SUPPORTING INFORMATION

Combining multivariate curve resolution and lumped kinetic modelling for the analysis of lignin degradation by copper-catalyzed Fenton-like systems

Andrea M. Berkovic [a,b*] , Mariana R. Costante [a], Fernando S. García Einschlag [a*]

Number of pages: 10
Number of figures: 13
Number of tables: 1

A. Description of the control experiments (Section 3.1)

In order to analyze the system behavior, in the absence of either the oxidant or the catalyst, several control experiments were conducted. Figure S1 compares the absorbance decay profiles at 280 nm recorded in the presence and in the absence of Cu(II). Results show that the initial rate of lignin transformation is about 30-fold higher in the presence of the catalyst.
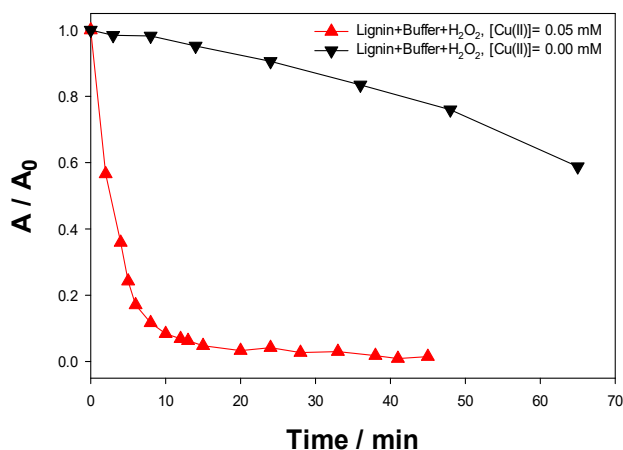

Figure S1. Comparison of kinetic profiles recorded in the presence and in the absence of Cu(II). Conditions: [Lignin] = 0.025 mM, [Buffer] = 0.05 M, [H_2O_2] = 50 mM, T= 80ºC, pH = 8.0.

With the aim of characterizing a possible chelation effect of Cu(II) by Lignin, the spectrum recorded for a mixture containing 0.1 mM of Cu(II) and 0.025 mM of lignin was compared with that calculated by summing the spectra of single solutions with identical concentrations. Within the experimental error, no spectroscopic evidence of complex formation between Cu(II) and Lignin was found (Fig. S2).
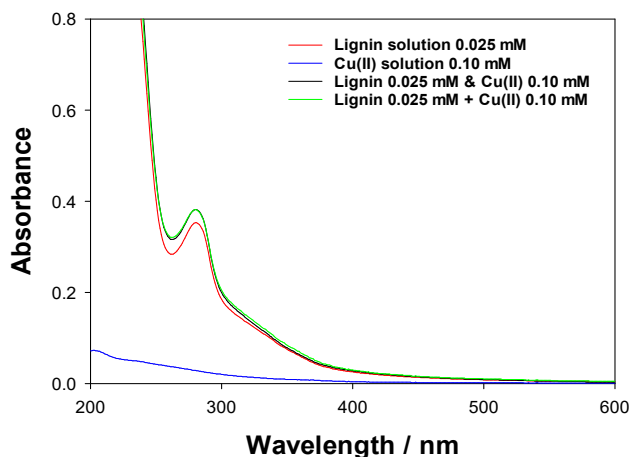

Figure S2. Comparison of the spectrum recorded for the Cu(II)/Lignin mixture (black line) with that calculated by adding individual spectra (green line). Conditions: [Lignin] = 0.025 mM, [Cu(II)] = 0.1 mM, T = 25°C, pH 7.0.

Given that the absence of spectroscopic evidence in the UV-vis range does completely not rule out some interaction of Cu(II) with Lignin and/or its intermediate transformation products, we have performed additional experiments to test the possible contribution of reaction pathways involving dissolved oxygen instead of H_2O_2. Figure S3A shows the time evolution of UV-vis spectra of a mixture containing both Lignin and Cu(II) but in the absence of added hydrogen peroxide. The results indicate only minor spectral changes after 27 hours.
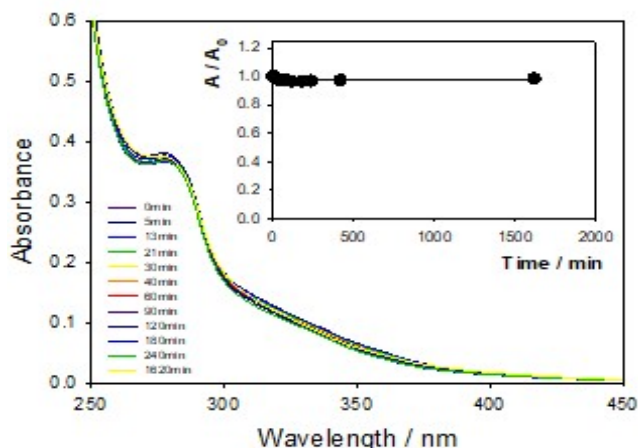

Figure S3. Time resolved spectra of a mixture of Cu(II) and Lignin in the absence of added H_2O_2. Inset: Kinetic profile recorded at 280 nm. Conditions: [Lignin] = 0.025 mM, [Cu(II)] = 0.05 mM T= 60°C, pH = 7.0.

A final assay was conducted to evaluate the contribution of Cu(II)-catalyzed reactions between intermediate lignin transformation products and dissolved oxygen. The experiment consisted of the stepwise addition of sub-stoichiometric amounts of H_2O_2. Briefly, small hydrogen peroxide amounts were spiked in the reaction mixture, at different times, in order to produce Lignin oxidation products. (Fig. S4). Upon H_2O_2 addition, fast absorbance decays were followed by long periods with relative constant absorbance values. Moreover, during the time-lapse of more than 20 hours, between the end of the second step (blue squares) and the beginning of the third step (red triangles), practically no absorbance changes were observed. The latter results suggest that, although Cu(II) species efficiently catalyze the oxidation of Lignin and its intermediate transformation product mediated by H_2O_2, no significant catalytic activity takes place for those reactions involving dissolved oxygen. Consequently, transformation reactions mediated by O_2 are negligible for the time scales associated with Cu(II) catalyzed Fenton-like systems.
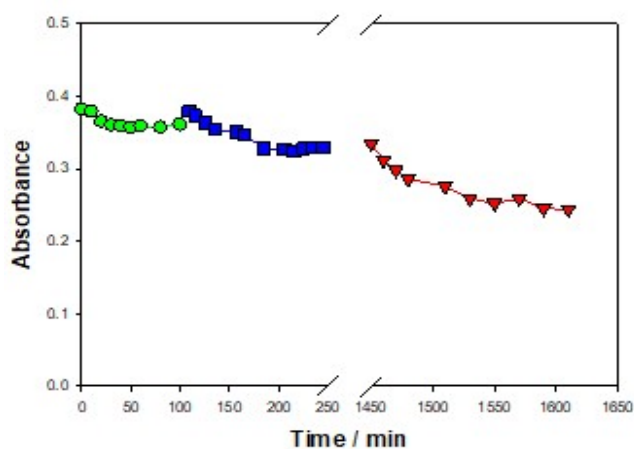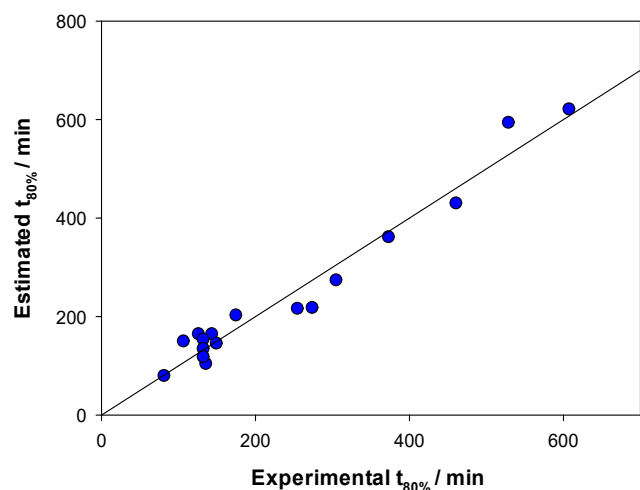

Figure S4. Pulse experiments performed by spiking sub-stoichiometric amounts of H_2O_2 at different time intervals (green circles: first pulse, blue squares: second pulse, red triangles: third pulse).
*Conditions: [Lignin] = 0.025 mM, [Cu(II)] = 0.07 mM, $[H_2O_2]_{EachPulse}$ = 4 mM, pH = 7.5 and T= 60°C.*

B. Results of the Experimental Design and the Surface Response Methodology (Section 3.2)

*Figure S5. Comparison between the experimental $t_{80\%}$ values and those estimated by the model.*
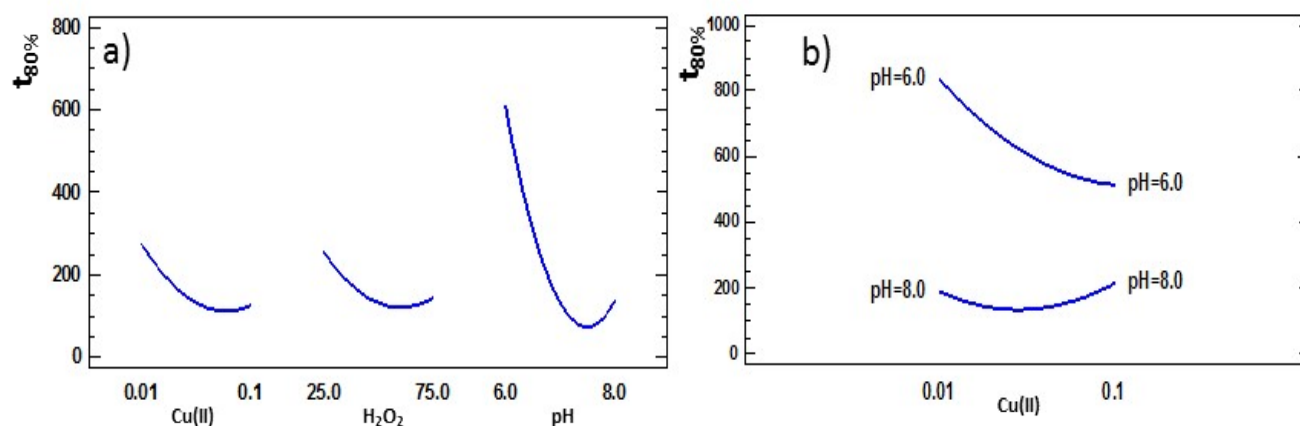
Figure S6: a) Graphical presentation of the main effects. b) Effect of the interaction between [Cu(II)] and pH on the removal time.
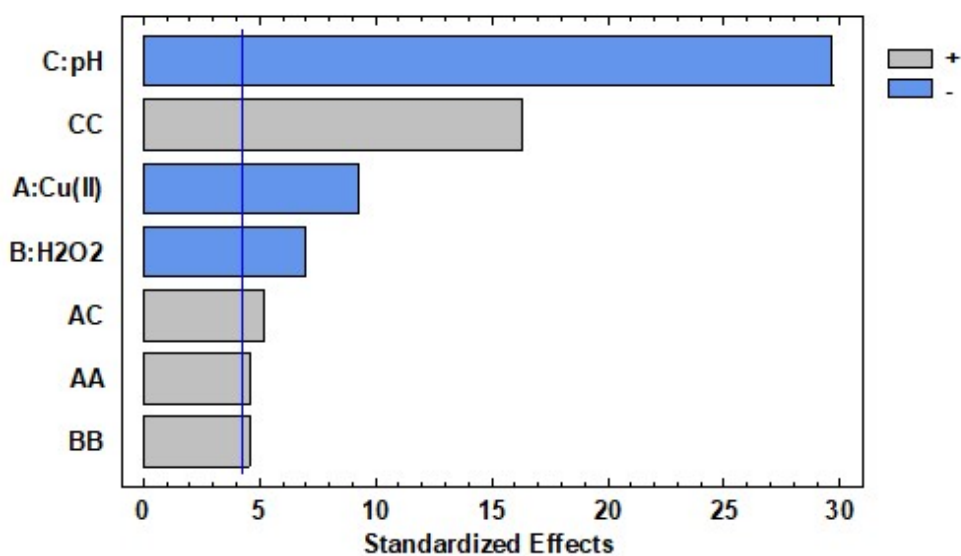

Figure S7: Pareto chart representing the standardized effects of individual factors and their interactions on the removal time of lignin. The vertical line represents the 95% confidence interval for a significant effect. The signs "-" and "+" indicate negative and positive effects, respectively.

C. Time-resolved UV-vis spectra recorded during the kinetic runs (Section 3.4.1)
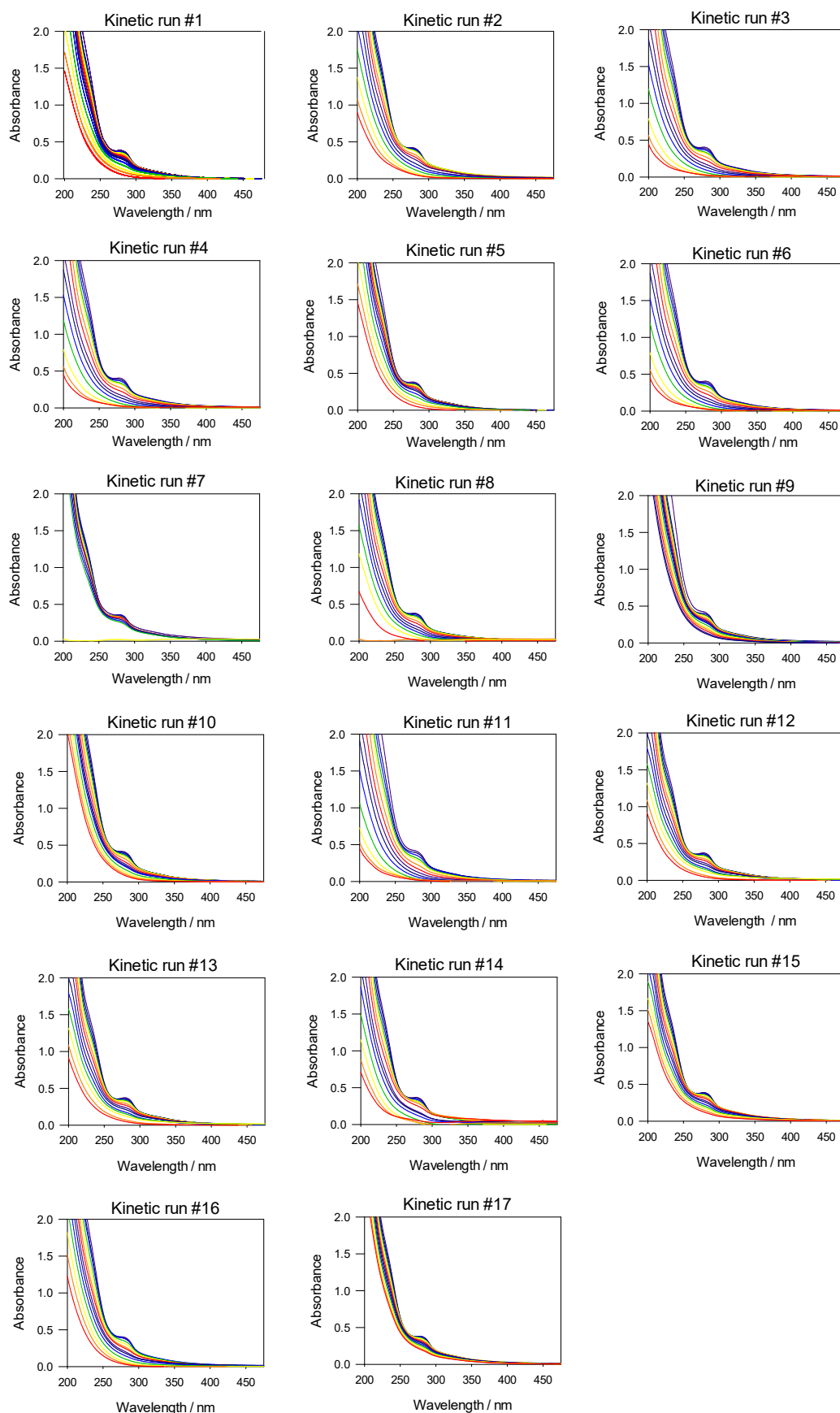
Figure S8. Time-resolved spectra recorded during the 17 kinetic runs performed under the conditions defined by the experimental design.

## D. Results obtained by MCR-ALS decomposition of time resolved spectra (Section 3.4.1)
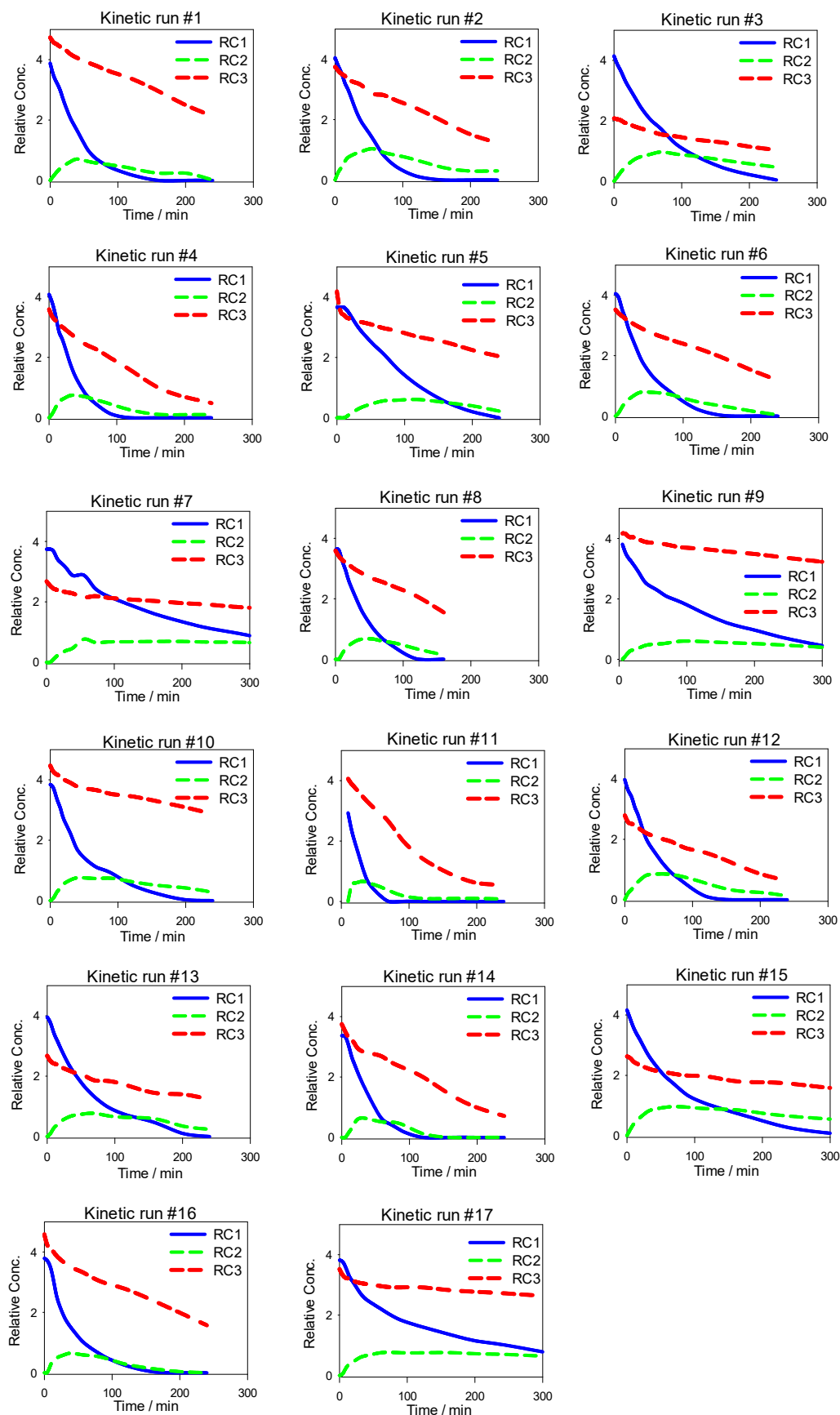

Figure S9. *Relative concentrations (RC) obtained, by MCR-ALS decomposition, for the 17 experimental runs.*

E. Parameter optimization and kinetic profiles derived from the lumped model (Section 3.4.3)

Table S1. Optimal values for the rate constants of the proposed mechanism calculated by non-linear regression fitting of the obtained kinetic profles.

Experiment #	k_1 $(mM^{-0.25}.min^{-1})$	k_2 $(mM^{-0.25}.min^{-1})$	k_3 $(mM^{-0.25}.min^{-1})$	k_4 $(mM^{+0.25}.min^{-1})$
01	3.41E-03	4.56E-03	6.73E-03	2.65E-03
02	1.13E-03	6.55E-03	6.87E-03	2.96E-03
03	1.22E-03	4.83E-03	5.47E-03	6.60E-04
04	4.32E-03	6.44E-03	9.52E-03	5.88E-03
05	1.98E-03	1.87E-03	3.58E-03	2.31E-03
06	2.33E-03	5.40E-03	7.69E-03	2.77E-03
07	2.15E-04	2.16E-03	3.48E-03	4.44E-04
08	3.81E-03	4.81E-03	7.49E-03	3.76E-03
09	9.84E-04	2.09E-03	3.67E-03	3.18E-04
10	2.94E-03	4.09E-03	4.26E-03	1.38E-03
11	2.42E-03	0.0157	0.0173	7.85E-03
12	2.48E-03	6.35E-03	7.47E-03	2.77E-03
13	2.13E-03	4.53E-03	6.00E-03	1.55E-03
14	4.13E-03	5.37E-03	0.0101	5.16E-03
15	1.34E-03	4.19E-03	3.55E-03	4.66E-04
16	4.26E-03	4.85E-03	8.35E-03	3.40E-03
17	3.14E-04	2.64E-03	3.40E-03	1.32E-04

* Simulations were performed using the following units: **mM** for concentrations, **min** for times and **mM.min^{-1}** for reaction rates.
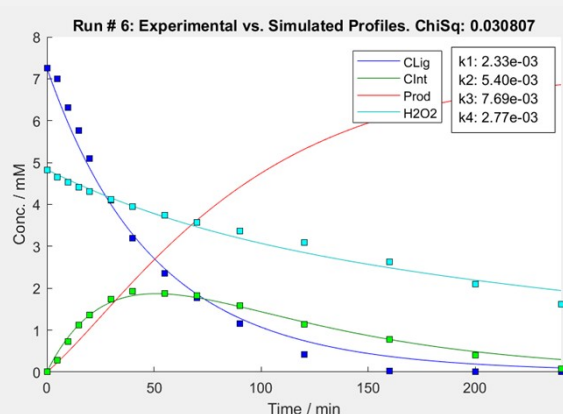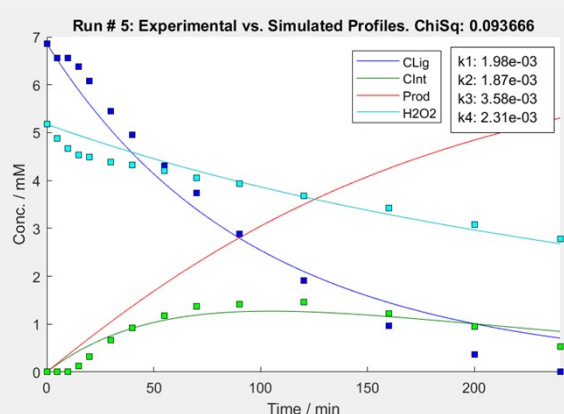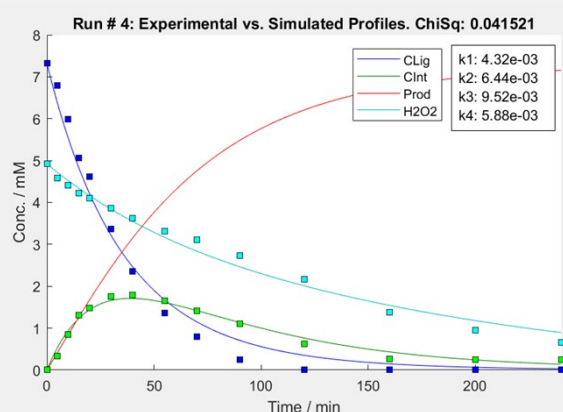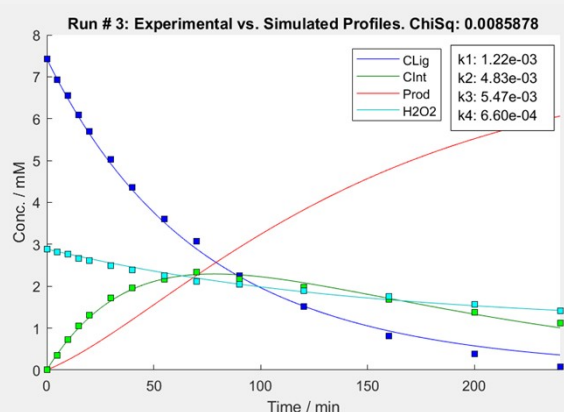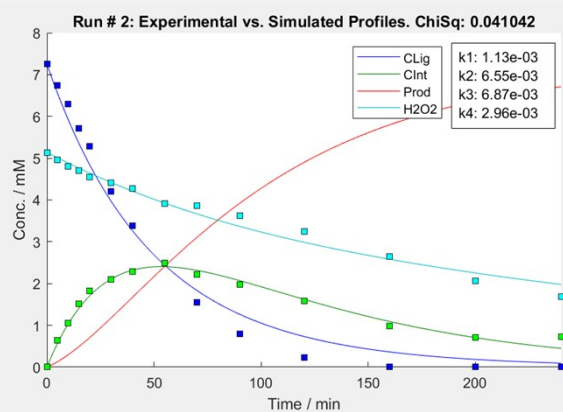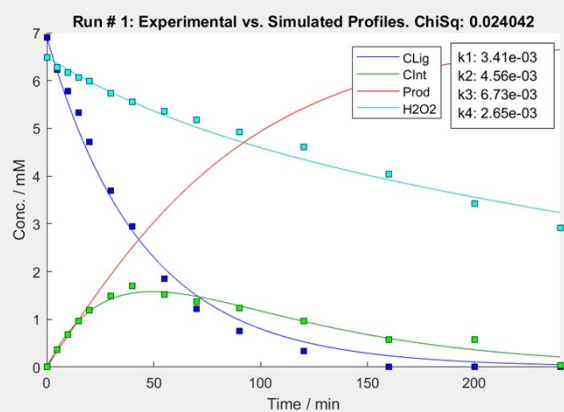
Figure S10. *Correlations between data obtained for the experimental runs 1-6 and traces simulated with the kinetic model. The red profiles correspond to the final reaction product (CO_2), whereas the profiles in blue, green, and cyan correspond to SP1, SP2, and SP3, respectively. The points represent the values obtained by the MCR-ALS algorithm (H_2O_2 profiles were scaled for comparison purposes), and the lines show the profiles calculated with the proposed mechanism.*
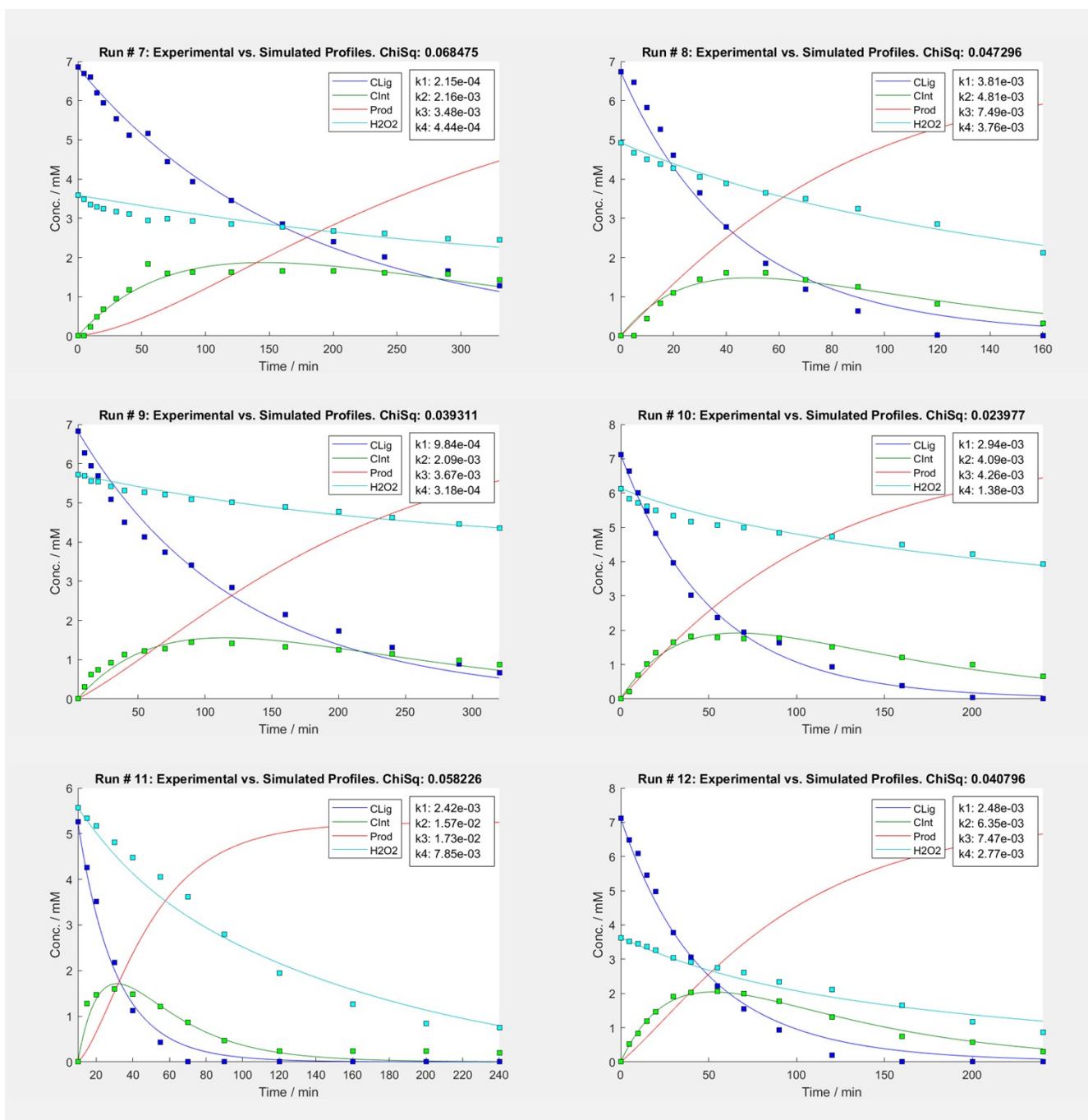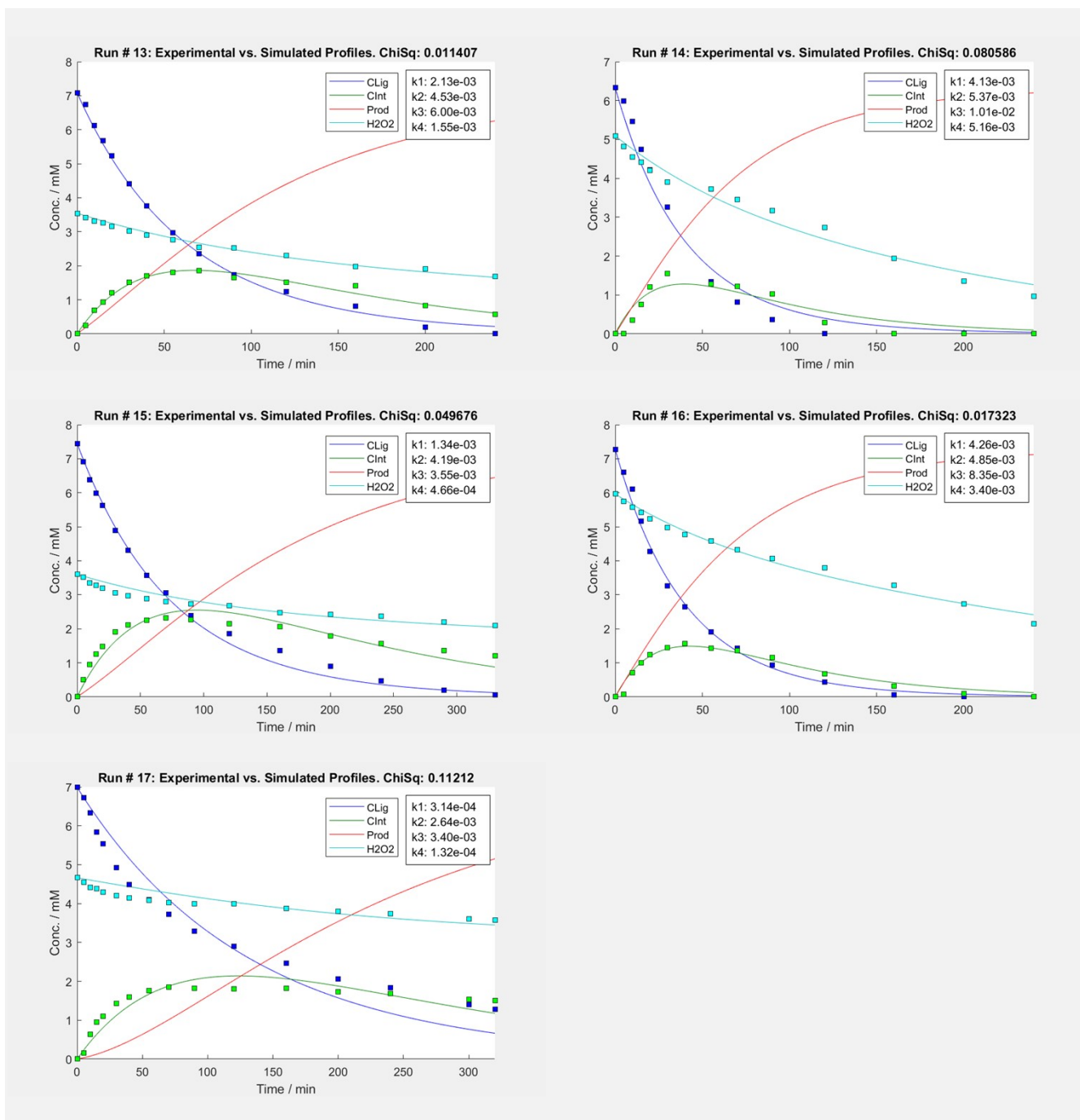
Figure S11. *Correlations between data obtained for the experimental runs 7-12 and traces simulated with the kinetic model. The red profiles correspond to the final reaction product (CO_2), whereas the profiles in blue, green, and cyan correspond to SP1, SP2, and SP3, respectively. The points represent the values obtained by the MCR-ALS algorithm (H_2O_2 profiles were scaled for comparison purposes), and the lines show the profiles calculated with the proposed mechanism.*

Figure S12. *Correlations between data obtained for the experimental runs 13-17 and traces simulated with the kinetic model. The red profiles correspond to the final reaction product (CO_2), whereas the profiles in blue, green, and cyan correspond to SP1, SP2, and SP3, respectively. The points represent the values obtained by the MCR-ALS algorithm (H_2O_2 profiles were scaled for comparison purposes), and the lines show the profiles calculated with the proposed mechanism.*

F. Evaluation of the relative contribution of hydroxyl radicals (Section 3.5)
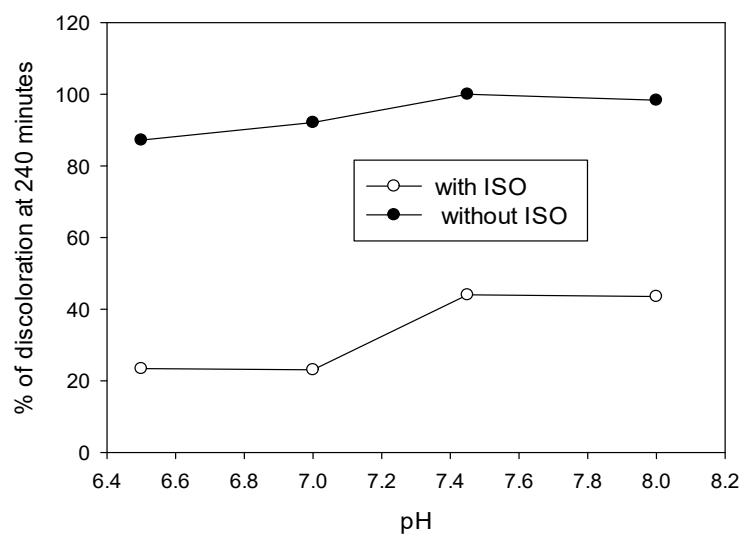
Figure S13. *Percentage of lignin discoloration (A/A$_0$x100) at 280 nm as a function of pH after 240 min of reaction, with (0.2 M) and without isopropanol. Reaction conditions: 0.025 mM of lignin, 0.055 mM of Cu(II), 50 mM of H$_2$O$_2$, pH = 6.5, 7, 7.45 y 8; and T = 60°C.*