



XXII CONGRESSO
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SENSITIVITY ANALYSIS OF A MODEL OF ADVANCED OXIDATION PROCESSES

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ABSTRACT – *This work focuses on the analytical sensitivity analysis (ASA) of a model of advanced oxidation processes (AOPs) applied to the treatment of ciprofloxacin (CIP) in aqueous solution by ozonation process. The ASA was carried out using the analytical Jacobian matrix of the system and the forward method of CVODES solver of SUNDIALS. The sensitivities of the model outputs were computed with respect to the model parameters: volumetric mass transfer coefficient in the liquid phase (k_{LA}) and the liquid fraction (β). As result, the influence of these parameters on the CIP and gas phase ozone concentrations was analyzed.*

1. INTRODUCTION

Mathematical models are used to describe complex processes. Using models it is possible to carry out process simulations, increasing the knowledge about the process itself and improving the understanding of the system behavior (McClean, McAuley, 2012). Sensitivity analyses are powerful tools in the development of models. The information generated by a sensitivity analysis (SA) is useful in the evaluation of optimization gradients and in uncertainty analysis in the process of parameter estimation (Petzold *et al.*, 2006; McClean, McAuley, 2012). Also, by means of a SA it is possible to study the influence of model parameters on the model predictions and to determine the parameters that have a greater influence on the model responses (Petzold *et al.*, 2006; Hindmarsh, Serban, 2009; Miao *et al.*, 2011). In addition, in models with a few number of parameters the sensitivity functions can be analyzed visually (McClean, McAuley, 2012).

A general model of advanced oxidation processes (AOPs) was developed in a previous work (Abreu *et al.*, 2017). It was based on the kinetic information and the mole balance equations of species in liquid and gas phases. The model was validated using available experimental data from the ciprofloxacin (CIP) degradation by ozonation process. In the present work, the analytical sensitivity analysis (ASA) of the model proposed by Abreu *et al.* (2017) is carried out. The sensitivities of the model outputs are computed with respect to the model parameters: volumetric mass transfer coefficient in the liquid phase (k_{LA}) and the liquid fraction (β). In the ASA the analytical Jacobian matrix of the system and the forward method of CVODES solver (Serban, Hindmarsh, 2005) of SUNDIALS (SUite of Nonlinear and Differential/ALgebraic equation Solvers) (Hindmarsh *et al.*, 2005) are used.

2. ANALYTICAL SENSITIVITY ANALYSIS



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The model outputs are the concentrations of species in liquid and gas phases in each tank that was assumed in order to represent the system (Abreu *et al.*, 2017). The ASA of the model outputs was carried out with respect to the model parameters: k_{LA} and β . Nominal values for these parameters are used ($k_{LA} = 7.5e-3 \text{ s}^{-1}$, and $\beta = 0.85$) (Beltrán *et al.*, 2000). In the analysis, the forward method of CVODES solver (Serban, Hindmarsh, 2005) of SUNDIALS (Hindmarsh *et al.*, 2005) is used. CVODES is an ODE solver for stiff and nonstiff problems and has incorporated sensitivity analysis capabilities (Hindmarsh, Serban, 2009). When using this method, CVODES computes the sensitivities with respect to the model parameters. This method is recommendable for problems with few parameters (Petzold *et al.*, 2006; Hindmarsh, Serban, 2009). In the forward sensitivity analysis (FSA), CVODES integrates a combined system of ODEs composed of the system of ODEs describing the dynamic process and the sensitivity equations (Hindmarsh, Serban, 2009). In order to perform the ASA it was necessary to obtain the analytical Jacobian matrix for the study case.

2.1. Analytical Jacobian Matrix

First, the general system's analytical Jacobian matrix was constructed based on the general model proposed by Abreu *et al.* (2017) using a block strategy. In this case, a square ($qxp+(q-1)$) matrix was obtained. This matrix was compared to the numerical Jacobian matrix computed by finite differences ($h = 10e-10$) in Matlab[®]. In the comparison process, a viable point for the concentrations of species and nominal values for model parameters were used. In addition, different number of tanks representing the system (q), number of species in the liquid phase (p) and number of reactions (n) were employed. In all cases, a relative error of $1e-4$ between the analytical and numerical Jacobian matrices was considered as acceptable. When applied to the case study ($q = 3$, $p = 12$, and $n = 24$) a 38-by-38 matrix was obtained. Equation 1 describes the analytical Jacobian matrix for the case study. Equations 2 to 8 illustrate the notation employed in the Jacobian matrix development. V_{co} , V_{lr} , Q_L , and Q_g are the column volume (L), the mixing tank volume (L), the liquid flowrate and the gas flowrate (L/s), respectively. He represents the dimensionless Henry's law constant, $\underline{\underline{\pi_r}}$ is the stoichiometric matrix, and $\underline{\underline{\psi_r}}$ corresponds with the analytical Jacobian matrix of the generation term.

2. RESULTS AND DISCUSSIONS

As result of the FSA, the sensitivities with respect to k_{LA} and β were computed. This information is available in each tank of the system. Figure 1 shows the sensitivity functions of CIP and gas phase ozone concentrations at the column outlet for one experiment. It is possible to observe that the influence of k_{LA} and β on the CIP concentration is insignificant for times higher than 150 s. This time corresponds to the time at which the CIP concentration takes a value equal to zero for the considered experiment. This indicates that experimental data for times above 150 s could be unnecessary for estimating the model parameters. However, k_{LA} as well as β have higher influence on the ozone concentration in the gas phase.

$$Jac_{syst} = \begin{bmatrix} \underline{P_{L_1}}_{(pxp)} & \alpha \underline{I}_{(pxp)} & \underline{[0]}_{(pxp)} & \underline{P_g}_{(px1)} & \underline{[0]}_{(px1)} \\ \underline{[0]}_{(pxp)} & \underline{P_{L_2}}_{(pxp)} & \underline{[0]}_{(pxp)} & \underline{[0]}_{(px1)} & \underline{P_g}_{(px1)} \\ \alpha_q \underline{I}_{(pxp)} & \underline{[0]}_{(pxp)} & \underline{P_{L_q}}_{(pxp)} & \underline{[0]}_{(px1)} & \underline{[0]}_{(px1)} \\ \delta \underline{[1 \dots 0]}_{(1xp)} & \underline{[0]}_{(1xp)} & \underline{[0]}_{(1xp)} & -\varepsilon - \left(\frac{\delta}{He}\right) & 0 \\ \underline{[0]}_{(1xp)} & \delta \underline{[1 \dots 0]}_{(1xp)} & \underline{[0]}_{(1xp)} & \varepsilon & -\varepsilon - \left(\frac{\delta}{He}\right) \end{bmatrix} \quad (1)$$

$$\underline{P_{L_{i=1 \dots (q-1)}}}_{(pxp)} = -\alpha \underline{I}_{(pxp)} - k_L a \begin{bmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{bmatrix}_{(pxp)} + \underline{\pi_r}_{(pxn)} \underline{\psi_{r_{i=1 \dots (q-1)}}}_{(npx)} \quad (2)$$

$$\underline{P_{L_q}}_{(pxp)} = -\alpha_q \underline{I}_{(pxp)} + \underline{\pi_r}_{(pxn)} \underline{\psi_r}_{(npx)} \quad (3)$$

$$\alpha = Q_L(q-1)/\beta V_{co} \quad (4)$$

$$\varepsilon = Q_g(q-1)/(1-\beta)V_{co} \quad (5)$$

$$\delta = \beta/(1-\beta) \quad (6)$$

$$\alpha_q = Q_L/V_{tr} \quad (7)$$

$$\underline{P_g}_{(px1)} = (k_L a/He) \underline{[10 \dots 0]}'_{(px1)} \quad (8)$$

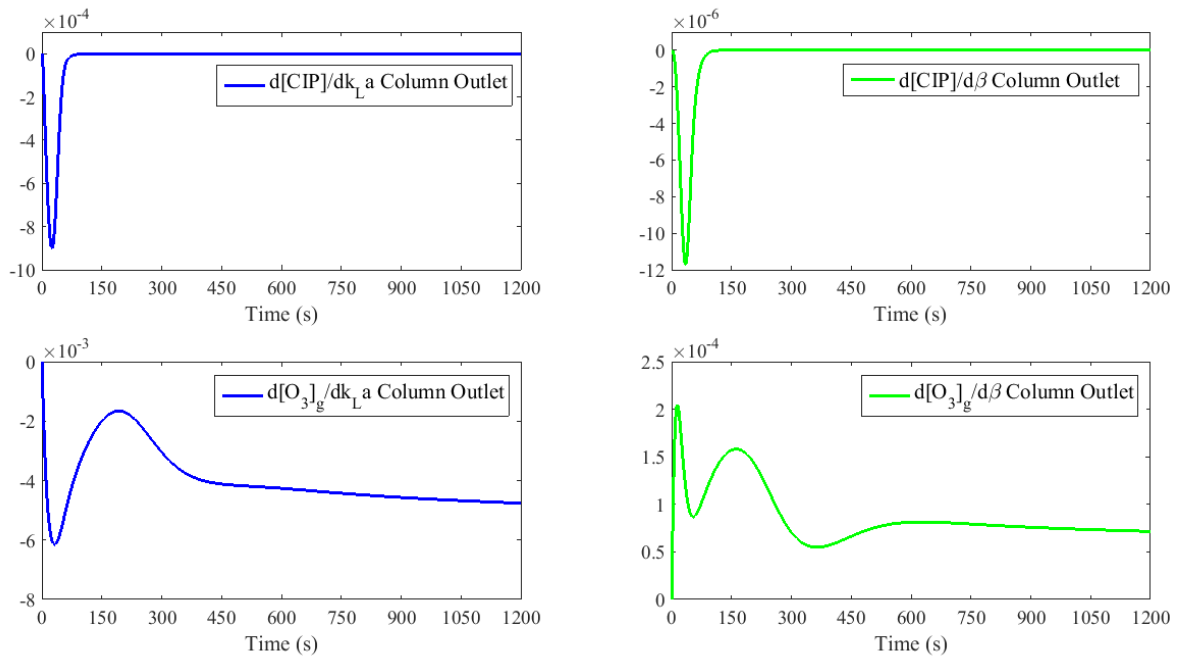


Figure 1 – Sensitivities of CIP and gas phase ozone concentrations at the column outlet with respect to the model parameters: $k_{L}a$ and β . Experimental conditions: $\text{pH} = 5.4$, $[\text{O}_3]_{g_0} = 4.69\text{e-}4 \text{ mol/L}$, and $[\text{CIP}]_0 = 1.50\text{e-}5 \text{ mol/L}$.



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4. CONCLUSIONS

The forward sensitivity analysis of the model describing the ciprofloxacin degradation by ozonation process was conducted. The general analytical Jacobian matrix was constructed and compared to the numerical Jacobian matrix. The Jacobian matrix was applied to the case study in order to compute the sensitivities. As result, the effect of the parameters k_{La} and β on the model outputs was analyzed. It was possible to observe that both parameters have a higher influence on the gas phase ozone concentration than ciprofloxacin concentration.

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6. ACKNOWLEDGMENTS

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