HO^\bullet + O_2 \xrightarrow{k_5} HQ + HO_2^\bullet$
$PH + HO^\bullet + O_2 \xrightarrow{k_6} RS + HO_2^\bullet$
$HQ + 2HO^\bullet + O_2 \xrightarrow{k_7} pBQ + 2H_2O$
$pBQ + 2H_2O \xrightarrow{k_8} HQ + 2HO^\bullet + O_2$
$HQ + HO^\bullet + O_2 \xrightarrow{k_9} MUC + CO_2$
$HQ + HO^\bullet + O_2 \xrightarrow{k_{10}} MLE + CO_2$
$pBQ + HO^\bullet + O_2 \xrightarrow{k_{11}} MUC + CO_2$
$pBQ + HO^\bullet + O_2 \xrightarrow{k_{12}} MLE + CO_2$
$CT + 2HO^\bullet \xrightarrow{k_{13}} oBQ + 2H_2O$
$oBQ + 2H_2O \xrightarrow{k_{14}} CT + 2HO^\bullet$
$CT + HO^\bullet + O_2 \xrightarrow{k_{15}} PG + HO_2^\bullet$
$CT + HO^\bullet + O_2 \xrightarrow{k_{16}} MUC + CO_2$
$CT + HO^\bullet + O_2 \xrightarrow{k_{17}} MLE + CO_2$
$oBQ + HO^\bullet + O_2 \xrightarrow{k_{18}} MUC + CO_2$
$RS + HO^\bullet + O_2 \xrightarrow{k_{19}} PG + HO_2^\bullet$
$PG + HO^\bullet + O_2 \xrightarrow{k_{20}} MUC + CO_2$
$PG + HO^\bullet + O_2 \xrightarrow{k_{21}} DHsBQ + CO_2$
$MUC + HO^\bullet + O_2 \xrightarrow{k_{22}} FUM + CO_2$
$MUC + HO^\bullet + O_2 \xrightarrow{k_{23}} SUC + CO_2$
$MUC + HO^\bullet + O_2 \xrightarrow{k_{24}} OBac + CO_2$
$MLE \xrightarrow{k_{25}} FUM$
$FUM \xrightarrow{k_{26}} MLE$
$MLE + HO^\bullet + O_2 \xrightarrow{k_{27}} OBac + CO_2$
$FUM + HO^\bullet + O_2 \xrightarrow{k_{28}} OBac + CO_2$

Table 6 (continued)

Reactions
$FUM + HO^\bullet + O_2 \xrightarrow{k_{29}} SUC + CO_2$
$SUC + HO^\bullet + O_2 \xrightarrow{k_{30}} PROP + CO_2$
$OBac + HO^\bullet + O_2 \xrightarrow{k_{31}} GLYOX + CO_2$
$PROP + HO^\bullet + O_2 \xrightarrow{k_{32}} CO_2 + H_2O$
$GLYOX + HO^\bullet + O_2 \xrightarrow{k_{33}} CO_2 + H_2O$
$DHsBQ + HO^\bullet + O_2 \xrightarrow{k_{34}} DHpBQ + CO_2$
$DHpBQ + HO^\bullet + O_2 \xrightarrow{k_{35}} DHOac + CO_2$
$DHOac + HO^\bullet + O_2 \xrightarrow{k_{36}} DHDac + CO_2$
$DHDac + HO^\bullet + O_2 \xrightarrow{k_{37}} DOB + CO_2$
$DOB + HO^\bullet + O_2 \xrightarrow{k_{38}} ACRac + CO_2$
$ACRac + HO^\bullet + O_2 \xrightarrow{k_{39}} HPac + CO_2$
$HPac + HO^\bullet + O_2 \xrightarrow{k_{40}} GLYOX + CO_2$
$HPac + HO^\bullet + O_2 \xrightarrow{k_{41}} OPac + CO_2$
$OPac + HO^\bullet + O_2 \xrightarrow{k_{42}} MLO + CO_2$
$MLO + HO^\bullet + O_2 \xrightarrow{k_{43}} TAR + CO_2$
$TAR + HO^\bullet + O_2 \xrightarrow{k_{44}} ACE + CO_2$
$TAR + HO^\bullet + O_2 \xrightarrow{k_{45}} KETO + CO_2$
$KETO + HO^\bullet + O_2 \xrightarrow{k_{46}} OXA + CO_2$
$ACE + HO^\bullet + O_2 \xrightarrow{k_{47}} OXA + CO_2$
$ACE + HO^\bullet + O_2 \xrightarrow{k_{48}} FOR + CO_2$
$ACE + HO^\bullet + O_2 \xrightarrow{k_{49}} CO_2 + H_2O$
$OXA + HO^\bullet + O_2 \xrightarrow{k_{50}} FOR + CO_2$
$OXA + HO^\bullet + O_2 \xrightarrow{k_{51}} CO_2 + H_2O$
$FOR + HO^\bullet + O_2 \xrightarrow{k_{52}} CO_2 + H_2O$

Table 7 – Numbered species according to the reaction mechanism involved in the phenol degradation by electro-Fenton process.

Species
$[H_2O_2] = c_{L1}$
$[HO\cdot] = c_{L2}$
$[PH] = c_{L3}$
$[CT] = c_{L4}$
$[HQ] = c_{L5}$
$[RS] = c_{L6}$
$[pBQ] = c_{L7}$
$[MUC] = c_{L8}$
$[MLE] = c_{L9}$
$[oBQ] = c_{L10}$
$[PG] = c_{L11}$
$[DHsBQ] = c_{L12}$
$[FUM] = c_{L13}$
$[SUC] = c_{L14}$
$[OBac] = c_{L15}$
$[PROP] = c_{L16}$
$[GLYOX] = c_{L17}$
$[DHpBQ] = c_{L18}$
$[DHOac] = c_{L19}$
$[DHDac] = c_{L20}$
$[DOB] = c_{L21}$
$[ACRac] = c_{L22}$
$[HPac] = c_{L23}$
$[OPac] = c_{L24}$
$[MLO] = c_{L25}$
$[TAR] = c_{L26}$
$[ACE] = c_{L27}$
$[KETO] = c_{L28}$
$[OXA] = c_{L29}$
$[FOR] = c_{L30}$

The general equations of the model (see Section 3.1.2) are applied to the case study. These equations are simplified since all the experiments were performed in batch mode and there was no gas phase, therefore there was no mass transfer. Thus, the mole balance equations of species in the liquid phase

are given by Equation 39. These equations are generated by using ν and α matrices (see Appendixes C and D).

$$\frac{d[c_i]_L}{dt} = R_{i_L} \quad (39)$$

As aforementioned, in the work of Mousset et al., (2016) the quasi-steady state approximation for the hydroxyl radical was assumed. In the current thesis, this hypothesis is not supposed (PANTEA et al., 2014). All the other hypotheses adopted by Mousset et al. (2016), are taken into account.

Based on the operating conditions (MOUSSET et al., 2016), the current intensity (I) and the surface of the electrode (A) are equal to 200 mA and 48 cm², respectively. From the experimental conditions, the initial concentration of Fe²⁺ ([Fe²⁺]) is equal to 0.1 mmol L⁻¹ and remains constant during the reaction time. In addition, the reaction medium is considered saturated with O₂. The concentration of dissolved O₂ is assumed to equal to its saturation value (2.8x10⁻⁴ mol L⁻¹).

New kinetic constants, based on the experimental conditions, were defined for the reactions involving [Fe²⁺], [H⁺] and [O₂] as reactants (see Table 6).

$$k'_1 = k_1 \left(\frac{I}{A} \right) [O_2][H^+]^2 \quad (40)$$

$$k'_2 = k_2 [Fe^{2+}][H^+] \quad (41)$$

$$k'_3 = k_3 [Fe^{2+}] \quad (42)$$

$$k'_l = k_l [O_2] \quad l = 4 - 7, 9 - 12, 15 - 24, 27 - 52 \quad (43)$$

[H⁺] in mol L⁻¹ is given by Equation 45.

$$pH = -\log([H^+]) \quad (44)$$

$$[H^+] = 10^{(-pH)} \quad (45)$$

The main characteristics of the model are listed in Table 8. The state variables are the concentrations of the 30 species and the model parameters are the kinetic rate constants of the 52 reactions involved in the reaction mechanism.

Table 8 – Main characteristics of the model when the computational tool is applied to the treatment of phenol by electro-Fenton process.

Number of ODEs: 30
Number of state variables: 30
Number of model parameters: 52

4.2.2. Parameter estimation and process simulations

The model parameters are estimated from real process data of PH degradation by electro-Fenton process (MOUSSET et al., 2016). The optimization problem is formulated according to Equations 29 and 30 by considering experimental and predicted concentrations of PH, CT, HQ and RS in the objective function. This function is minimized by using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab® function and the PSO method.

$$\min_{\theta'} OF = \sum_{i=1}^N \left(\frac{[PH]_{exp} - [PH]_{pred}(\theta')}{MV_{[PH]_{exp}}} \right)^2 + \left(\frac{[CT]_{exp} - [CT]_{pred}(\theta')}{MV_{[CT]_{exp}}} \right)^2 + \left(\frac{[HQ]_{exp} - [HQ]_{pred}(\theta')}{MV_{[HQ]_{exp}}} \right)^2 + \left(\frac{[RS]_{exp} - [RS]_{pred}(\theta')}{MV_{[RS]_{exp}}} \right)^2 \quad (46)$$

$$\text{subject to: } lb \leq \theta' \leq ub$$

$$\theta' = [\ln(k_l)]^T \quad l = 1, \dots, 52 \quad (47)$$

being $MV_{[PH]_{exp}}$, $MV_{[CT]_{exp}}$, $MV_{[HQ]_{exp}}$ and $MV_{[RS]_{exp}}$ the maximum values of the experimental concentrations of PH, CT, HQ and RS, correspondingly.

Initial concentrations of species are given by the experimental conditions. The initial concentration of PH is equal to 2.5 mmol L⁻¹ and for the remaining species, the initial concentrations are assumed to be equal to zero.

With the adjusted parameters, simulations of the PH degradation by the electro-Fenton process are carried out. All the simulations are performed in Matlab® using a desktop computer with a CORE i5-2400, processor 3.10 GHz and 8 GB of RAM.

Parameter estimation by using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab® function

When using the lsqnonlin Matlab® function with the trust-region-reflective algorithm, the analytical Jacobian matrix of the residuals is supplied. It is formulated according to Equation 31 and evaluated by using the information of the sensitivity matrices. The validity of this matrix is checked by employing the DerivativeCheck function of Matlab®.

$$Jac_{\theta'} R = \begin{bmatrix} -MV_{[PH]exp}^{-1} \frac{\partial ([PH]_{pred}(\theta'))}{\partial \theta'} \\ -MV_{[CT]exp}^{-1} \frac{\partial ([CT]_{pred}(\theta'))}{\partial \theta'} \\ -MV_{[HQ]exp}^{-1} \frac{\partial ([HQ]_{pred}(\theta'))}{\partial \theta'} \\ -MV_{[RS]exp}^{-1} \frac{\partial ([RS]_{pred}(\theta'))}{\partial \theta'} \end{bmatrix} \quad (48)$$

where $\partial ([PH]_{pred}(\theta'))/\partial \theta'$, $\partial ([CT]_{pred}(\theta'))/\partial \theta'$, $\partial ([HQ]_{pred}(\theta'))/\partial \theta'$ and $\partial ([RS]_{pred}(\theta'))/\partial \theta'$ are the sensitivity matrices of the predicted concentrations of PH, CT, HQ and RS, respectively.

The system of ODEs describing the dynamic process along with the sensitivity equations is integrated by using the CVODES solver of SUNDIALS (Section 3.2.1.1). As a result, predicted concentration profiles of species (see Table 7) and their sensitivities with respect to the model parameters are obtained. Predicted concentrations and sensitivity matrices of PH, CT, HQ, and RS are employed in the construction of the objective function and in the evaluation of the Jacobian matrix of the residuals, respectively.

In order to generate the sensitivity equations, the general analytical Jacobian matrix of the model and the derivatives of the right-hand side of the model differential equations with respect to the model parameters θ' are applied to the specific case. The analytical Jacobian matrix is only composed of the $Jac_{c_L c_L}$ block (see Appendix B). This matrix was compared to the numerical one computed by forward finite differences. On the other hand, only derivatives of

the right-hand side of the model equations with respect to the kinetic constants are considered (see Appendix A).

Initial guesses for the model parameters are defined. These values are established based on previous knowledge (LIU et al., 2007; MEIJIDE et al., 2017; QIU et al., 2015). Lower and upper bounds for the model parameters are also established (see Appendix E). The algorithm to estimate the parameters is executed. The stopping criteria are that the relative changes in the objective function or the step size values between two successive iterations are less or equal than a tolerance value equal to 10^{-8} . The computation time is measured by the *tic* and *toc* Matlab® function.

Parameter estimation by using the PSO method

When the PSO method is used, the system of ODEs that describes the process is integrated by using the ode15s solver of Matlab®. In the parameter estimation, upper and lower bounds for the parameters are defined (see Appendix E). The inertial weight is computed according to Equation 37 by using the maximum and minimum values listed in Table 9. Three different population sizes are used. The maximum number of iterations to be performed is used as the stopping criteria. Table 9 summarizes the values of the parameters used in the implementation of the PSO method.

Table 9 – Parameter values used in the parameter estimation by using the particle swarm method.

Parameter	Value
N_{p1}	30
N_{p2}	45
N_{p3}	60
$MaxIter$	200
c_1	2
c_2	2
w_{min}	0.4
w_{max}	0.9

Estimated kinetic parameters by using the trust-region-reflective algorithm and the PSO method considering different population sizes are shown in Table 10. The adjusted values of k_2 reached its upper bound. The same behavior was observed for the values of k_1 , except when the PSO method with 30 particles was used. It is possible to observe that for lsqnonlin, as it uses the trust-region algorithm, parameters whose sensitivity is small were practically unchanged from their initial guess value (parameters k_{10} to k_{52}). With the adjusted parameters, process simulations are performed. These simulations are carried out in Matlab® using a desktop computer with a CORE i5-2400 processor 3.10 GHz and 8GB of RAM.

Table 10 – Estimated kinetic constants for the treatment of phenol by electro-Fenton process. N_p : number of particles.

Kinetic constants (mol ⁻¹ L s ⁻¹)	Initial guesses	Estimated values			
		lsqnonlin	PSO		
			$N_p = 30$	$N_p = 45$	$N_p = 60$
k_1	6.6	10	9.26	10	10
k_2	63	81	81	81	81
k_3	3.20x10 ⁸	1.74x10 ⁹	1.00x10 ⁹	1.00x10 ⁹	1.10x10 ⁹
k_4	2.85x10 ⁹	1.00x10 ¹⁰	1.00x10 ¹⁰	1.00x10 ¹⁰	1.00x10 ¹⁰
k_5	2.85x10 ⁹	2.15x10 ⁹	2.30x10 ⁹	2.30x10 ⁹	2.29x10 ⁹
k_6	2.85x10 ⁹	5.23x10 ⁷	5.85x10 ⁷	5.44x10 ⁷	5.94x10 ⁷
k_7	4.50x10 ⁹	4.50x10 ⁹	1.00x10 ¹⁰	1.00x10 ⁹	9.79x10 ⁹
k_8	4.00x10 ⁸	4.00x10 ⁸	1.00x10 ⁸	1.00x10 ¹⁰	1.00x10 ⁸
k_9	2.50x10 ⁹	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹
k_{10}	2.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁸
k_{11}	1.50x10 ¹⁰	1.50x10 ¹⁰	1.00x10 ¹¹	1.00x10 ¹¹	1.00x10 ¹⁰
k_{12}	5.00x10 ⁹	5.00x10 ⁹	1.00x10 ¹⁰	1.00x10 ⁹	9.91x10 ⁹
k_{13}	8.70x10 ⁹	8.70x10 ⁹	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹
k_{14}	9.00x10 ⁵	9.00x10 ⁵	1.00x10 ⁶	1.00x10 ⁵	1.00x10 ⁵
k_{15}	8.90x10 ⁸	1.00x10 ⁹	5.80x10 ⁸	1.00x10 ⁹	1.00x10 ⁷
k_{16}	4.00x10 ⁸	1.30x10 ⁸	3.92x10 ⁸	1.00x10 ⁷	1.00x10 ⁹
k_{17}	5.00x10 ⁷	2.99x10 ⁷	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶
k_{18}	2.50x10 ⁹	2.50x10 ⁹	4.35x10 ⁹	1.90x10 ⁹	1.00x10 ¹⁰
k_{19}	8.10x10 ⁸	8.48x10 ⁹	8.90x10 ⁹	7.59x10 ⁹	9.21x10 ⁹

Table 10 (continued)

Kinetic constants (mol ⁻¹ L s ⁻¹)	Initial guesses	Estimated values			
		lsqnonlin	PSO		
			N _p = 30	N _p = 45	N _p = 60
k_{20}	5.00x10 ⁹	5.10x10 ⁹	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ¹⁰
k_{21}	4.00x10 ¹⁰	4.82x10 ¹⁰	1.00x10 ¹¹	1.00x10 ¹¹	1.00x10 ¹¹
k_{22}	2.70x10 ⁷	2.72x10 ⁷	1.00x10 ⁸	1.00x10 ⁷	1.00x10 ⁸
k_{23}	3.40x10 ⁸	3.56x10 ⁸	1.00x10 ⁹	1.00x10 ⁸	1.00x10 ⁹
k_{24}	6.00x10 ⁸	6.44x10 ⁸	1.00x10 ⁸	1.00x10 ⁹	1.00x10 ⁸
k_{25}	2.40x10 ⁷	2.40x10 ⁷	1.00x10 ⁸	1.00x10 ⁷	1.00x10 ⁷
k_{26}	1.80x10 ⁶	1.80x10 ⁶	1.00x10 ⁶	1.00x10 ⁷	1.00x10 ⁶
k_{27}	4.00x10 ⁸	4.00x10 ⁸	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹
k_{28}	8.50x10 ⁷	8.47x10 ⁷	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁸
k_{29}	3.30x10 ⁷	3.29x10 ⁷	1.00x10 ⁷	1.00x10 ⁸	1.03x10 ⁷
k_{30}	7.00x10 ⁸	6.59x10 ⁸	9.18x10 ⁸	1.00x10 ⁸	1.00x10 ⁹
k_{31}	5.00x10 ⁷	4.87x10 ⁷	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁷
k_{32}	2.00x10 ⁸	1.99x10 ⁸	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁹
k_{33}	3.00x10 ⁹	2.99x10 ⁹	3.24x10 ⁹	1.00x10 ⁹	1.00x10 ¹⁰
k_{34}	5.00x10 ⁷	4.80x10 ⁷	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁷
k_{35}	2.00x10 ⁸	1.99x10 ⁸	1.00x10 ⁹	1.00x10 ⁹	9.97x10 ⁸
k_{36}	7.00x10 ⁸	6.97x10 ⁸	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁸
k_{37}	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁹	1.00x10 ⁸	1.00x10 ⁹
k_{38}	9.00x10 ⁷	9.00x10 ⁷	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹
k_{39}	1.10x10 ⁸	1.10x10 ⁸	1.00x10 ⁸	1.00x10 ⁸	5.47x10 ⁸
k_{40}	2.00x10 ⁷	2.00x10 ⁷	1.00x10 ⁷	1.13x10 ⁷	1.00x10 ⁷
k_{41}	1.10x10 ⁸	1.10x10 ⁸	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁸
k_{42}	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁹	8.88x10 ⁸	1.00x10 ⁸
k_{43}	1.10x10 ⁸	1.10x10 ⁸	1.00x10 ⁹	1.00x10 ⁸	5.73x10 ⁸
k_{44}	1.20x10 ⁸	1.20x10 ⁸	1.00x10 ⁹	1.93x10 ⁸	1.00x10 ⁹
k_{45}	9.00x10 ⁷	9.00x10 ⁷	1.00x10 ⁷	1.00x10 ⁹	1.00x10 ⁹
k_{46}	8.00x10 ⁷	8.00x10 ⁷	1.00x10 ⁷	1.00x10 ⁷	1.00x10 ⁹
k_{47}	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁷	3.08x10 ⁶
k_{48}	1.10x10 ⁶	1.10x10 ⁶	1.00x10 ⁷	8.24x10 ⁶	1.00x10 ⁶
k_{49}	5.00x10 ⁷	5.00x10 ⁷	3.18x10 ⁷	1.00x10 ⁸	1.00x10 ⁷
k_{50}	3.00x10 ⁷	3.00x10 ⁷	1.00x10 ⁷	1.00x10 ⁷	1.00x10 ⁸
k_{51}	7.50x10 ⁹	7.50x10 ⁹	1.00x10 ¹⁰	1.00x10 ¹⁰	1.00x10 ⁹
k_{52}	6.70x10 ⁷	6.70x10 ⁷	1.00x10 ⁷	1.00 x10 ⁷	1.02x10 ⁷
OF value		0.833101	1.293718	1.311553	1.291745

Figures 8 and 9 show the predicted and experimental concentration profiles of PH, CT, HQ and RS when the set of parameters estimated by using the trust-

region-reflective algorithm is used (see Table 10). Figures 10 and 11 display these concentration profiles when the set of parameters estimated by using the PSO method, for which the lowest value of the objective function was obtained, is employed.

Figure 8 – Experimental and predicted concentration profiles of phenol (PH) and catechol (CT) by using the set of adjusted parameters when the trust-region-reflective algorithm was employed.

Figure 9 – Experimental and predicted concentration profiles of hydroquinone (HQ) and resorcinol (RS) by using the set of adjusted parameters when the trust-region-reflective algorithm was employed.

Figure 10 – Experimental and predicted concentration profiles of phenol (PH) and catechol (CT) by using the set of adjusted parameters when the PSO method was employed.

Figure 11 – Experimental and predicted concentration profiles of hydroquinone (HQ) and resorcinol (RS) by using the set of adjusted parameters when the PSO method was employed.

From these figures, it is possible to conclude that the model with the adjusted parameters by using both optimization algorithms predicts reasonably well the experimental concentrations of PH and its aromatic intermediates. When comparing the objective function values, the lowest value was reached when the trust-region-reflective algorithm was used leading to the best adjust. Table 11 summarizes the RMSE values calculated for each measured variable when simulations considering the set of parameters estimated by using the trust-region-reflective algorithm (see Table 10).

Table 11 – Root mean square error (RMSE) values calculated for the phenol ($RMSE_{[PH]}$) and its aromatic intermediates: catechol ($RMSE_{[CT]}$), hydroquinone ($RMSE_{[HQ]}$) and resorcinol ($RMSE_{[RS]}$).

RMSE	Values
$RMSE_{[PH]}$	2.77×10^{-4}
$RMSE_{[CT]}$	2.52×10^{-4}
$RMSE_{[HQ]}$	1.85×10^{-5}
$RMSE_{[RS]}$	1.54×10^{-4}

4.2. Partial conclusions

- The proposed computational tool was applied to the treatment of phenol by electro-Fenton process. It was validated by using real process data.
- The kinetic parameters of the degradation model were estimated by using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab[®] function and the particle swarm optimization method considering three different population sizes (30, 45, and 60).
- When the particle swarm optimization method was used, the lowest value of the objective function was equal to 1.291745 and was achieved when 60 particles were considered. The value of the objective function by employing the trust-region-reflective algorithm was equal to 0.833101. This value was less than the lowest value achieved by using the particle swarm optimization method. Therefore, a better fit of the experimental concentrations of phenol and its aromatic intermediates was obtained.
- The results of the process simulations illustrated that the model with the adjusted parameters was able to predict relatively well the experimental concentrations of phenol (PH) and its aromatic intermediates: catechol (CT), hydroquinone (HQ) and resorcinol (RS).

Chapter 5. Second case study: treatment of ciprofloxacin in aqueous solution by ozonation process

This chapter presents the application of the previously presented methodology to the treatment of ciprofloxacin (CIP) in aqueous solution by ozonation process (BARDAUIL, 2012).

The antibiotic CIP (molecular formula: $C_{17}H_{18}FN_3O_3$) presents a low biodegradability (AL-AHMAD; DASCHNER; KÜMMERER, 1999; DEWITTE et al., 2008; GUO et al., 2013; VASCONCELOS et al., 2009a). CIP has been frequently detected in effluents from wastewater treatment plants, from pharmaceutical manufacturing plants and hospital effluents (DE WITTE et al., 2009; DEWITTE et al., 2008; DORIVAL-GARCÍA et al., 2013; LIU et al., 2012; VASCONCELOS et al., 2009b).

Various papers have been published concerning the CIP degradation by AOPs in general (AN et al., 2010a; LESTER et al., 2011; MONDAL; SAHA; SINHA, 2018; PEREIRA et al., 2007; VASCONCELOS et al., 2009a; YUAN et al., 2011 GUO et al., 2013; OU et al., 2016) and ozonation process in particular (DE WITTE et al., 2010; DEWITTE et al., 2008; DODD; BUFFLE; VON GUNTEN, 2006; LIU; NANABOINA; KORSHIN, 2012; VASCONCELOS et al., 2009b). In some of these works, the pathways of degradation were studied, some of the intermediate compounds were qualitatively identified and also the kinetics of ozone and hydroxyl radical reactions with CIP was measured. Values of the second-order reaction rates of the reactions of ozone (k_{O_3}) and hydroxyl radical ($k_{HO^\bullet}$) with CIP are summarized in Table 12.

The studied system and the available experimental data are presented in the next sections.

Table 12 – Second-order reaction rate constants for the ozone (k_{O_3}) and hydroxyl radical ($k_{HO^\bullet}$) reactions with ciprofloxacin.

Process	k_{O_3} ($\text{mol}^{-1} \text{ L s}^{-1}$)	$k_{HO^\bullet}$ ($\text{mol}^{-1} \text{ L s}^{-1}$)	Reference
O_3	1.9×10^4	4.1×10^9	(DODD; BUFFLE; VON GUNTEN, 2006)
UV and UV/ H_2O_2		6.22×10^9	(PEREIRA et al., 2007)
Pulse radiation and photocatalytic experiments		$(2.15 \pm 0.10) \times 10^{10}$	(AN et al., 2010b)
UV/ H_2O_2	2.2×10^4	5.0×10^9	(LESTER et al., 2011)
UV/ H_2O_2		7.5×10^9	(YUAN et al., 2011)
UV/ H_2O_2		$(5.94 \pm 1.72) \times 10^9$	(WOLS; HOFMAN-CARIS, 2012)

5.1. Description of the system

In the current work, experiments of the CIP degradation in aqueous solution by ozonation process are considered. All the ozonation experiments were performed by Bardaui (2012) in an experimental set-up mounted by the Research Group in Advanced Oxidation Processes (AdOx), Department of Chemical Engineering at Polytechnic School of the University of São Paulo. Figure 12 shows a schematic representation of the set-up. The system is mainly composed of a bubble column reactor, a mixing tank, a mechanical stirrer, an ozone generator, an oxygen cylinder, and a spectrophotometer. The total volume of aqueous solution of CIP in the system was equal to 6 L. The column and mixing tank volumes were equal to 3.8 L and 1 L, respectively. Therefore, in tubes and connections, there was 1.2 L of aqueous solution. In the column, the liquid flow was descendent and a gas mixture of O_2 and O_3 was continuously supplied by the bottom. The pH value was adjusted at the beginning of each experiment and manually controlled remaining constant during the reaction time. The system temperature was kept constant at 25 °C. In all the experiments the volumetric flow rates in gas and liquid phases were constant.

Figure 12 – Schematic representation of the experimental set-up. SP: sampling point and M: mechanical stirrer (modified from Bardauli (2012)).

5.2. Available experimental data

The ozonation experiments were performed with the system operating in closed loop mode operation. These experiments were carried out following a Doehlert experimental design where the ozone concentration in the gas phase at the column inlet ($[O_3]_{G_{inlet}}$), the pH and the initial concentration of CIP ($[CIP]_0$) were the independent variables. CIP removal at two minutes and the total organic carbon (TOC) removal at 30 minutes of experiment were the dependent variables. All the experimental conditions are displayed in Table 13.

The ozone concentration in the gas phase at the column outlet (top of the column, see Figure 12) was measured by the spectrophotometer. Samples of aqueous solution, at different time intervals (0, 2, 4, 6, 8, 10, 15, 20, 25 and 30 minutes), were taken at the column outlet (bottom of the column, see Figure 12) and concentrations of CIP and TOC ($[CIP]$ and $[TOC]$) were determined by using High-performance liquid chromatography (HPLC) and a TOC Analyzer, respectively. Hence, the available experimental data comprise measurements of concentrations of CIP, TOC, and ozone in the gas phase leaving the column at each sampling time. In the current thesis, it was used data of nine ozonation experiments (experiments 1, 2, 4, 5, 6, 8, 9, 12 and 13, see Table 13).

Table 13 – Experimental conditions of the ozonation experiments (modified from Bardauil (2012)).

Experiment	$[O_3]_{G_{inlet}}$ (mgO ₃ /L)	pH	$[CIP]_0$ (mg/L)
1	17.1	7.0	15.6
2	24.9	7.0	15.8
3	22.4	10.5	15.2
4	23.3	8.2	25.9
5	8.0	7.0	15.7
6	13.9	3.5	15.7
7	14.2	5.8	5.3
8	22.3	3.4	16.5
9	22.5	5.7	5.0
10	17.2	9.3	5.0
11	14.1	10.5	15.6
12	14.3	8.4	24.9
13	16.2	4.7	25.8

A more detailed description of the experimental procedure can be found in Bardauil (2012).

5.3. Results and discussion

5.3.1. Modeling

For the particular case study, it is supposed that the reaction medium is saturated with O₂ and the water concentration ([H₂O]) is constant. In agreement with the experimental conditions (BARDAUIL, 2012), the system is considered isothermal and the gas phase in the column is supposed as composed of ozone diluted in oxygen. Concentrations of H⁺ and OH⁻ ([H⁺] and [OH⁻]) are constant since the pH value remains constant during each experiment. The column volume (V_{co}) is equal to 3.8 L and the mixing tank volume (V_{mt}) is assumed to be equal to 2.2 L. This later volume includes the volume of aqueous solution in tubes and connections. Constant volumetric flow rates in gas and liquid phases are equal to 0.033 L/s and 0.028 L/s, respectively.

The reaction mechanism is established by considering the CIP ozonation in aqueous solution at acidic to neutral and basic conditions based on the experimental conditions (see Table 13).

As aforementioned in Section 2.1.1, in the ozonation process, the organic compound can be oxidized by molecular O_3 , $HO^\bullet$ or a combination of both oxidants. Hence, the mechanism involved in the CIP ozonation is composed of the ozone decomposition reactions in water for acidic to neutral and basic conditions (see Table 14) and the second order reactions of O_3 and $HO^\bullet$ with CIP and its intermediate compounds (VON GUNTEN, 2003). These later reactions are considered according to a proposed scheme that takes into account the decrease of carbon atoms until the formation of the species with four carbon atoms ($C_4H_5FN_3O_3$) (see Table 15). The equilibrium reactions were treated as two different reactions, one forward and the other one backward.

With the reaction mechanism established, it was proceeded to identify and number the species (see Table 16). There are 23 species in the liquid phase ($p = 23$) that undergo 48 chemical reactions ($n = 48$) in the same phase and O_3 is the only species in the gas phase. Afterward, the stoichiometry matrix ($\nu_{(23 \times 48)}$ matrix) and the matrix of partial orders of the reactions ($\alpha_{(48 \times 23)}$ matrix) are constructed. These matrices are listed in Appendixes F and G.

The model is formulated from equations listed in Section 3.1.2 by using the information of ν and α matrices. The ozone mass transfer from gas to the liquid phase is considered. Then, the ozone absorption rate is calculated by means of Equation 23. The dimensional Henry's law constant He in $\text{atm}(\text{mole fraction})^{-1}$ is calculated by using the Roth and Sullivan correlation (Equation 49) (see Table 4) (ROTH; SULLIVAN, 1981).

$$He = 3.84 \times 10^7 [OH^-]^{0.035} \exp\left(\frac{-2428}{T}\right) \quad (49)$$

being $[OH^-]$ the hydroxide ion concentration in mol L^{-1} and T the temperature in K.

The He in $\text{atm}(\text{mole fraction})^{-1}$ is converted to atm L mol^{-1} by dividing its value by the constant water concentration ($[\text{H}_2\text{O}] = 55.5 \text{ mol L}^{-1}$) (SANDER, 2015).

$$[c_{O_3}]_G = x \frac{\rho_{H_2O}}{M_{H_2O}} \quad (50)$$

$$[c_{O_3}]_G = 55.5x \quad (51)$$

$$He(\text{atm L mol}^{-1}) = He(\text{atm/mole fraction})/55.5 \quad (52)$$

where x , ρ_{H_2O} , and M_{H_2O} are the mole fraction (dimensionless), the water density (1000 kg/m^3) and the molar mass of the water (18.01528 g/mol), respectively.

Table 14 – Ozone decomposition reactions in water for acidic to neutral and basic conditions (modified from Lovato et al., (2009)).

Reaction	Rate constant	Unit
$O_3 + OH^- \xrightarrow{k_1} HO_2^- + O_2$	70	$\text{mol}^{-1} \text{ L s}^{-1}$
$O_3 + HO_2^- \xrightarrow{k_2} HO_2^\bullet + O_3^{\bullet-}$	2.20×10^6	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO_2^\bullet \xrightarrow{k_3} O_2^{\bullet-} + H^+$	7.90×10^5	s^{-1}
$O_2^{\bullet-} + H^+ \xrightarrow{k_4} HO_2^\bullet$	5.00×10^{10}	$\text{mol}^{-1} \text{ L s}^{-1}$
$O_3 + O_2^{\bullet-} \xrightarrow{k_5} O_3^{\bullet-} + O_2$	1.60×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$
$O_3^{\bullet-} + H^+ \xrightarrow{k_6} HO_3^\bullet$	5.20×10^{10}	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO_3^\bullet \xrightarrow{k_7} O_3^{\bullet-} + H^+$	$(3.7 \pm 0.3) \times 10^4$	s^{-1}
$HO_3^\bullet \xrightarrow{k_8} HO^\bullet + O_2$	1.01×10^5	s^{-1}
$O_3 + HO^\bullet \xrightarrow{k_9} HO_4^\bullet$	2.00×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO_4^\bullet \xrightarrow{k_{10}} HO_2^\bullet + O_2$	2.80×10^4	s^{-1}
$HO_2^- + H^+ \xrightarrow{k_{11}} H_2O_2$	5.00×10^{10}	$\text{mol}^{-1} \text{ L s}^{-1}$
$H_2O_2 \xrightarrow{k_{12}} HO_2^- + H^+$	0.125	s^{-1}
$HO_4^\bullet + HO_4^\bullet \xrightarrow{k_{13}} H_2O_2 + 2O_3$	5.00×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO_4^\bullet + HO_3^\bullet \xrightarrow{k_{14}} H_2O_2 + O_2 + O_3$	5.00×10^9	$\text{mol}^{-1} \text{ L s}^{-1}$
$HO^\bullet + H_2O_2 \xrightarrow{k_{15}} HO_2^\bullet + H_2O$	2.70×10^7	$\text{mol}^{-1} \text{ L s}^{-1}$

Table 14 (continued)

Reaction	Rate constant	Unit
$HO^\bullet + HO_2^- \xrightarrow{k_{16}} HO_2^\bullet + OH^-$	7.50×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO^\bullet + HO^\bullet \xrightarrow{k_{17}} H_2O_2$	5.20×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO_2^\bullet + HO_2^\bullet \xrightarrow{k_{18}} H_2O_2 + O_2$	8.30×10^5	$\text{mol}^{-1} \text{L s}^{-1}$
$O_3^{\bullet-} + H_2O \xrightarrow{k_{19}} HO^\bullet + O_2 + OH^-$	$(20 - 30)$	$\text{mol}^{-1} \text{L s}^{-1}$
$O_3^{\bullet-} + HO^\bullet \xrightarrow{k_{20}} HO_2^\bullet + O_2^{\bullet-}$	6×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$HO^\bullet + O_3 \xrightarrow{k_{21}} HO_2^\bullet + O_2$	3.00×10^9	$\text{mol}^{-1} \text{L s}^{-1}$
$O_3^{\bullet-} + HO^\bullet \xrightarrow{k_{22}} O_3 + OH^-$	2.50×10^9	$\text{mol}^{-1} \text{L s}^{-1}$

Table 15 – Second order reactions of ozone and hydroxyl radical with ciprofloxacin and its intermediate compounds until the formation of the species with four carbon atoms.

Reactions
$C_{17}H_{18}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{23}} C_{16}H_{17}FN_3O_3 + CO_2 + H_2O$
$C_{17}H_{18}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{24}} C_{16}H_{17}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_{16}H_{17}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{25}} C_{15}H_{16}FN_3O_3 + CO_2 + H_2O$
$C_{16}H_{17}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{26}} C_{15}H_{16}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_{15}H_{16}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{27}} C_{14}H_{15}FN_3O_3 + CO_2 + H_2O$
$C_{15}H_{16}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{28}} C_{14}H_{15}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_{14}H_{15}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{29}} C_{13}H_{14}FN_3O_3 + CO_2 + H_2O$
$C_{14}H_{15}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{30}} C_{13}H_{14}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_{13}H_{14}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{31}} C_{12}H_{13}FN_3O_3 + CO_2 + H_2O$
$C_{13}H_{14}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{32}} C_{12}H_{13}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_{12}H_{13}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{33}} C_{11}H_{12}FN_3O_3 + CO_2 + H_2O$
$C_{12}H_{13}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{34}} C_{11}H_{12}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_{11}H_{12}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{35}} C_{10}H_{11}FN_3O_3 + CO_2 + H_2O$
$C_{11}H_{12}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{36}} C_{10}H_{11}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$

Table 15 (continued)

Reactions
$C_{10}H_{11}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{37}} C_9H_{10}FN_3O_3 + CO_2 + H_2O$
$C_{10}H_{11}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{38}} C_9H_{10}FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_9H_{10}FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{39}} C_8H_9FN_3O_3 + CO_2 + H_2O$
$C_9H_{10}FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{40}} C_8H_9FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_8H_9FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{41}} C_7H_8FN_3O_3 + CO_2 + H_2O$
$C_8H_9FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{42}} C_7H_8FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_7H_8FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{43}} C_6H_7FN_3O_3 + CO_2 + H_2O$
$C_7H_8FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{44}} C_6H_7FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_6H_7FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{45}} C_5H_6FN_3O_3 + CO_2 + H_2O$
$C_6H_7FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{46}} C_5H_6FN_3O_3 + CO_2 + \frac{1}{2}H_2O$
$C_5H_6FN_3O_3 + O_2 + HO^\bullet \xrightarrow{k_{47}} C_4H_5FN_3O_3 + CO_2 + H_2O$
$C_5H_6FN_3O_3 + \frac{10}{12}O_3 \xrightarrow{k_{48}} C_4H_5FN_3O_3 + CO_2 + \frac{1}{2}H_2O$

Table 16 – Numbered species according to the reaction mechanism.

Species in the liquid phase	Species in the gas phase
$[O_3] = c_{1L}$	$[O_3]_G = c_{1G}$
$[HO_2^-] = c_{2L}$	
$[HO_2^\bullet] = c_{3L}$	
$[O_3^{\bullet-}] = c_{4L}$	
$[O_2^{\bullet-}] = c_{5L}$	
$[HO_3^\bullet] = c_{6L}$	
$[HO^\bullet] = c_{7L}$	
$[HO_4^\bullet] = c_{8L}$	
$[H_2O_2] = c_{9L}$	
$[C_{17}H_{18}FN_3O_3] = [CIP] = c_{10L}$	
$[C_{16}H_{17}FN_3O_3] = c_{11L}$	

Table 16 (continued)

Species in the liquid phase	Species in the gas phase
$[C_{15}H_{16}FN_3O_3]$	$= c_{12L}$
$[C_{14}H_{15}FN_3O_3]$	$= c_{13L}$
$[C_{13}H_{14}FN_3O_3]$	$= c_{14L}$
$[C_{12}H_{13}FN_3O_3]$	$= c_{15L}$
$[C_{11}H_{12}FN_3O_3]$	$= c_{16L}$
$[C_{10}H_{11}FN_3O_3]$	$= c_{17L}$
$[C_9H_{10}FN_3O_3]$	$= c_{18L}$
$[C_8H_9FN_3O_3]$	$= c_{19L}$
$[C_7H_8FN_3O_3]$	$= c_{20L}$
$[C_6H_7FN_3O_3]$	$= c_{21L}$
$[C_5H_6FN_3O_3]$	$= c_{22L}$
$[C_4H_5FN_3O_3]$	$= c_{23L}$

New kinetic constants (k'_1 , k'_4 , k'_6 , k'_{11} , and k'_{19}) are defined for the second order reactions involving $[H^+]$, $[OH^-]$ and $[H_2O]$ as reactants (reactions 1, 4, 6, 11, and 19, see Table 14). These reactions are first order with respect to each reactant and according to the experimental conditions and model hypotheses, $[H^+]$, $[OH^-]$ and $[H_2O]$ are constant. The $[H^+]$ and $[OH^-]$ in mol L^{-1} are expressed by Equations 55 and 56, respectively. The water concentration was equal to 55.5 mol L^{-1} .

$$pH = -\log([H^+]) \quad (53)$$

$$pH + pOH = 14 \quad (54)$$

$$[H^+] = 10^{(-pH)} \quad (55)$$

$$[OH^-] = 10^{(pH-14)} \quad (56)$$

Then, the kinetic constants are given by the following equations:

$$k'_1 = k_1 [OH^-] = k_1 10^{(pH-14)} \quad (57)$$

$$k'_4 = k_4 [H^+] = k_4 10^{-pH} \quad (58)$$

$$k'_6 = k_6 [H^+] = k_6 10^{-pH} \quad (59)$$

$$k'_{11} = k_{11}[H^+] = k_{11} 10^{-pH} \quad (60)$$

$$k'_{19} = k_{19} [H_2O] \quad (61)$$

When defining these new kinetic constants the reaction rates are given by the following equations:

$$r'_1 = k'_1 [O_3] \quad (62)$$

$$r'_4 = k'_4 [O_2^{\bullet-}] \quad (63)$$

$$r'_6 = k'_6 [O_3^{\bullet-}] \quad (64)$$

$$r'_{11} = k'_{11} [HO_2^-] \quad (65)$$

$$r'_{19} = k'_{19} [O_3^{\bullet-}] \quad (66)$$

It is necessary to highlight that the proposed model is general thus, changes in $[H^+]$, $[OH^-]$ and $[H_2O]$ values during the reaction time could be considered.

Initial concentrations of CIP are given by the experimental data. For the remaining species in both phases (see Table 16), the initial concentrations are assumed equal to zero. Table 17 summarizes the main characteristics of the model when different values of q are considered. The state variables are the species concentrations in each tank that composes the system.

Table 17 – Main characteristics of the model when the computational tool was applied to the treatment of ciprofloxacin by ozonation process considering different numbers of tanks representing the system (q).

Characteristics	$q = 2$	$q = 3$	$q = 4$
Number of ODEs	47	71	95
Number of state variables	47	71	95

5.3.2. Parameter estimation and process simulations

The optimization problems are formulated according to Equations 29 and 30. In a first approach, experimental and predicted concentrations of CIP and TOC are considered in the objective function (OF_1 , Equation 67). In a second moment, experimental and predicted concentrations of ozone in the gas phase are also accounted for in the objective function (OF_2 , Equation 68).

It is worth noting that the TOC concentration is not an estate variable of the model. However, the model is capable to predict the TOC removal. Its predicted concentration at each sampling time is determined as the sum of the TOC concentration of each organic compound (see Table 15), which is calculated multiplying its concentration by its respective number of carbon atoms. Besides, for each experiment, the initial TOC concentration is calculated from the initial concentration of CIP. The calculated value was compared to the measured one and differences were found. Hence, a correction factor for each experiment was determined by dividing the calculated value by the measured one. Finally, the experimental values of TOC concentrations were affected by the correction factor (see Appendix H).

$$\min_{\theta'} OF_1 = \sum_{i=1}^{n_{exp}} \left[\left(\frac{[CIP]_{exp_i} - [CIP]_{pred_i}(\theta')}{MV_{[CIP]_{exp_i}}} \right)^2 + \left(\frac{[TOC]_{exp_i} - [TOC]_{pred_i}(\theta')}{MV_{[TOC]_{exp_i}}} \right)^2 \right] \quad (67)$$

subject to: $lb \leq \theta' \leq ub$

$$\min_{\theta'} OF_2 = \sum_{i=1}^{n_{exp}} \left[\left(\frac{[CIP]_{exp_i} - [CIP]_{pred_i}(\theta')}{MV_{[CIP]_{exp_i}}} \right)^2 + \left(\frac{[TOC]_{exp_i} - [TOC]_{pred_i}(\theta')}{MV_{[TOC]_{exp_i}}} \right)^2 + \left(\frac{[O_3]_{G_{exp_i}} - [O_3]_{G_{pred_i}}(\theta')}{MV_{[O_3]_{G_{exp_i}}}} \right)^2 \right] \quad (68)$$

subject to: $lb \leq \theta' \leq ub$

in which $[CIP]_{exp_i}$, $[TOC]_{exp_i}$, and $[O_3]_{G_{exp_i}}$ are the experimental concentrations of CIP, TOC and ozone in the gas phase for the i^{th} experiment, respectively. $[CIP]_{pred_i}$, $[TOC]_{pred_i}$, and $[O_3]_{G_{pred_i}}$ are the predicted concentrations of CIP, TOC and ozone in the gas phase for the i^{th} experiment, correspondingly. $MV_{[CIP]_{exp_i}}$, $MV_{[TOC]_{exp_i}}$, and $MV_{[O_3]_{G_{exp_i}}}$ represent the maximum experimental

values of concentrations of CIP, TOC and ozone in the gas phase for the j^{th} experiment, respectively.

It is worthwhile to remember that all the experimental data were measured at the column outlet (see Figure 12). This means, top and bottom of the column for gas and liquid phases, respectively. Therefore, all the predicted concentrations in OF_1 and OF_2 corresponded to the column outlet as well.

The parameter estimation is followed by simulations taking into account all the experimental conditions. Desktop computers with CORE i5-2400 processors, 3.10 GHz and 8 GB of RAM are used. In all cases, the computation time is determined by the *tic* and *toc* Matlab® function.

Parameter estimation by using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab® function

The model parameters are estimated from experimental data. Firstly, the parameters: $k_L a$, β and kinetic constants corresponding to the reactions of O_3 and $HO^\bullet$ with CIP and its intermediate compounds (reactions in Table 15) are estimated. The kinetic constants of the radical formation mechanism are fixed at their reported values in the literature (reactions and kinetic constant values in Table 14). In this case, 28 parameters were estimated (θ'_1 , Equation 69). Secondly, estimates of all the model parameters ($k_L a$, β and kinetic constants of reactions in Tables 14 and 15) are obtained. A total of 50 parameters are estimated (θ'_2 , Equation 70).

$$\theta'_1 = \begin{bmatrix} k_L a \\ \beta \\ \ln(k_l) \end{bmatrix} \quad l = 23, \dots, 48 \quad (69)$$

$$\theta'_2 = \begin{bmatrix} k_L a \\ \beta \\ \ln(k_l) \end{bmatrix} \quad l = 1, \dots, 48 \quad (70)$$

Both sets of parameters: θ'_1 and θ'_2 are estimated by using both objective functions (Equations 67 and 68) and the three different values of q listed in Table 17. As a result, 12 optimization problems are formulated and solved by using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab®

function. In each case, the system of ODEs describing the process along with the sensitivity equations are solved by using CVODES solver according to the proceeding described in Section 3.2.1.1.

In order to generate the sensitivity equations, the general Jacobian matrix of the model as well as the derivatives of the right-hand side of the model differential equations with respect to the parameters (see Appendixes A and B) are applied to the case study. In all cases, the analytical Jacobian matrix is validated by its comparison with the numerical one computed by forward finite differences. In the comparison process, nominal values of the model parameters (initial guesses for the parameters when θ'_2 is estimated, see Tables 18 and 21) and a feasible value of the species concentrations (1×10^{-3} mol L⁻¹) are used.

Consequently, concentrations of species in both phases and their sensitivity coefficients with respect to the model parameters are obtained. Sensitivity matrices of the concentrations of CIP, TOC, and ozone in the gas phase are used to compute the analytical Jacobian matrices of the residuals correspondent to OF_1 and OF_2 ($Jac_{\theta'} R_1$ and $Jac_{\theta'} R_2$ matrices, Equations 71 and 72). Their validity was checked by using the DerivativeCheck Matlab[®] function.

The initial guesses for parameters are established according to values reported in the literature (see Table 11 for the kinetic constants). In addition, lower and upper bounds are defined (see Appendix I) (GOTTSCALK; LIBRA; SAUPE, 2000; JIN; PELDSZUS; HUCK, 2012; RIVERA-UTRILLA et al., 2013). The stopping criteria were that relative changes of the objective function or the step size values between two consecutive iterations are less or equal than a tolerance value equal to 10^{-6} . It is also used the maximum number of iterations as a stopping criterion.

$$Jac_{\theta'} R_1 = \begin{bmatrix} -MV_{[CIP]_{exp_i}}^{-1} \frac{\partial ([CIP]_{pred_i}(\theta'))}{\partial \theta'} \\ -MV_{[TOC]_{exp_i}}^{-1} \frac{\partial ([TOC]_{pred_i}(\theta'))}{\partial \theta'} \end{bmatrix} \quad (71)$$

$$Jac_{\theta'} R_2 = \begin{bmatrix} -MV_{[CIP]_{exp_i}}^{-1} \frac{\partial ([CIP]_{pred_i}(\theta'))}{\partial \theta'} \\ -MV_{[TOC]_{exp_i}}^{-1} \frac{\partial ([TOC]_{pred_i}(\theta'))}{\partial \theta'} \\ -MV_{[O_3]_{G_{exp_i}}}^{-1} \frac{\partial ([O_3]_{G_{pred_i}}(\theta'))}{\partial \theta'} \end{bmatrix} \quad (72)$$

$\partial[CIP]_{pred_i}/\partial\theta'$, $\partial[TOC]_{pred_i}/\partial\theta'$, and $\partial[O_3]_{G_{pred_i}}/\partial\theta'$ are the sensitivity coefficients of the predicted concentrations of CIP, TOC and ozone in the gas phase with respect to the model parameters θ' .

Estimates of θ'_1 using both objective functions are summarized in Tables 18 and 19. It can be seen from Table 18 that the lowest value of the OF_1 was obtained for q equal to three. On the other hand, the lowest value of the OF_2 was attained when four tanks for representing the system are considered. The estimated values of k_La and β by using OF_1 are in the order of reported values in the literature (BELTRÁN et al., 2000; BELTRÁN; AGUINACO; GARCÍA-ARAYA, 2010). When the estimated values of k_La by using OF_1 are compared to the values estimated by using OF_2 , an increase is observed probably due to an attempt to adjust the ozone concentration in the gas phase. Estimates of the kinetic constants of the reactions of CIP with ozone and hydroxyl radical were also in the order of reported values in literature (see Table 11). Regarding to the estimated values of the kinetic constants of the reactions of the intermediate compounds with the two oxidant species is valid to say that there are no values of these constants reported in the literature. Therefore, it was difficult to establish an interval for them.

Once the sets of θ'_1 were estimated, simulations are performed. Figures 13 to 21 illustrate the concentration profiles of CIP, TOC and ozone in the gas phase by using the set of parameters listed in Table 18 for which OF_1 achieved the lowest value. In these figures, it is also shown the comparison of the predicted concentrations to the experimental data. The predicted concentrations profiles for the remaining species (see Table 16) in the liquid phase at the column are also available.

Table 18 – Adjusted parameters (θ'_1) by considering experimental and predicted concentrations of CIP and TOC in the objective function (OF_1) by using the trust-region-reflective algorithm. q : number of tanks representing the system.

Parameter	Unit	Initial guesses	Estimated values		
			q = 2	q = 3	q = 4
$k_L a$	s^{-1}	0.75×10^{-2}	1.72×10^{-2}	1.45×10^{-2}	1.38×10^{-2}
β	Dimensionless	0.85	0.99	0.99	0.99
k_{23}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.01×10^9	2.22×10^{10}	2.25×10^{10}
k_{24}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^4	1.00×10^4	1.00×10^4
k_{25}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	2.30×10^6	1.17×10^6
k_{26}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.24×10^4	1.50×10^4	1.49×10^4
k_{27}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.01×10^6	1.83×10^6	1.06×10^6
k_{28}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.95×10^4	2.10×10^4	2.29×10^4
k_{29}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.02×10^6	1.37×10^6	1.05×10^8
k_{30}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	6.93×10^1	7.09×10^1	6.96×10^1
k_{31}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.02×10^6	1.02×10^6	7.81×10^6
k_{32}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	5.31×10^2	5.74×10^2	1.15×10^3
k_{33}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.07×10^6	1.03×10^6	6.44×10^6
k_{34}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.06×10^3	1.14×10^3	7.46×10^2
k_{35}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.16×10^6	1.06×10^6	1.55×10^6
k_{36}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	2.71×10^3	6.13×10^3	1.93×10^2
k_{37}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
k_{38}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.01×10^{-1}	1.00×10^{-1}	1.0×10^{-1}
k_{39}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.01×10^6	1.09×10^6	5.00×10^6
k_{40}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	6.63×10^6	8.72×10^6	7.08×10^5
k_{41}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.10×10^6	1.00×10^6	5.28×10^6
k_{42}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	5.82×10^6	7.96×10^6	1.61×10^5
k_{43}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.02×10^6	1.01×10^6	1.01×10^6
k_{44}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	5.08×10^6	7.69×10^6	1.27×10^5
k_{45}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.02×10^6	1.01×10^6	1.00×10^6
k_{46}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	3.87×10^6	6.68×10^6	1.45×10^4
k_{47}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.02×10^6	1.01×10^6	1.17×10^6
k_{48}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	2.60×10^6	5.71×10^6	3.23×10^3
OF ₁ value			0.539912	0.533293	0.534946
Computation time	h		1.24	2.02	1.85

Table 19 – Adjusted parameters (θ'_1) by considering experimental and predicted concentrations of CIP, TOC and ozone in the gas phase in the objective function (OF_2) by using the trust-region-reflective algorithm. q : number of tanks representing the system.

Parameter	Unit	Initial guesses	Estimated values		
			q = 2	q = 3	q = 4
$k_L a$	s^{-1}	0.75×10^{-2}	2.55×10^{-1}	1.43×10^{-1}	1.22×10^{-1}
β	Dimensionless	0.85	0.99	0.99	0.99
k_{23}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^9	1.00×10^9	1.00×10^9
k_{24}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	4.62×10^4	1.00×10^4	1.00×10^4
k_{25}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{26}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	6.34×10^2	5.41×10^2	1.76×10^2
k_{27}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{28}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.80×10^3	1.35×10^3	3.06×10^3
k_{29}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{30}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	6.88×10^3	1.29×10^4	1.09×10^4
k_{31}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{32}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^7	4.91×10^6	1.94×10^4
k_{33}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{34}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.06×10^2	7.32×10^1	3.78×10^4
k_{35}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{36}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	9.85×10^6	9.53×10^6	3.04×10^6
k_{37}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{38}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^7	9.82×10^6	9.94×10^6
k_{39}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{40}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	9.99×10^6	9.97×10^6	1.00×10^7
k_{41}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{42}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^7	9.99×10^6	4.31×10^1
k_{43}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{44}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^7	1.00×10^7	1.00×10^7
k_{45}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{46}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^7	1.00×10^7	1.00×10^7
k_{47}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{48}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^7	1.00×10^7	1.00×10^7
OF_2 value			17.1117	16.8801	16.8297
Computation time	h		1.40	1.04	1.96

Figure 13 – Concentration profiles of ciprofloxacin (CIP) for the experiments 1 to 4. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 14 – Concentration profiles of ciprofloxacin (CIP) for experiments 4 to 8. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 15 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 16 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 17 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 18 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 19 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 20 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 21 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_1 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

As can be noticed from these figures, the model with θ'_1 estimated by using OF_1 predicts reasonably well the experimental concentrations of CIP and TOC. However, it is not capable to predict adequately the ozone concentrations in the gas phase. Predicted ozone concentrations are, in all cases, higher than the experimental values. It is necessary to mention that this concentration was not accounted for in the objective function (OF_1). A better fit for this variable when considered in the objective function (OF_2) is expected.

Table 20 reports the RMSE values for the concentrations of CIP, TOC, and ozone in the gas phase.

Table 20 – Root mean square error values for concentrations of ciprofloxacin ($RMSE_{[CIP]}$), total organic carbon ($RMSE_{[TOC]}$) and ozone in the gas phase ($RMSE_{[O_3]_G}$).

Experiment	$RMSE_{[CIP]}$	$RMSE_{[TOC]}$	$RMSE_{[O_3]_G}$
1	1.91×10^{-6}	3.14×10^{-5}	1.60×10^{-4}
2	1.16×10^{-6}	9.96×10^{-5}	1.78×10^{-4}
3	4.69×10^{-6}	7.98×10^{-5}	2.62×10^{-4}
4	3.37×10^{-6}	3.68×10^{-5}	8.09×10^{-5}
5	1.93×10^{-6}	5.11×10^{-5}	1.42×10^{-4}
6	1.53×10^{-6}	3.11×10^{-5}	1.42×10^{-4}
7	2.77×10^{-8}	3.07×10^{-5}	8.42×10^{-5}
8	2.65×10^{-6}	3.86×10^{-5}	1.35×10^{-4}
9	1.89×10^{-6}	1.21×10^{-4}	1.07×10^{-4}

The small RMSE values obtained for CIP and TOC concentrations reflect the ability of the model with the adjusted parameters to adequately predict these experimental concentrations.

Below are depicted the results of the simulations with θ_1' estimated by using OF_2 and $q = 4$ (see Table 19) that was the case with the lowest value of the objective function. Figures 22 to 30 show the predicted concentration profiles of CIP, TOC and ozone in the gas phase compared to the experimental data.

Figure 22 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ_1' adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 23 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ_1' adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 24 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 25 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 26 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 27 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 28 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 29 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 30 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_1 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

From these figures, it can be concluded that in fact there is an attempt to adjust the ozone concentration in the gas phase, however, the adjustments of CIP and TOC concentrations worsen.

Later, it is proceeded to estimate all the kinetic constants of the reaction mechanism along with $k_L a$ and β (θ'_2). As mentioned before, these parameters are estimated using OF_1 and OF_2 and the three different values of q . When estimating θ'_2 , the initial guesses of the kinetic constants correspondent to the radical formation mechanism are the reported values in the literature (see Table 14).

Estimates of θ'_2 are listed in Tables 21 and 22. The values of OF_1 decrease with the increment of the number of tanks. On the other hand, the lowest value of OF_2 was reached for q equal to three.

When the estimates of θ'_2 , considering and neglecting the ozone concentration in the gas phase in the objective function are compared, an increase in the estimated values of $k_L a$ is observed probably due to an attempt to adjust the experimental concentration of ozone in the gas phase.

Table 21 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of CIP and TOC in the objective function (OF_1) by using the trust-region-reflective algorithm. q : number of tanks representing the system.

Parameter	Unit	Initial guesses	Estimated values		
			$q = 2$	$q = 3$	$q = 4$
$k_L a$	s^{-1}	0.75×10^{-2}	1.51×10^{-2}	1.32×10^{-2}	1.27×10^{-2}
β	Dimensionless	0.85	0.99	0.99	0.99
k_1	$\text{mol}^{-1} \text{ L s}^{-1}$	7.00×10^1	8.00×10^1	8.00×10^1	7.99×10^1
k_2	$\text{mol}^{-1} \text{ L s}^{-1}$	2.20×10^6	1.51×10^6	2.91×10^6	1.63×10^6
k_3	s^{-1}	7.90×10^5	7.90×10^5	8.25×10^5	8.00×10^5
k_4	$\text{mol}^{-1} \text{ L s}^{-1}$	5.00×10^{10}	5.00×10^{10}	2.42×10^{10}	4.06×10^{10}
k_5	$\text{mol}^{-1} \text{ L s}^{-1}$	1.60×10^9	1.60×10^9	2.25×10^9	1.76×10^9
k_6	$\text{mol}^{-1} \text{ L s}^{-1}$	5.20×10^{10}	5.20×10^{10}	5.87×10^{10}	5.38×10^{10}
k_7	s^{-1}	3.7×10^4	3.70×10^4	3.64×10^4	3.68×10^4
k_8	s^{-1}	1.01×10^5	1.01×10^5	1.55×10^5	1.14×10^5
k_9	$\text{mol}^{-1} \text{ L s}^{-1}$	2.00×10^9	1.05×10^8	1.33×10^8	1.05×10^8
k_{10}	s^{-1}	2.80×10^4	2.80×10^4	3.55×10^4	3.00×10^4
k_{11}	$\text{mol}^{-1} \text{ L s}^{-1}$	5.00×10^{10}	7.38×10^9	1.25×10^{10}	7.74×10^9
k_{12}	s^{-1}	0.125	0.178	0.165	0.183
k_{13}	$\text{mol}^{-1} \text{ L s}^{-1}$	5.00×10^9	5.00×10^9	2.42×10^9	4.06×10^9
k_{14}	$\text{mol}^{-1} \text{ L s}^{-1}$	5.00×10^9	5.00×10^9	2.42×10^9	4.06×10^9
k_{15}	$\text{mol}^{-1} \text{ L s}^{-1}$	2.70×10^7	2.41×10^7	1.73×10^7	2.29×10^7
k_{16}	$\text{mol}^{-1} \text{ L s}^{-1}$	7.50×10^9	6.37×10^9	3.68×10^9	5.94×10^9
k_{17}	$\text{mol}^{-1} \text{ L s}^{-1}$	5.20×10^9	5.20×10^9	2.49×10^9	4.22×10^9
k_{18}	$\text{mol}^{-1} \text{ L s}^{-1}$	8.30×10^5	8.30×10^5	3.65×10^5	6.57×10^5
k_{19}	$\text{mol}^{-1} \text{ L s}^{-1}$	25	2.50×10^1	2.58×10^1	2.52×10^1
k_{20}	$\text{mol}^{-1} \text{ L s}^{-1}$	6.00×10^9	6.00×10^9	3.06×10^9	4.93×10^9
k_{21}	$\text{mol}^{-1} \text{ L s}^{-1}$	3.00×10^9	1.03×10^8	1.34×10^8	1.05×10^8
k_{22}	$\text{mol}^{-1} \text{ L s}^{-1}$	2.50×10^9	2.49×10^9	1.37×10^9	2.11×10^9
k_{23}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.59×10^9	7.59×10^9	3.80×10^9
k_{24}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^4	1.00×10^4	1.00×10^4
k_{25}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	5.54×10^6	1.87×10^8	1.98×10^7
k_{26}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	3.46×10^3	4.20×10^3	4.51×10^3
k_{27}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.46×10^9	3.57×10^9	3.20×10^9
k_{28}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	5.54×10^6	4.24×10^6	8.22×10^6

Table 21 (continued)

Parameter	Unit	Initial guesses	Estimated values		
			q = 2	q = 3	q = 4
k_{29}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.11×10^9	6.08×10^9	3.40×10^9
k_{30}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	3.82×10^6	2.38×10^6	6.52×10^6
k_{31}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.52×10^6	6.30×10^6	1.81×10^6
k_{32}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	7.80×10^1	7.79×10^1	7.88×10^1
k_{33}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	2.20×10^6	1.91×10^7	3.99×10^6
k_{34}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.32×10^2	1.38×10^2	1.40×10^2
k_{35}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	7.48×10^6	9.85×10^7	4.33×10^7
k_{36}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.55×10^3	1.11×10^4	6.43×10^3
k_{37}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	9.99×10^9	9.98×10^9	9.97×10^9
k_{38}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.00×10^{-1}	1.01×10^{-1}	1.00×10^{-1}
k_{39}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.60×10^9	3.22×10^9	1.71×10^9
k_{40}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	2.43×10^5	3.37×10^4	1.44×10^5
k_{41}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.50×10^9	1.14×10^9	1.62×10^9
k_{42}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	2.09×10^5	2.90×10^4	1.21×10^5
k_{43}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.17×10^9	8.52×10^8	2.01×10^9
k_{44}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.65×10^5	2.35×10^4	3.25×10^5
k_{45}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	1.02×10^9	8.40×10^8	1.31×10^9
k_{46}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	1.27×10^5	1.39×10^4	7.43×10^4
k_{47}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.1×10^9	8.68×10^8	7.64×10^8	9.58×10^8
k_{48}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.9×10^4	8.89×10^4	9.15×10^3	4.45×10^4
OF_1 value			0.556006	0.54907	0.547417
Computation time	h		2.01	1.42	3.59

Table 22 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of CIP, TOC and ozone in the gas phase in the objective function (OF_2) by using the trust-region-reflective algorithm. q : number of tanks representing the system.

Parameter	Unit	Initial guesses	Estimated values		
			q = 2	q = 3	q = 4
$k_L a$	s^{-1}	0.75×10^{-2}	1.50×10^{-1}	1.15×10^{-1}	8.05×10^{-2}
β	Dimensionless	0.85	0.99	0.99	0.99
k_1	$\text{mol}^{-1} \text{ L s}^{-1}$	7.00×10^1	8.00×10^1	8.00×10^1	8.00×10^1
k_2	$\text{mol}^{-1} \text{ L s}^{-1}$	2.20×10^6	1.00×10^7	1.00×10^7	1.00×10^7

Table 22 (continued)

Parameter	Unit	Initial guesses	Estimated values		
			q = 2	q = 3	q = 4
k_3	s ⁻¹	7.90x10 ⁵	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶
k_4	mol ⁻¹ L s ⁻¹	5.00x10 ¹⁰	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹
k_5	mol ⁻¹ L s ⁻¹	1.60x10 ⁹	1.00x10 ¹⁰	1.00E+10	1.00x10 ¹⁰
k_6	mol ⁻¹ L s ⁻¹	5.20x10 ¹⁰	1.00x10 ⁹	4.20x10 ⁹	7.48x10 ¹⁰
k_7	s ⁻¹	3.7x10 ⁴	4.00x10 ⁴	3.81x10 ⁴	3.48x10 ⁴
k_8	s ⁻¹	1.01x10 ⁵	9.36x10 ⁵	4.67x10 ⁵	1.00x10 ⁴
k_9	mol ⁻¹ L s ⁻¹	2.00x10 ⁹	1.00x10 ¹⁰	1.00E+10	1.00x10 ¹⁰
k_{10}	s ⁻¹	2.80x10 ⁴	1.00x10 ⁵	1.52x10 ⁴	1.02x10 ³
k_{11}	mol ⁻¹ L s ⁻¹	5.00x10 ¹⁰	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹
k_{12}	s ⁻¹	0.125	0.250	0.250	0.250
k_{13}	mol ⁻¹ L s ⁻¹	5.00x10 ⁹	9.78x10 ⁸	2.21x10 ⁹	1.60x10 ⁹
k_{14}	mol ⁻¹ L s ⁻¹	5.00x10 ⁹	1.22x10 ⁸	1.00x10 ⁸	1.00x10 ¹⁰
k_{15}	mol ⁻¹ L s ⁻¹	2.70x10 ⁷	1.00x10 ⁸	5.52x10 ⁶	1.00x10 ⁸
k_{16}	mol ⁻¹ L s ⁻¹	7.50x10 ⁹	1.00x10 ⁸	1.00x10 ¹⁰	1.00x10 ⁸
k_{17}	mol ⁻¹ L s ⁻¹	5.20x10 ⁹	1.00x10 ⁸	1.00x10 ⁸	1.00x10 ⁸
k_{18}	mol ⁻¹ L s ⁻¹	8.30x10 ⁵	1.37x10 ⁴	1.42x10 ⁴	1.00x10 ⁴
k_{19}	mol ⁻¹ L s ⁻¹	25	20	20	30
k_{20}	mol ⁻¹ L s ⁻¹	6.00x10 ⁹	1.00x10 ¹⁰	1.00x10 ⁸	1.00x10 ¹⁰
k_{21}	mol ⁻¹ L s ⁻¹	3.00x10 ⁹	1.00x10 ¹⁰	1.00x10 ¹⁰	1.00x10 ¹⁰
k_{22}	mol ⁻¹ L s ⁻¹	2.50x10 ⁹	1.00x10 ¹⁰	9.95x10 ⁹	1.00x10 ⁸
k_{23}	mol ⁻¹ L s ⁻¹	4.1x10 ⁹	1.00x10 ⁹	1.00x10 ⁹	1.00x10 ⁹
k_{24}	mol ⁻¹ L s ⁻¹	1.9x10 ⁴	5.00x10 ⁴	5.00x10 ⁴	5.00x10 ⁴
k_{25}	mol ⁻¹ L s ⁻¹	4.1x10 ⁹	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶
k_{26}	mol ⁻¹ L s ⁻¹	1.9x10 ⁴	7.67x10 ⁶	5.12x10 ²	1.00x10 ⁷
k_{27}	mol ⁻¹ L s ⁻¹	4.1x10 ⁹	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶
k_{28}	mol ⁻¹ L s ⁻¹	1.9x10 ⁴	8.45x10 ⁶	2.29x10 ³	1.00x10 ⁷
k_{29}	mol ⁻¹ L s ⁻¹	4.1x10 ⁹	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶
k_{30}	mol ⁻¹ L s ⁻¹	1.9x10 ⁴	7.19x10 ⁶	1.91x10 ³	1.00x10 ⁷
k_{31}	mol ⁻¹ L s ⁻¹	4.1x10 ⁹	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶
k_{32}	mol ⁻¹ L s ⁻¹	1.9x10 ⁴	5.81x10 ²	2.85x10 ²	1.00x10 ⁷
k_{33}	mol ⁻¹ L s ⁻¹	4.1x10 ⁹	1.00x10 ⁶	1.00x10 ⁶	1.00x10 ⁶
k_{34}	mol ⁻¹ L s ⁻¹	1.9x10 ⁴	6.86x10 ²	4.00x10 ²	2.63x10 ²

Table 22 (continued)

Parameter	Unit	Initial guesses	Estimated values		
			q = 2	q = 3	q = 4
k_{35}	$\text{mol}^{-1} \text{L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{36}	$\text{mol}^{-1} \text{L s}^{-1}$	1.9×10^4	8.30×10^2	5.57×10^2	7.38×10^1
k_{37}	$\text{mol}^{-1} \text{L s}^{-1}$	4.1×10^9	1.00×10^6	1.00×10^6	1.00×10^6
k_{38}	$\text{mol}^{-1} \text{L s}^{-1}$	1.9×10^4	1.10×10^3	8.38×10^2	1.00×10^7
k_{39}	$\text{mol}^{-1} \text{L s}^{-1}$	4.1×10^9	1.01×10^6	1.00×10^6	1.00×10^6
k_{40}	$\text{mol}^{-1} \text{L s}^{-1}$	1.9×10^4	9.93×10^6	1.23×10^3	1.00×10^7
k_{41}	$\text{mol}^{-1} \text{L s}^{-1}$	4.1×10^9	1.01×10^6	1.00×10^6	1.00×10^6
k_{42}	$\text{mol}^{-1} \text{L s}^{-1}$	1.9×10^4	9.68×10^6	1.23×10^2	1.00×10^7
k_{43}	$\text{mol}^{-1} \text{L s}^{-1}$	4.1×10^9	1.01×10^6	1.00×10^6	1.00×10^6
k_{44}	$\text{mol}^{-1} \text{L s}^{-1}$	1.9×10^4	9.85×10^6	1.43×10^2	1.00×10^7
k_{45}	$\text{mol}^{-1} \text{L s}^{-1}$	4.1×10^9	1.01×10^6	2.08×10^8	1.00×10^6
k_{46}	$\text{mol}^{-1} \text{L s}^{-1}$	1.9×10^4	9.87×10^6	2.17×10^2	1.00×10^7
k_{47}	$\text{mol}^{-1} \text{L s}^{-1}$	4.1×10^9	1.01×10^6	6.39×10^8	1.00×10^6
k_{48}	$\text{mol}^{-1} \text{L s}^{-1}$	1.9×10^4	9.90×10^6	1.08×10^2	1.00×10^7
OF_2 value			11.5769	11.4589	13.9124
Computation time	h		9.21	7.45	3.53

Simulations with the two sets of θ'_2 for which the lowest values of the objective functions were attained are shown as following. Figures 31 to 39 display the predicted concentration profiles of CIP, TOC and ozone in the gas phase employing θ'_2 estimated by using the OF_1 and $q = 4$.

Figure 31 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 32 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 33 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 34 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 35 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 36 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 37 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 38 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Figure 39 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_1 using trust-region-reflective algorithm.

Results of the simulations with the adjusted parameters using the OF_2 and $q = 3$ are shown as follows. Figures 40 to 48 depict the predicted concentrations of CIP, TOC and ozone in the gas phase.

Figure 40 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ_2' adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 41 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ_2' adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 42 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 43 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 44 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 45 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 46 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 47 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Figure 48 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_2 using trust-region-reflective algorithm.

Parameter estimation by using the PSO method

When using the PSO method, the set of parameters θ'_2 is estimated by using OF_1 and OF_2 according to the procedure described in section 3.2.2. Three different population sizes are employed and the number of tanks forming the system is equal to four. Besides, the maximum number of iterations to be performed (*MaxIter*) is used as a stopping criterion. In addition, upper and lower bounds for the parameters are defined (see Appendix I). Table 23 reports the values of the parameters used in the PSO implementation.

Table 23 – Values of parameters used in the PSO implementation.

Parameter	Value
N_{p1}	30
N_{p2}	45
N_{p3}	60
<i>MaxIter</i>	150
c_1	2
c_2	2
w_{max}	0.9
w_{min}	0.4

The adjusted parameters by using OF_1 and OF_2 are listed in Tables 24 and 25, respectively. In both cases, the estimated values of k_La increased with the increase of the population size. The lowest values of OF_1 and OF_2 are reached for $N_p = 45$ and $N_p = 60$, correspondingly.

Table 24 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of ciprofloxacin and total organic carbon in the objective function (OF_1) using the PSO method. N_p : number of particles.

Parameter	Unit	Estimated values		
		$N_p = 30$	$N_p = 45$	$N_p = 60$
k_La	s^{-1}	1.25×10^{-2}	1.37×10^{-2}	1.37×10^{-2}
β	Dimensionless	0.99	0.99	0.99
k_1	$mol^{-1} L s^{-1}$	40	80	80
k_2	$mol^{-1} L s^{-1}$	1.04×10^5	1.00×10^7	1.00×10^7
k_3	s^{-1}	1.54×10^4	1.19×10^4	1.41×10^4
k_4	$mol^{-1} L s^{-1}$	2.42×10^{10}	6.29×10^9	9.06×10^9
k_5	$mol^{-1} L s^{-1}$	1.01×10^8	1.00×10^{10}	1.10×10^8
k_6	$mol^{-1} L s^{-1}$	9.95×10^{10}	1.01×10^9	1.00×10^{11}
k_7	s^{-1}	4.00×10^4	3.40×10^4	3.98×10^4
k_8	s^{-1}	1.00×10^4	1.00×10^6	1.38×10^4
k_9	$mol^{-1} L s^{-1}$	1.04×10^9	1.00×10^8	1.00×10^8
k_{10}	s^{-1}	1.72×10^3	7.57×10^3	6.73×10^3
k_{11}	$mol^{-1} L s^{-1}$	1.58×10^9	1.00×10^{11}	1.00×10^{11}
k_{12}	s^{-1}	0.103	0.250	0.250
k_{13}	$mol^{-1} L s^{-1}$	1.00×10^{10}	9.54×10^9	1.00×10^{10}
k_{14}	$mol^{-1} L s^{-1}$	1.00×10^{10}	6.04×10^8	1.00×10^{10}
k_{15}	$mol^{-1} L s^{-1}$	3.09×10^7	2.05×10^6	1.00×10^8
k_{16}	$mol^{-1} L s^{-1}$	2.02×10^8	1.00×10^8	1.00×10^8
k_{17}	$mol^{-1} L s^{-1}$	1.00×10^8	9.40×10^9	1.22×10^9
k_{18}	$mol^{-1} L s^{-1}$	5.40×10^5	1.00×10^6	1.00×10^4
k_{19}	$mol^{-1} L s^{-1}$	30	20.1	28.9
k_{20}	$mol^{-1} L s^{-1}$	1.00×10^8	1.00×10^8	1.00×10^{10}
k_{21}	$mol^{-1} L s^{-1}$	1.00×10^8	1.00×10^8	1.92×10^8
k_{22}	$mol^{-1} L s^{-1}$	5.35×10^9	2.50×10^8	1.00×10^{10}
k_{23}	$mol^{-1} L s^{-1}$	1.00×10^9	2.25×10^{10}	1.48×10^{10}
k_{24}	$mol^{-1} L s^{-1}$	1.00×10^4	1.00×10^4	1.00×10^4

Table 24 (continued)

Parameter	Unit	Estimated values		
		$N_p = 30$	$N_p = 45$	$N_p = 60$
k_{25}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	2.68×10^9	6.48×10^9
k_{26}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.71×10^4	1.57×10^4	1.62×10^4
k_{27}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.08×10^6	1.00×10^6
k_{28}	$\text{mol}^{-1} \text{ L s}^{-1}$	2.92×10^3	2.07×10^4	1.95×10^4
k_{29}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	9.49×10^9	1.00×10^6
k_{30}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	7.43×10^1	7.38×10^1
k_{31}	$\text{mol}^{-1} \text{ L s}^{-1}$	3.77×10^7	1.85×10^7	1.00×10^{10}
k_{32}	$\text{mol}^{-1} \text{ L s}^{-1}$	8.93×10^1	3.84×10^2	5.64×10^2
k_{33}	$\text{mol}^{-1} \text{ L s}^{-1}$	4.28×10^9	1.00×10^{10}	1.00×10^{10}
k_{34}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.37×10^2	9.90×10^6	1.19×10^3
k_{35}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^6	1.00×10^{10}
k_{36}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	8.97×10^6	1.00×10^7
k_{37}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
k_{38}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.126	0.100	0.100
k_{39}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	2.81×10^7	1.00×10^6
k_{40}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.31×10^{-1}	1.16×10^6	1.00×10^7
k_{41}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
k_{42}	$\text{mol}^{-1} \text{ L s}^{-1}$	9.65×10^6	1.00×10^7	1.00×10^7
k_{43}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^{10}	1.00×10^{10}
k_{44}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	1.00×10^{-1}
k_{45}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.12×10^6	1.51×10^7	1.00×10^6
k_{46}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.03×10^{-1}	3.66×10^3
k_{47}	$\text{mol}^{-1} \text{ L s}^{-1}$	9.19×10^9	1.00×10^6	1.00×10^{10}
k_{48}	$\text{mol}^{-1} \text{ L s}^{-1}$	9.77×10^6	1.00×10^7	1.00×10^7
OF ₁ value		0.555531	0.53434	0.534786

Table 25 – Adjusted parameters (θ'_2) by considering experimental and predicted concentrations of ciprofloxacin, total organic carbon and ozone in the gas phase in the objective function (OF_2) using the PSO method. N_p : number of particles.

Parameter	Unit	Estimated values		
		$N_p = 30$	$N_p = 45$	$N_p = 60$
$k_L a$	s^{-1}	8.13×10^{-2}	1.15×10^{-1}	1.11×10^{-1}
β	Dimensionless	0.99	0.80	0.99

Table 25 (continued)

Parameter	Unit	Estimated values		
		$N_p = 30$	$N_p = 45$	$N_p = 60$
k_1	$\text{mol}^{-1} \text{ L s}^{-1}$	80	80	80
k_2	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	1.00×10^7
k_3	s^{-1}	1.00×10^6	1.00×10^6	1.00×10^6
k_4	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^9	1.00×10^{11}	1.00×10^9
k_5	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
k_6	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{11}	1.00×10^9	1.00×10^{11}
k_7	s^{-1}	4.00×10^4	4.00×10^4	3.40×10^4
k_8	s^{-1}	1.00×10^6	1.00×10^6	1.00×10^4
k_9	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
k_{10}	s^{-1}	1.00×10^5	1.00×10^5	1.00×10^3
k_{11}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^9	1.00×10^9	1.00×10^9
k_{12}	s^{-1}	0.100	0.100	0.250
k_{13}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^8	1.00×10^8	3.11×10^9
k_{14}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^8	1.00×10^8	1.00×10^8
k_{15}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^8	2.00×10^6	1.00×10^8
k_{16}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^8	1.00×10^{10}	1.00×10^{10}
k_{17}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^8	1.00×10^8
k_{18}	$\text{mol}^{-1} \text{ L s}^{-1}$	5.25×10^4	1.00×10^6	1.00×10^4
k_{19}	$\text{mol}^{-1} \text{ L s}^{-1}$	30	20	20
k_{20}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^8	1.00×10^{10}	1.00×10^8
k_{21}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^8
k_{22}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
k_{23}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^9	1.00×10^9	1.00×10^9
k_{24}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^4	1.00×10^4	1.00×10^4
k_{25}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
k_{26}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	1.00×10^7
k_{27}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^{10}	1.00×10^6
k_{28}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	5.97×10^1
k_{29}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^6	1.00×10^{10}
k_{30}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	1.00×10^7
k_{31}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^6	1.00×10^6
k_{32}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.78×10^2	1.00×10^7

Table 25 (continued)

Parameter	Unit	Estimated values		
		$N_p = 30$	$N_p = 45$	$N_p = 60$
k_{33}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^6	1.00×10^6
k_{34}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	2.05×10^2	1.00×10^7
k_{35}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^6	1.00×10^{10}
k_{36}	$\text{mol}^{-1} \text{ L s}^{-1}$	2.31×10^2	1.00×10^7	1.00×10^7
k_{37}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^6	1.00×10^6
k_{38}	$\text{mol}^{-1} \text{ L s}^{-1}$	2.71×10^2	1.00×10^7	1.00×10^7
k_{39}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^{10}	1.00×10^6
k_{40}	$\text{mol}^{-1} \text{ L s}^{-1}$	3.11×10^2	1.00×10^7	1.00×10^7
k_{41}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^6	1.00×10^6
k_{42}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	2.87×10^3	1.00×10^7
k_{43}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^6	1.00×10^6	1.00×10^6
k_{44}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	3.42×10^3
k_{45}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^6	1.00×10^6
k_{46}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	1.00×10^7
k_{47}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^{10}	1.00×10^6	1.00×10^6
k_{48}	$\text{mol}^{-1} \text{ L s}^{-1}$	1.00×10^7	1.00×10^7	1.00×10^7
OF_2 value		13.54203	14.08333	13.30037

Simulations with the adjusted parameters were performed. Results of the simulations with the two sets of parameters listed in Tables 24 and 25 for which the lowest values of the objective function were obtained are presented as follows.

Figure 49 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 50 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 51 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 52 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ_2' adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 53 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ_2' adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 54 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 55 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 56 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 57 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_1 using the particle swarm optimization method.

Figure 58 – Concentration profiles of ciprofloxacin (CIP) for experiments 1 to 4. θ_2' adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 59 – Concentration profiles of ciprofloxacin (CIP) for experiments 5 to 8. θ_2' adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 60 – Concentration profiles of ciprofloxacin (CIP) for experiment 9. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 61 – Concentration profiles of ozone in the gas phase for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 62 – Concentration profiles of ozone in the gas phase for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 63 – Concentration profiles of ozone in the gas phase for experiment 9. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 64 – Concentration profiles of total organic carbon (TOC) for experiments 1 to 4. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 65 – Concentration profiles of total organic carbon (TOC) for experiments 5 to 8. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.

Figure 66 – Concentration profiles of total organic carbon (TOC) for experiment 9. θ'_2 adjusted by minimizing OF_2 using the particle swarm optimization method.

From these figures, it can be noticed that the model performance is very similar to the one that was observed when the parameters were estimated by using the trust-region-reflective algorithm. When the ozone concentration in the gas phase is not accounted for in the objective function, the model fits adequately the CIP and TOC experimental concentrations and overestimates the ozone concentrations in the gas phase for all the experimental conditions. On the other hand, when this later concentration is considered in the objective function there is an attempt to adjust it, nevertheless, the fits of CIP and TOC concentrations worsen. Thus, it is possible to suspect that the three experimental concentration profiles (CIP, TOC and ozone in the gas phase) cannot be adjusted adequately by using the model based on the available experimental data because there could be a systematic experimental error in the measurement of the concentrations of ozone in the gas phase. Unfortunately, as the experimental set-up is no more available it is impossible to confirm this hypothesis.

5.4. Partial conclusions

- The proposed computational tool was applied to the treatment of ciprofloxacin (CIP) in aqueous solution by ozonation process. The model parameters: volumetric mass transfer coefficient in the liquid phase ($k_L a$), liquid holdup (β) and kinetic constants of the degradation model (θ'_1 and θ'_2) were

estimated from real process data by using the trust-region-reflective algorithm implemented in the `lsqnonlin` Matlab[®] function and the particle swarm optimization (PSO) method.

- When using the trust-region-reflective algorithm, three different numbers of tanks (2, 3, and 4) representing the system were considered. When the PSO method was employed, three different population sizes (30, 45, and 60) were taken into account.

- Simulations with the adjusted parameters were performed. The model with the two sets of parameters (θ'_1 and θ'_2) estimated by neglecting the ozone concentration in the gas phase in the objective function was able to adjust adequately the experimental concentrations of ciprofloxacin (CIP) and total organic carbon (TOC). However, predicted concentrations of ozone in the gas phase were higher than the experimental values for all the experimental conditions. These behaviors were observed in both scenarios: model parameter estimation using trust-region-reflective and PSO methods.

- The results of simulations, using the adjusted parameters (θ'_1 and θ'_2) when the ozone concentration in the gas phase was accounted for in the objective function, showed that there was an attempt to adjust this experimental concentration, nevertheless, the adjustments of CIP and TOC concentrations worsened. The three experimental concentration profiles (CIP, TOC and ozone in the gas phase) cannot be adjusted adequately by using the model based on the available experimental data because there could be a systematic experimental error in the measurement of the concentrations of ozone in the gas phase.

Chapter 6. Conclusions and recommendations for future works

6.1. Conclusions

- In this work, a computational tool for the modeling and parameter estimation of advanced oxidation process was proposed. The tool, developed in Matlab[®], contains four main modules:

- Module I: process modeling module. In this module, the model differential equations are generated based on the mole balance of species and the kinetic expressions.

- Modules II and III: parameter estimation modules. These modules are dedicated to the estimation of the model parameters from available experimental data by minimizing the objective function (weighted least squares), using the trust-region-reflective algorithm implemented in the lsqnonlin Matlab[®] function (Module II) and the particle swarm optimization (PSO) method (Module III).

- Module IV: simulation module. Simulations with the estimated parameters in Modules II or III or parameters supplied by the user are performed.

- The proposed computational tool was applied to the treatment of phenol by electro-Fenton process.

- The kinetic constants of the reactions involved in the mechanism were estimated by using the trust-region-reflective algorithm and the PSO method considering three different population sizes (30, 45 and 60 particles).

- When the PSO method was used, the lowest value of the objective function was equal to 1.291745 and was achieved when 60 particles were considered. The objective function by employing the trust-region-reflective algorithm was equal to 0.833101.

- The results of the process simulations, illustrated that the model with the adjusted parameters by using both optimization algorithms was able to fit relatively well the experimental concentrations of phenol and its aromatic intermediates: catechol (CT), hydroquinone (HQ) and resorcinol (RS).

- The tool was also applied to the treatment of ciprofloxacin (CIP) in aqueous solution by ozonation process. The model parameters: volumetric mass transfer coefficient in the liquid phase (k_La), liquid holdup (β) and kinetic constants of the degradation model were estimated.

- When using the trust-region-reflective algorithm, three different numbers of tanks (2, 3, and 4) representing the system were considered. On the other hand, when the PSO method was employed, three different population sizes (30, 45, and 60) were taken into account.

- The model with the adjusted parameters by neglecting the ozone concentration in the gas phase in the objective function was able to adjust adequately the experimental concentrations of CIP and total organic carbon (TOC). However, the predicted concentrations of ozone in the gas phase were higher than the experimental values for all the experimental conditions. These behaviors were observed in both scenarios: model parameter estimation using trust-region-reflective and PSO methods.

- The results of simulations, by using the adjusted parameters when the ozone concentration in the gas phase was accounted for in the objective function, showed that there was an attempt to adjust this experimental concentration, nevertheless, the adjustments of CIP and TOC concentrations worsened. The three experimental concentration profiles (CIP, TOC and ozone in the gas phase) cannot be adjusted adequately by using the model based on the available experimental data because there could be a systematic experimental error in the measurement of the concentrations of ozone in the gas phase.

- An important conclusion of the current work is that the developed tool can be used to describe other AOPs, and it is expected that it will be helpful for process and equipment design.

6.2. Recommendations for future works

- Extend the proposed computational tool to photochemical advanced oxidation processes by considering the photochemical reactions.
- Test different weights in the objective function or different objective functions.
- Test different degradation models (different reaction mechanisms) with available experimental data of the intermediate compounds to obtain better estimates of the parameters.
- Consider more case studies in order to test and evaluate the performance of the proposed computational tool.
- Consider a distribution of gas holdups for the tanks forming the gas-liquid contact column. This is translated into different values of β for each tank.
- Quantification of the uncertainties by using the information generated by the sensitivity analysis.

The proposed computational tool will allow those hypotheses to be easily implemented.

References

- AL-AHMAD, A.; DASCHNER, F. D.; KÜMMERER, K. Biodegradability of cefotiam, ciprofloxacin, meropenem, penicillin G, and sulfamethoxazole and inhibition of waste water bacteria. **Archives of Environmental Contamination and Toxicology**, v. 37, n. 2, p. 158–163, 1999.
- ALNAIZY, R.; AKGERMAN, A. Advanced oxidation of phenolic compounds. **Advances in Environmental Research**, v. 4, n. 3, p. 233–244, 2000.
- AN, T.; YANG, H.; LI, G.; SONG, W.; COOPER, W. J.; NIE, X. Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water. **Applied Catalysis B: Environmental**, v. 94, n. 3–4, p. 288–294, 2010.
- ANDREOZZI, R. Advanced oxidation processes (AOP) for water purification and recovery. **Catalysis Today**, v. 53, n. 1, p. 51–59, 1999.
- ANDREOZZI, R.; D'APUZZO, A.; MAROTTA, R. A kinetic model for the degradation of benzothiazole by Fe^{3+} -photo-assisted Fenton process in a completely mixed batch reactor. **Journal of Hazardous Materials**, v. 80, n. 1–3, p. 241–257, 2000.
- BARD, Y. **Nonlinear Parameter Estimation**. Academic Press, 1974.
- BARDAUIL, C. **Degradação do antibiótico ciprofloxacina em solução aquosa por meio de processo oxidativo avançado baseado em ozônio**. Tese de mestrado, Departamento de Engenharia Química, Universidade de São Paulo, 2012.
- BEERS, K. J. **Numerical Methods for Chemical Engineering. Applications in MATLAB®**. Cambridge University Press, 2007.
- BELTRAN DE HEREDIA, J. et al. Kinetic model for phenolic compound oxidation by Fenton's reagent. **Chemosphere**, v. 45, n. 1, p. 85–90, 2001.
- BELTRÁN, F. et al. A kinetic model for advanced oxidation processes of aromatic hydrocarbons in water: application to phenanthrene and nitrobenzene. **Industrial & Engineering Chemistry Research**, v. 38, p. 4189–4199, 1999.

BELTRÁN, F. J. et al. Modelling Industrial Wastewater Ozonation In Bubble Contactors. 1. Rate Coefficient Determination. **Ozone: Science & Engineering**, v. 17, n. 4, p. 355–378, 1995.

BELTRÁN, F. J. et al. Aqueous Degradation of Atrazine and Some of Its Main By-products with Ozone/Hydrogen Peroxide. 1998.

BELTRÁN, F. J. et al. Kinetic modelling of aqueous atrazine ozonation processes in a continuous flow bubble contactor. **Journal of Hazardous Materials**, v. 80, n. 1–3, p. 189–206, 2000.

BELTRÁN, F. J. et al. An Attempt to Model the Kinetics of the Ozonation of Simazine in Water. **Industrial & Engineering Chemistry Research**, p. 1723–1732, 2002.

BELTRÁN, F. J. **Ozone Reaction Kinetics for Water and Wastewater Systems**. Lewis Publishers, 2004.

BELTRÁN, F. J.; AGUINACO, A.; GARCÍA-ARAYA, J. F. Kinetic modelling of TOC removal in the photocatalytic ozonation of diclofenac aqueous solutions. **Applied Catalysis B: Environmental**, v. 100, n. 1–2, p. 289–298, 2010.

BELTRÁN, F. J.; ENCINAR, J. M.; GARCÍA-ARAYA, J. F. Modelling Industrial WasteWater Ozonation in Bubble Contactors. 2. Scale-up From Bench to Pilot-Plant. **Ozone-Science & Engineering**, v. 17, n. 4, p. 379–398, 1995.

BELTRÁN, F. J.; GÓMEZ-SERRANO, V.; DURÁN, A. Degradation kinetics of p-nitrophenol ozonation in water. **Water Research**, v. 26, n. 1, p. 9–17, 1992.

BIEGLER, L. T.; DAMIANO, J. J.; BLAU, G. E. Nonlinear parameter estimation: A case study comparison. **AIChE Journal**, v. 32, n. 1, p. 29–45, 1986.

BIÑ, A. K. Ozone dissolution in aqueous systems treatment of the experimental data. **Experimental Thermal and Fluid Science**, v. 28, p. 395–405, 2004.

BIÑ, A. K. Ozone Solubility in Liquids. **Ozone: Science & Engineering**, v. 28, n. 2, p. 67–75, 2006.

CARELL MORRIS, J. The aqueous solubility of ozone - A review. **Ozone News**,

n. 1, 1988.

CARINI, D. et al. Modeling Ozonation as Pre-Treatment Step for the Biological Batch Degradation of Industrial Wastewater Containing 3-Methyl-Pyridine. **Ozone: Science & Engineering**, v. 23, p. 359–368, 2001.

CHU, W.; CHAN, K. H.; KWAN, C. Y. Modeling the ozonation of herbicide 2,4-D through a kinetic approach. **Chemosphere**, v. 55, n. 5, p. 647–652, 2004.

CLERC, M. The swarm and the queen: Towards a deterministic and adaptive particle swarm optimization. **Proceedings of the 1999 Congress on Evolutionary Computation, CEC 1999**, v. 3, p. 1951–1957, 1999.

CRITTENDEN, J. C. et al. A kinetic model for H_2O_2 /UV process in a completely mixed batch reactor. **Water Research**, v. 33, n. 10, p. 2315–2328, 1999.

DA, S. et al. A comparison among stochastic optimization algorithms for parameter estimation of biochemical kinetic models. **Applied Soft Computing Journal**, v. 13, n. 5, p. 2205–2214, 2013.

DE TORRES-SOCÍAS, E. et al. Dynamic modelling for cork boiling wastewater treatment at pilot plant scale. **Environmental Science and Pollution Research**, p. 12182–12189, 2014.

DE WITTE, B. et al. Ozonation and advanced oxidation by the peroxone process of ciprofloxacin in water. **Journal of Hazardous Materials**, v. 161, n. 2–3, p. 701–708, 2009.

DE WITTE, B. et al. Ciprofloxacin ozonation in hospital wastewater treatment plant effluent: Effect of pH and H_2O_2 . **Chemosphere**, v. 78, n. 9, p. 1142–1147, 2010.

DEWIL, R. et al. New perspectives for Advanced Oxidation Processes. **Journal of Environmental Management**, v. 195, p. 93–99, 2017.

DEWITTE, B. et al. Ozonation of ciprofloxacin in water: HRMS identification of reaction products and pathways. **Environmental Science and Technology**, v. 42, n. 13, p. 4889–4895, 2008.

DODD, M. C.; BUFFLE, M. O.; VON GUNTEN, U. Oxidation of antibacterial molecules by aqueous ozone: Moiety-specific reaction kinetics and application to ozone-based wastewater treatment. **Environmental Science and Technology**, v. 40, n. 6, p. 1969–1977, 2006.

DOMÈNECH, X.; JARDIM, W. F.; LITTER, M. I. Procesos avanzados de oxidación para la eliminación de contaminantes. **Eliminación de Contaminantes por Fotocatálisis Heterogénea**, p. 3–26, 2001.

DORIVAL-GARCÍA, N. et al. Simultaneous determination of 13 quinolone antibiotic derivatives in wastewater samples using solid-phase extraction and ultra performance liquid chromatography-tandem mass spectrometry. **Microchemical Journal**, v. 106, p. 323–333, 2013.

EBERHART, R.; KENNEDY, J. A new optimizer using particle swarm theory. **MHS'95. Proceedings of the Sixth International Symposium on Micro Machine and Human Science**, p. 39–43, 1995.

EDALATMANESH, M.; DHIB, R.; MEHRVAR, M. Kinetic modeling of aqueous Phenol degradation by UV/H₂O₂ process. **International Journal of Chemical Kinetics**, v. 40, n. 1, p. 34–43, 2008.

ESPLUGAS, S. et al. Comparison of different advanced oxidation processes for phenol degradation. **Water Research**, v. 36, n. 4, p. 1034–1042, 2002.

FERRE-ARACIL, J. et al. Ozonation of hospital raw wastewaters for cytostatic compounds removal. Kinetic modelling and economic assessment of the process. **Science of the Total Environment**, v. 556, p. 70–79, 2016.

FOGLER, H. S. **Elements of Chemical Reaction Engineering**. Prentice Hall, 2006.

GLAZE, W. H. et al. Chemical Models of Advanced Oxidation Processes. v. 27, n. 1, p. 23–42, 1992.

GLAZE, W. H.; KANG, J.-W. Advanced Oxidation Processes. Description of a kinetic model for the oxidation of hazardous materials in aqueous media with ozone and hydrogen peroxide in a semibatch reactor. **Society**, v. 28, n. 2, p.

1573–1580, 1989a.

GLAZE, W. H.; KANG, J.-W.; CHAPIN, D. H. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. **Ozone: Science & Engineering**, v. 9, n. 4, p. 335–352, 1987.

GLAZE, W. H.; KANG, J. Advanced Oxidation Processes. Test of a Kinetic Model for the Oxidation of Organic Compounds with Ozone and Hydrogen Peroxide in a Semibatch Reactor. **Industrial & Engineering Chemistry Research**, v. 28, p. 1580–1587, 1989b.

GLAZE, W. H.; LAY, Y.; KANG, J.-W. Advanced Oxidation Processes. A Kinetic Model for the Oxidation Hydrogen Peroxide and U V Radiation. **Industrial & Engineering Chemistry Research**, v. 37, p. 2314–2323, 1995.

GOTTSCHALK, C.; LIBRA, J. A.; SAUPE, A. **Ozonation of Water and Waste Water. A Practical Guide to Understanding Ozone and its Application**. WILEY-VCH, 2000.

GUO, H. G. et al. Photochemical degradation of ciprofloxacin in UV and UV/H₂O₂ process: Kinetics, parameters, and products. **Environmental Science and Pollution Research**, v. 20, n. 5, p. 3202–3213, 2013.

HAMBY, D. M. A review of techniques for parameter sensitivity analysis of environmental models. p. 135–154, 1994.

HINDMARSH, A. C. et al. SUNDIALS: Suite of Nonlinear and Differential/Algebraic Equation Solvers. **ACM Transactions on Mathematical Software**, v. 31, n. 3, p. 363–396, 2005.

HINDMARSH, A. C.; SERBAN, R. User Documentation for cvodes v2.6.0. **Center for Applied Scientific Computing Lawrence Livermore National Laboratory**, 2009.

HOFMAN-CARIS, C. H. M. et al. Prediction of advanced oxidation performance in UV/H₂O₂ reactor systems with LP-UV lamps. **Water Science and Technology: Water Supply**, v. 11, n. 4, p. 460–467, 2011.

HOFMAN-CARIS, C. H. M. et al. Prediction of Advanced Oxidation

Performance in Pilot UV/H₂O₂ Reactor Systems with MP- and LP-UV Lamps. **Ozone: Science and Engineering**, v. 34, n. 2, p. 120–124, 2012a.

HOFMAN-CARIS, R. C. H. M. et al. Prediction of advanced oxidation performance in various pilot UV/H₂O₂ reactor systems with MP- and LP- and DBD-UV lamps. **Chemical Engineering Journal**, v. 210, p. 520–528, 2012b.

HOIGNÉ, J.; BADER, H. Ozone and hydroxyl radical-initiated oxidations of organic and organometallic trace impurities in water. p. 292–313, 1978.

JIN, X.; PELDSZUS, S.; HUCK, P. M. Reaction kinetics of selected micropollutants in ozonation and advanced oxidation processes. **Water Research**, v. 46, n. 19, p. 6519–6530, 2012.

KALLAS, J. et al. Ozonation And AOP Parameter Estimation From Countercurrent Film Absorber Data. **Ozone: Science & Engineering**, v. 17, n. 5, p. 527–550, 1995.

KANG, N.; LEE, D. S.; YOON, J. Kinetic modeling of Fenton oxidation of phenol and monochlorophenols. **Chemosphere**, v. 47, p. 915–924, 2002.

KANTARCI, N.; BORAK, F.; ULGEN, K. O. Bubble column reactors. **Process Biochemistry**, v. 40, n. 7, p. 2263–2283, 2005.

KENNEDY, J.; EBERHART, R. Particle Swarm Optimization. p. 1942–1948, 1995.

KUOSA, M.; LAARI, A.; KALLAS, J. Determination of the Henry's coefficient and mass transfer for ozone in a bubble column at different pH values of water. **Ozone: Science and Engineering**, v. 26, n. 3, p. 277–286, 2004.

LEE, C. J.; PRASAD, V.; LEE, J. M. Stochastic Nonlinear Optimization for Robust Design of Catalysts. **Industrial & Engineering Chemistry Research**, p. 3938–3946, 2011.

LESTER, Y. et al. Removal of pharmaceuticals using combination of UV/H₂O₂/O₃ advanced oxidation process. **Water science and technology: a journal of the International Association on Water Pollution Research**, v. 64, p. 2230–2238, 2011.

LEVENSPIEL, O. **Chemical Reaction Engineering**. New York: John Wiley & Sons, Inc, 1999.

LEWIS, W. K.; WHITMAN, W. G. Principles of Gas Absorption. **Industrial & Engineering Chemistry**, v. 16, n. 12, p. 1215–1220, 1924.

LIU, C. et al. Spectroscopic study of degradation products of ciprofloxacin, norfloxacin and lomefloxacin formed in ozonated wastewater. **Water Research**, v. 46, n. 16, p. 5235–5246, 2012.

LIU, C.; NANABOINA, V.; KORSHIN, G. V. **Spectroscopic study of degradation products of ciprofloxacin, norfloxacin and lomefloxacin formed in ozonated wastewater (SM)**, 2012.

LIU, H. et al. Kinetic modeling of electro-Fenton reaction in aqueous solution. **Water Research**, v. 41, n. 5, p. 1161–1167, 2007.

LOVATO, M. E.; MARTÍN, C. A.; CASSANO, A. E. A reaction kinetic model for ozone decomposition in aqueous media valid for neutral and acidic pH. **Chemical Engineering Journal**, v. 146, n. 3, p. 486–497, 2009.

MANDAL, S. Reaction Rate Constants of Hydroxyl Radicals with Micropollutants and Their Significance in Advanced Oxidation Processes. **Journal of Advanced Oxidation Technologies**, v. 21, n. 1, p. 178–195, 2018.

MARINI, F.; WALCZAK, B. Chemometrics and Intelligent Laboratory Systems Particle swarm optimization (PSO). A tutorial. **Chemometrics and Intelligent Laboratory Systems**, v. 149, p. 153–165, 2015.

MATHWORKS. **Matlab Documentation PSO**. Disponível em: <<https://www.mathworks.com/matlabcentral/fileexchange/57286-video-tutorial-of-particle-swarm-optimization-pso-in-matlab?focused=6373855&tab=function>>. Acesso em: 1 out. 2018.

MATHWORKS. **Matlab Documentation Isqnonlin**. Disponível em: <<https://www.mathworks.com/help/optim/ug/Isqnonlin.html>>. Acesso em: 24 out. 2018a.

MATHWORKS. **Matlab Documentation ODE15S**. Disponível em:

<<https://www.mathworks.com/help/matlab/ref/ode15s.html>>. Acesso em: 11 fev. 2016b.

MCLEAN, K. A. P.; MCAULEY, K. B. Mathematical modelling of chemical processes-obtaining the best model predictions and parameter estimates using identifiability and estimability procedures. **Canadian Journal of Chemical Engineering**, v. 90, n. 2, p. 351–366, 2012.

MEIJIDE, J. et al. p-Nitrophenol degradation by electro-Fenton process: Pathway, kinetic model and optimization using central composite design. **Chemosphere**, v. 185, p. 726–736, 2017.

MIZUNO, T.; TSUNO, H. Evaluation of solubility and the gas-liquid equilibrium coefficient of high concentration gaseous ozone to water. **Ozone: Science and Engineering**, v. 32, n. 1, p. 3–15, 2010.

MONDAL, S. K.; SAHA, A. K.; SINHA, A. Removal of ciprofloxacin using modified advanced oxidation processes: Kinetics, pathways and process optimization. **Journal of Cleaner Production**, v. 171, p. 1203–1214, 2018.

MOUSSET, E. et al. A complete phenol oxidation pathway obtained during electro-Fenton treatment and validated by a kinetic model study. **Applied Catalysis B, Environmental**, v. 180, p. 189–198, 2016.

OLLER, I.; MALATO, S.; SÁNCHEZ-PÉREZ, J. A. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. **Science of the Total Environment**, v. 409, n. 20, p. 4141–4166, 2011.

OPPENLÄNDER, T. **Photochemical Purification of Water and Air. Advanced Oxidation Processes (AOPs): Principles, Reaction Mechanisms, Reactor Concepts**. WILEY-VCH, 2003.

OUEDERNI, A.; MORA, J. C.; BES, R. S. Ozone absorption in water: Mass transfer and solubility. **Ozone Science & Engineering**, 1987.

PANTEA, C. et al. The QSSA in chemical kinetics: as taught and as practiced. **Discrete and Topological Models in Molecular Biology, Natural Computing**

Series, p. 419–442, 2014.

PERA-TITUS, M. et al. Degradation of chlorophenols by means of advanced oxidation processes: A general review. **Applied Catalysis B: Environmental**, v. 47, n. 4, p. 219–256, 2004.

PEREIRA, V. J. et al. UV Degradation Kinetics and Modeling of Pharmaceutical Compounds in Laboratory Grade and Surface Water via Direct and Indirect Photolysis at 254 nm. **Environmental Science & Technology**, v. 41, n. 5, p. 1682–1688, 2007.

PETZOLD, L. et al. Sensitivity analysis of differential-algebraic equations and partial differential equations. **Computers & Chemical Engineering**, v. 30, n. 10–12, p. 1553–1559, 2006.

POCOSTALES, J. P.; ÁLVAREZ, P.; BELTRÁN, F. J. Kinetic modeling of granular activated carbon promoted ozonation of a food-processing secondary effluent. **Chemical Engineering Journal**, v. 183, p. 395–401, 2012.

POCOSTALES, J. P.; ALVAREZ, P. M.; BELTRÁN, F. J. Kinetic modeling of powdered activated carbon ozonation of sulfamethoxazole in water. **Chemical Engineering Journal**, v. 164, n. 1, p. 70–76, 2010.

PONTES, R. F. F. et al. A mechanistic kinetic model for phenol degradation by the Fenton process. **Journal of Hazardous Materials**, v. 176, n. 1–3, p. 402–413, 2010.

POPLI, K.; PRASAD, V. Robust design of experiments using constrained stochastic optimization. **IFAC-PapersOnLine**, v. 28, n. 8, p. 106–111, 2015.

POYATOS, J. M. et al. Advanced oxidation processes for wastewater treatment: State of the art. **Water, Air, and Soil Pollution**, v. 205, n. 1–4, p. 187–204, 2010.

POZA-NOGUEIRAS, V. et al. Current advances and trends in electro-Fenton process using heterogeneous catalysts – A review. **Chemosphere**, v. 201, p. 399–416, 2018.

QIU, S. et al. Kinetic Modeling of the Electro-Fenton Process: Quantification of

Reactive Oxygen Species Generation. **Electrochimica Acta**, v. 176, p. 51–58, 2015.

QUERO-PASTOR, M. J. et al. Ozonation of ibuprofen: A degradation and toxicity study. **Science of the Total Environment**, v. 466–467, p. 957–964, 2014.

RAO, S. S. **Engineering Optimization. Theory and Practice**. John Wiley & Sons, Inc, 2009.

REINIK, J.; JAKOBSSON, K.; KALLAS, J. 2,4-Xylidine Degradation with Ozonation: Mass Transfer and Reaction Kinetics. **Ozone: Science & Engineering**, v. 26, n. 5, p. 499–509, 2004.

RHIM J.-A. Equilibrium concentration and overall henry's law constant of ozone. **Environmental Engineering Research**, v. 9, n. 2, p. 88–95, 2004.

RISCHBIETER, E.; STEIN, H.; SCHUMPE, A. Ozone solubilities in water and aqueous salt solutions. **Journal of Chemical and Engineering Data**, v. 45, n. 2, p. 338–340, 2000.

RIVERA-UTRILLA, J. et al. Pharmaceuticals as emerging contaminants and their removal from water. A review. **Chemosphere**, v. 93, n. 7, p. 1268–1287, 2013.

ROTH, J. A.; SULLIVAN, D. E. Solubility of ozone in water. **Industrial and Engineering Chemistry Fundamentals**, v. 20, n. 2, p. 137–140, 1981.

SANDER, R. Compilation of Henry's law constants (version 4.0) for water as solvent. **Atmospheric Chemistry and Physics**, v. 15, p. 4399–4981, 2015.

SCHWAAB, M. et al. Nonlinear parameter estimation through particle swarm optimization. v. 63, p. 1542–1552, 2008.

SEFERLIS, P. Sensitivity Analysis for Chemical Process. v. 20, n. 10, p. 1177–1200, 1996.

SERBAN, R.; HINDMARSH, A. C. **CVODES: The Sensitivity-Enabled ODE Solver in SUNDIALS**, 2005.

SHI, Y.; EBERHART, R. A modified particle swarm optimizer. **1998 IEEE International Conference on Evolutionary Computation Proceedings. IEEE World Congress on Computational Intelligence**, p. 69–73, 1998.

STAEHELIN, J.; HOIGNE, J. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. **Environmental Science and Technology**, v. 19, n. 12, p. 1206–1213, 1985.

VAN LANGENHOVE, H. et al. Formal Bimolecular Kinetic Model for the Ozonation of Ciprofloxacin in the Liquid Phase. **Journal of Advanced Oxidation Technologies**, v. 14, n. 1, 2016.

VASCONCELOS, T. G. et al. Photo-degradation of the antimicrobial ciprofloxacin at high pH: Identification and biodegradability assessment of the primary by-products. **Chemosphere**, v. 76, n. 4, p. 487–493, 2009a.

VASCONCELOS, T. G. et al. Ciprofloxacin in hospital effluent: Degradation by ozone and photoprocesses. **Journal of Hazardous Materials**, v. 169, n. 1–3, p. 1154–1158, 2009b.

VON GUNTEN, U. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. **Water Research**, v. 37, n. 7, p. 1443–1467, 2003.

WANG, H. et al. Kinetic modeling for the deactivation of TiO₂ during the photocatalytic removal of low concentration SO₂. **Chemical Engineering Journal**, v. 303, p. 425–432, 2016.

WANG, J. et al. Mathematical model involving chemical reaction and mass transfer for the ozonation of dimethyl phthalate in water in a bubble column reactor. **Journal of Advanced Oxidation Technologies**, v. 20, n. 1, 2017.

WANG, J. L.; XU, L. J. Advanced oxidation processes for wastewater treatment: Formation of hydroxyl radical and application. **Critical Reviews in Environmental Science and Technology**, v. 42, n. 3, p. 251–325, 2012a.

WANG, J. L.; XU, L. J. Advanced oxidation processes for wastewater treatment: Formation of hydroxyl radical and application. **Critical Reviews in Environmental Science and Technology**, v. 42, n. 3, p. 251–325, 2012b.

WOLS, B. A. et al. Degradation of 40 selected pharmaceuticals by UV/H₂O₂. **Water Research**, v. 47, n. 15, p. 5876–5888, 2013.

WOLS, B. A. et al. Predicting pharmaceutical degradation by UV (LP)/ H₂O₂ processes : A kinetic model. **Chemical Engineering Journal**, v. 255, p. 334–343, 2014.

WOLS, B. A. et al. Predicting pharmaceutical degradation by UV (MP)/H₂O₂ processes: A kinetic model. **Chemical Engineering Journal**, v. 263, p. 336–345, 2015.

WOLS, B. A.; HOFMAN-CARIS, C. H. M. Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water. **Water Research**, v. 46, n. 9, p. 2815–2827, 2012.

YUAN, F. et al. Photodegradation and toxicity changes of antibiotics in UV and UV/H₂O₂ process. **Journal of Hazardous Materials**, v. 185, n. 2–3, p. 1256–1263, 2011.

ZAZO, J. A. et al. Chemical pathway and kinetics of phenol oxidation by Fenton's reagent. **Environmental Science and Technology**, v. 39, n. 23, p. 9295–9302, 2005.

ZAZO, J. A. et al. Semicontinuous Fenton oxidation of phenol in aqueous solution. A kinetic study. **Water Research**, v. 43, n. 16, p. 4063–4069, 2009.

ZHANG, T. et al. Modeling the oxidation of phenolic compounds by hydrogen peroxide photolysis. **Chemosphere**, v. 161, p. 349–357, 2016.

Appendix A. Derivatives of the right-hand side of the model differential equations with respect to the model parameters

The information related in this Appendix is used to generate the right-hand side of the forward sensitivity equations.

To obtain the general analytical derivatives of the right-hand side of the model differential equations (see Section 3.1.2) with respect to the model parameters (θ' , see Equation 30), the following notation is considered:

- f_{iLj} depicts the right-hand side of the model equations correspondent to the mole balance equations for species in the liquid phase ($i = 1, \dots, p$) in each tank that form the system ($j = 1, \dots, q$) (see Figure 3).

- f_{Gj} represents the right-hand side of the model equations which correspond to the mole balance equations for species in the gas phase in the tanks forming the column ($j = 1, \dots, (q - 1)$) (see Figure 3).

Derivatives of f_{iLj} are summarized as follows. Equations 73 and 74 show these derivatives with respect to $k_L a$ for the first species ($i = 1$) and the remaining species ($i = 2, \dots, p$) in the tanks that form the column ($j = 1, \dots, (q - 1)$). Derivatives with respect to β for all the species in the liquid phase ($i = 1, \dots, p$) are given by Equation 75.

$$\frac{df_{1Lj}}{dk_L a} = \left(\frac{[c]_{Gj} RT}{He} - [c_1]_{Lj} \right) \quad (73)$$

$$\frac{df_{iLj}}{dk_L a} = 0 \quad (74)$$

$$\frac{df_{iLj}}{d\beta} = -\frac{Q_L(q-1)}{V_{co}\beta^2} ([c_i]_{L(j+1)} - [c_i]_{Lj}) \quad (75)$$

The derivatives of f_{iLj} with respect to $k_L a$ and β in the mixing tank ($j = q$) are equal to zero (Equations 76 and 77). Since the parameter $k_L a$ characterizes the mass transfer from gas to liquid phase and in the mixing tank there is no gas phase and β is related to the liquid volume in each tank that was considered in order to represent the column.

$$\frac{df_{i_L q}}{dk_L a} = 0 \quad (76)$$

$$\frac{df_{i_L q}}{d\beta} = 0 \quad (77)$$

Derivatives with respect to $\ln(k_l)$ ($l = 1, \dots, n$) can be written as the product of the stoichiometry matrix ($v_{(p \times n)}$ matrix) and a diagonal matrix with elements defined by Equation 78.

$$Derv = diag \left(\prod_{i=1}^p [c_i]_{L_j}^{\alpha_{i,l}} \right)_{(n \times n)} \quad (78)$$

Derivatives of f_{G_j} with respect to $k_L a$ in each tank that forms the column ($j = 1, \dots, (q - 1)$) are given by Equation 79.

$$\frac{df_{G_j}}{dk_L a} = \frac{-\beta}{(1 - \beta)} \left(\frac{[c]_{G_j} RT}{He} - [c_1]_{L_j} \right) \quad (79)$$

Equation 80 summarizes these derivatives with respect to β in the tanks forming the column ($j = 1, \dots, (q - 1)$). For the first tank ($j = 1$), $[c]_{G_{(j-1)}} = [c]_{G_{inlet}}$.

$$\frac{df_{G_j}}{d\beta} = \frac{Q_G(q-1)}{V_{co}(1-\beta)^2} ([c]_{G_{(j-1)}} - [c]_{G_j}) - \frac{k_L a \beta + k_L a (1 - \beta)}{(1 - \beta)^2} \left(\frac{[c]_{G_j} RT}{He} - [c_1]_{L_j} \right) \quad (80)$$

Appendix B. Analytical Jacobian matrix of the model

The analytical Jacobian matrix of the model (Jac_{model} , square matrix with dimension equal to the number of model equations) is also used in the generation of the right-hand side of the sensitivity equations. This matrix is constructed according to a block strategy by deriving the right-hand side of the model differential equations with respect to the state variables.

The blocks' description is given as follows:

- $Jac_{c_L c_L}$ and $Jac_{c_G c_G}$ are $(q * p)$ and $(q - 1)$ square matrices, correspondingly. The former relates the derivatives of $f_{i_L j}$ with respect to the species concentrations in the same phase in each tank forming the system ($j = 1, \dots, q$). The latter denotes the derivatives of $f_{G j}$ with respect to the species concentrations in the same phase in the tanks forming the column ($j = 1, \dots, (q - 1)$).

- $Jac_{c_L c_G}$ is a $((q * p) \times (q - 1))$ matrix that contains the derivatives of $f_{i_L j}$ with respect to the species concentrations in the gas phase in the tanks that represent the column ($j = 1, \dots, (q - 1)$).

- $Jac_{c_G c_L}$ is a $((q - 1) \times (q * p))$ matrix and summarizes the derivatives of $f_{G j}$ with respect to the species concentrations in the liquid phase in the tanks that form the system ($j = 1, \dots, q$).

The blocks together with the notation employed are given by Equations 81 to 95.

$$\begin{aligned}
 & Jac_{c_L c_L} \\
 &= \begin{bmatrix} P_{L1(pxp)} & \alpha I_{(pxp)} & [0]_{(pxp)} & \cdots & [0]_{(pxp)} & [0]_{(pxp)} \\ [0]_{(pxp)} & P_{L2(pxp)} & \alpha I_{(pxp)} & \cdots & [0]_{(pxp)} & [0]_{(pxp)} \\ [0]_{(pxp)} & [0]_{(pxp)} & P_{L3(pxp)} & \cdots & [0]_{(pxp)} & [0]_{(pxp)} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ [0]_{(pxp)} & [0]_{(pxp)} & [0]_{(pxp)} & \cdots & P_{L(q-1)(pxp)} & \alpha I_{(pxp)} \\ \alpha_q I_{(pxp)} & [0]_{(pxp)} & [0]_{(pxp)} & \cdots & [0]_{(pxp)} & P_{Lq(pxp)} \end{bmatrix}_{((q*p) \times (q*p))} \quad (81)
 \end{aligned}$$

$$Jac_{c_L c_G} = \begin{bmatrix} P_{G_1(px1)} & [0]_{(px1)} & [0]_{(px1)} & \cdots & [0]_{(px1)} \\ [0]_{(px1)} & P_{G_2(px1)} & [0]_{(px1)} & \cdots & [0]_{(px1)} \\ [0]_{(px1)} & [0]_{(px1)} & P_{G_3(px1)} & \cdots & [0]_{(px1)} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ [0]_{(px1)} & [0]_{(px1)} & [0]_{(px1)} & \cdots & P_{G_{(q-1)}(px1)} \\ [0]_{(px1)} & [0]_{(px1)} & [0]_{(px1)} & \cdots & [0]_{(px1)} \end{bmatrix}_{((q*p) \times (q-1))} \quad (82)$$

$$Jac_{c_G c_L} = \begin{bmatrix} \gamma_{(1xp)} & [0]_{(1xp)} & [0]_{(1xp)} & \cdots & [0]_{(1xp)} & [0]_{(1xp)} \\ [0]_{(1xp)} & \gamma_{(1xp)} & [0]_{(1xp)} & \cdots & [0]_{(1xp)} & [0]_{(1xp)} \\ [0]_{(1xp)} & [0]_{(1xp)} & \gamma_{(1xp)} & \cdots & [0]_{(1xp)} & [0]_{(1xp)} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ [0]_{(1xp)} & [0]_{(1xp)} & [0]_{(1xp)} & \cdots & \gamma_{(1xp)} & [0]_{(1xp)} \end{bmatrix}_{((q-1) \times (q*p))} \quad (83)$$

$$Jac_{c_G c_G} = \begin{bmatrix} \sigma & 0 & 0 & \cdots & 0 \\ \varepsilon & \sigma & 0 & \cdots & 0 \\ 0 & \varepsilon & \sigma & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \sigma \end{bmatrix}_{((q-1) \times (q-1))} \quad (84)$$

$$Jac_{model} = \begin{bmatrix} Jac_{c_L c_L} & Jac_{c_L c_G} \\ Jac_{c_G c_L} & Jac_{c_G c_G} \end{bmatrix}_{((q*p+(q-1)) \times (q*p+(q-1)))} \quad (85)$$

$$\alpha = \frac{Q_L(q-1)}{\beta V_{co}} \quad (86)$$

$$\alpha_q = \frac{Q_L}{V_{mt}} \quad (87)$$

$$\varepsilon = \frac{Q_G(q-1)}{(1-\beta)V_{co}} \quad (88)$$

$$\delta = \frac{k_L a \beta}{(1-\beta)} \quad (89)$$

$$\gamma_{(1 \times p)} = \delta [1 \quad 0 \quad \cdots \quad 0]_{(1 \times p)} \quad (90)$$

$$\sigma = -\varepsilon - \frac{\delta}{He} \quad (91)$$

$$\psi_{r(n \times p)} = \frac{dr_l}{d[c_i]_{L_j}} = \frac{d}{d[c_i]_{L_j}} \left(k_l \prod_{i=1}^p [c_i]_{L_j}^{\alpha_{i,l}} \right) \quad (92)$$

$$P_{Lj=1 \dots (q-1)(p \times p)} = -\alpha I_{(p \times p)} - k_L a \begin{bmatrix} 1 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 0 \end{bmatrix}_{(p \times p)} + v_{(p \times n)} \psi_{r(n \times p)} \quad (93)$$

$$P_{Lj=q(p \times p)} = -\alpha_q I_{(p \times p)} + v_{(p \times n)} \psi_{r(n \times p)} \quad (94)$$

$$P_{G(p \times 1)} = \frac{k_L a R T}{H e} \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}_{(p \times 1)} \quad (95)$$

being I the identity matrix and ψ_r an $n \times p$ matrix (Equation 94) that relates the derivatives of the vector of reaction rates r_l with respect to the state variables in each tank that forms the system ($j = 1, \dots, q$).

Stoichiometry matrix for the first case study: phenol degradation by electro-Fenton process (final)

Species\Reaction	R27	R28	R29	R30	R31	R32	R33	R34	R35	R36	R37	R38	R39	R40	R41	R42	R43	R44	R45	R46	R47	R48	R49	R50	R51	R52
[PROP]	0	0	0	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[GLYOX]	0	0	0	0	1	0	-1	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
[DHpBQ]	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[DHOac]	0	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[DHDac]	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[DOB]	0	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[ACRac]	0	0	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0
[HPac]	0	0	0	0	0	0	0	0	0	0	0	0	1	-1	-1	0	0	0	0	0	0	0	0	0	0	0
[OPac]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0	0	0	0	0
[MLO]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0	0	0	0
[TAR]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	-1	-1	0	0	0	0	0	0	0
[ACE]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	-1	-1	-1	0	0	0
[KETO]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	0
[OXA]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	-1	-1	0
[FOR]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	-1

Appendix E. Lower and upper bounds for the parameter estimation in the first case study

Table 26 – Lower and upper bounds established for the parameter estimation in the first case study.

Kinetic constants (mol ⁻¹ L s ⁻¹)	Lower bound	Upper bound
k_1	1.5	10
k_2	55	81
k_3	1x10 ⁹	1x10 ¹⁰
k_4	1x10 ⁹	1x10 ¹⁰
k_5	1x10 ⁹	1x10 ¹⁰
k_6	1x10 ⁶	1x10 ⁹
k_7	1x10 ⁹	1x10 ¹⁰
k_8	1x10 ⁸	1x10 ¹⁰
k_9	1x10 ⁹	1x10 ¹⁰
k_{10}	1x10 ⁸	1x10 ¹⁰
k_{11}	1x10 ¹⁰	1x10 ¹¹
k_{12}	1x10 ⁹	1x10 ¹⁰
k_{13}	1x10 ⁹	1x10 ¹¹
k_{14}	1x10 ⁵	1x10 ⁶
k_{15}	1x10 ⁷	1x10 ⁹
k_{16}	1x10 ⁷	1x10 ⁹
k_{17}	1x10 ⁶	1x10 ⁸
k_{18}	1x10 ⁹	1x10 ¹⁰
k_{19}	1x10 ⁹	1x10 ¹²
k_{20}	1x10 ⁹	1x10 ¹⁰
k_{21}	1x10 ¹⁰	1x10 ¹¹
k_{22}	1x10 ⁷	1x10 ⁸
k_{23}	1x10 ⁸	1x10 ⁹
k_{24}	1x10 ⁸	1x10 ⁹
k_{25}	1x10 ⁷	1x10 ⁸
k_{26}	1x10 ⁶	1x10 ⁷
k_{27}	1x10 ⁸	1x10 ⁹
k_{28}	1x10 ⁷	1x10 ⁸
k_{29}	1x10 ⁷	1x10 ⁸
k_{30}	1x10 ⁸	1x10 ⁹
k_{31}	1x10 ⁷	1x10 ⁹
k_{32}	1x10 ⁸	1x10 ⁹

Table 26 (continued)

Kinetic constants (mol⁻¹ L s⁻¹)	Lower bound	Upper bound
k_{33}	1×10^9	1×10^{10}
k_{34}	1×10^7	1×10^8
k_{35}	1×10^8	1×10^9
k_{36}	1×10^8	1×10^9
k_{37}	1×10^8	1×10^9
k_{38}	0.1×10^8	1×10^9
k_{39}	1×10^8	1×10^9
k_{40}	1×10^7	1×10^8
k_{41}	1×10^8	1×10^9
k_{42}	1×10^8	1×10^9
k_{43}	1×10^8	1×10^9
k_{44}	1×10^8	1×10^9
k_{45}	0.1×10^8	1×10^9
k_{46}	0.1×10^8	1×10^9
k_{47}	1×10^6	1×10^7
k_{48}	1×10^6	1×10^7
k_{49}	1×10^7	1×10^8
k_{50}	1×10^7	1×10^8
k_{51}	1×10^9	1×10^{10}
k_{52}	1×10^7	1×10^8

Stoichiometry matrix for the second case study: treatment of ciprofloxacin in aqueous solution by ozonation process (final)

Species\Reaction	R41	R42	R43	R44	R45	R46	R47	R48
[O ₃]	0	-1	0	-1	0	-1	0	-1
[HO ₂ ⁻]	0	0	0	0	0	0	0	0
[HO ₂ [•]]	0	0	0	0	0	0	0	0
[O ₃ ^{-•}]	0	0	0	0	0	0	0	0
[O ₂ ^{-•}]	0	0	0	0	0	0	0	0
[HO ₃ [•]]	0	0	0	0	0	0	0	0
[HO [•]]	-1	0	-1	0	-1	0	-1	0
[HO ₄ [•]]	0	0	0	0	0	0	0	0
[H ₂ O ₂]	0	0	0	0	0	0	0	0
[CIP]	0	0	0	0	0	0	0	0
[C ₁₆ H ₁₇ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₁₅ H ₁₆ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₁₄ H ₁₅ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₁₃ H ₁₄ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₁₂ H ₁₃ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₁₁ H ₁₂ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₁₀ H ₁₁ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₉ H ₁₀ FN ₃ O ₃]	0	0	0	0	0	0	0	0
[C ₈ H ₉ FN ₃ O ₃]	-1	-1	0	0	0	0	0	0
[C ₇ H ₈ FN ₃ O ₃]	1	1	-1	-1	0	0	0	0
[C ₆ H ₇ FN ₃ O ₃]	0	0	1	1	-1	-1	0	0
[C ₅ H ₆ FN ₃ O ₃]	0	0	0	0	1	1	-1	-1
[C ₄ H ₅ FN ₃ O ₃]	0	0	0	0	0	0	1	1

Appendix H. Correction of the experimental concentrations of TOC

In each experiment of CIP ozonation, the initial concentration of TOC is due to the CIP presence. According to its molecular formula ($C_{17}H_{18}FN_3O_3$), this antibiotic has 17 carbon atoms. Therefore, the initial TOC value was calculated from the initial CIP concentration as follows:

$$[TOC]_0 = 17[CIP]_0 \quad (96)$$

given the initial concentrations of CIP and TOC in mol L^{-1} .

The result for each experiment was compared to its respective measured value. Differences between both values were found. Then, the initial calculated value was divided by the initial measured one and a correction factor was determined. Afterward, the remaining values of TOC concentrations corresponding to the same experiment were corrected by this factor. This correction procedure was carried out for each one experiment. In this study, all the work was made using the corrected values of TOC concentrations.

Table 27 – Calculated initial concentrations of TOC and correction factors.

Experiment	$[CIP]_0$ (mol L^{-1})	Measured $[TOC]_0$ (mol L^{-1}) (Bardauil, 2012)	Calculated $[TOC]_0$ (mol L^{-1}) (present work)	Relative error (%)	Correction factor
1	4.72×10^{-5}	9.16×10^{-4}	8.02×10^{-4}	14.14	8.76×10^{-1}
2	4.78×10^{-5}	8.25×10^{-4}	8.12×10^{-4}	1.55	9.85×10^{-1}
3	4.59×10^{-5}	9.82×10^{-4}	7.80×10^{-4}	25.97	$7. \times 10^{-1}$
4	7.83×10^{-5}	1.38×10^{-3}	1.33×10^{-3}	3.86	9.63×10^{-1}
5	4.73×10^{-5}	1.01×10^{-3}	8.04×10^{-4}	25.98	7.94×10^{-1}
6	4.74×10^{-5}	1.06×10^{-3}	8.07×10^{-4}	31.92	7.58×10^{-1}
8	4.98×10^{-5}	9.50×10^{-4}	8.47×10^{-4}	12.22	8.91×10^{-1}
9	1.50×10^{-5}	3.18×10^{-4}	2.56×10^{-4}	24.30	8.04×10^{-1}
10	1.51×10^{-5}	2.54×10^{-4}	2.57×10^{-4}	1.07	1.01
11	4.70×10^{-5}	8.85×10^{-4}	8.00×10^{-4}	10.69	9.03×10^{-1}
12	7.52×10^{-5}	1.49×10^{-3}	1.28×10^{-3}	16.16	8.61×10^{-1}
13	7.79×10^{-5}	1.48×10^{-3}	1.32×10^{-3}	11.51	8.97×10^{-1}

Appendix I. Lower and upper bounds used in the parameter estimation for the second case study

Table 28 – Lower and upper bounds established for the parameter estimation in the second case study.

Parameter	Unit	Lower bound	Upper bound
$k_L a$	s^{-1}	0	15×10^{-2}
β	Dimensionless	0.8	0.99
k_1	$\text{mol}^{-1} \text{ L s}^{-1}$	40	80
k_2	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^5	1×10^7
k_3	s^{-1}	1×10^4	1×10^6
k_4	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^9	1×10^{11}
k_5	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_6	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^9	1×10^{11}
k_7	s^{-1}	3.4×10^4	4×10^4
k_8	s^{-1}	1×10^4	1×10^6
k_9	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{10}	s^{-1}	1×10^3	1×10^5
k_{11}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^9	1×10^{11}
k_{12}	s^{-1}	0.100	0.250
k_{13}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{14}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{15}	$\text{mol}^{-1} \text{ L s}^{-1}$	2×10^6	1×10^8
k_{16}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{17}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{18}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^4	1×10^6
k_{19}	$\text{mol}^{-1} \text{ L s}^{-1}$	20	30
k_{20}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{21}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{22}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^8	1×10^{10}
k_{23}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^9	2.25×10^{10}
k_{24}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^4	5×10^4
k_{25}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{26}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{27}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}

Table 28 (continued)

Parameter	Unit	Lower bound	Upper bound
k_{28}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{29}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{30}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{31}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{32}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{33}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{34}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{35}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{36}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{37}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{38}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{39}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{40}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{41}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{42}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{43}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{44}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{45}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{46}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7
k_{47}	$\text{mol}^{-1} \text{ L s}^{-1}$	1×10^6	1×10^{10}
k_{48}	$\text{mol}^{-1} \text{ L s}^{-1}$	0.1	1×10^7

When the trust-region-reflective algorithm was used and θ'_1 was estimated, the upper bound for the volumetric mass transfer coefficient $k_L a$ was equal to 1.