chemengineering

Supplementary Material: Bicarbonate-Activated Hydrogen Peroxide for an Azo Dye Degradation: Experimental Design

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1. Experimental design - Adequacy check of the model

Plots of “Actual and Predicted" values for decolorization, mineralization, and total nitrogen removal are shown in Figures S1, S2, and S3, respectively. In these plots, most data were well distributed around the straight-line X = Y in a narrow area, indicating that the proposed models had an adequate approximation to the actual value.

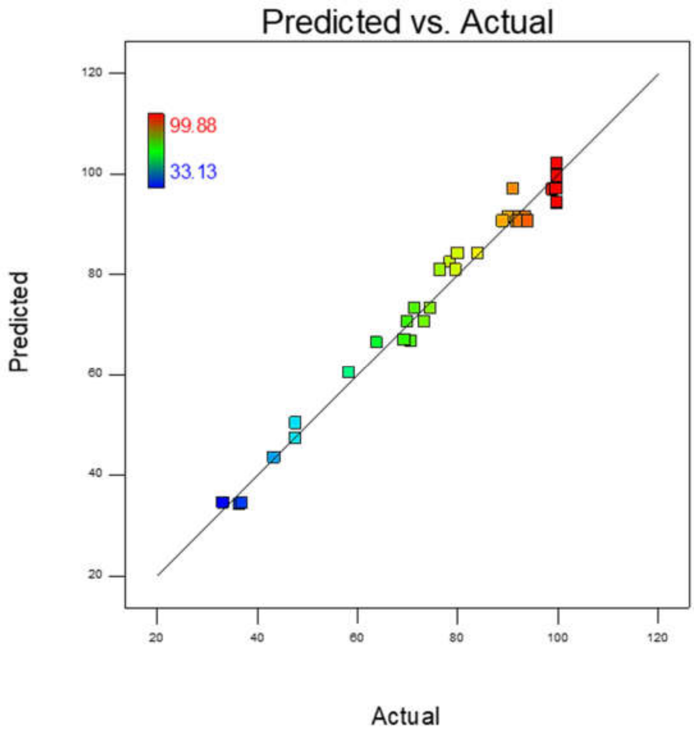

Figure S1. Predicted vs. actual values plot for decolorization.

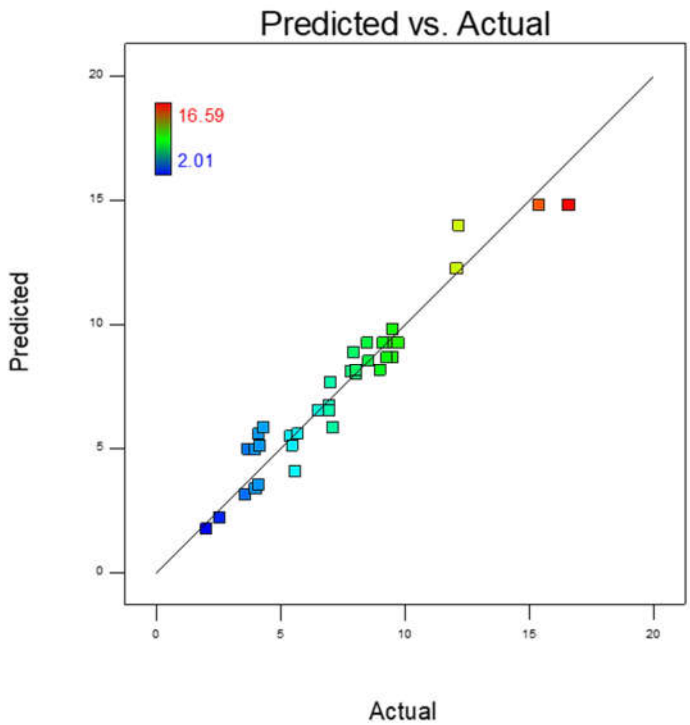

Figure S2. Predicted vs. actual values plot for mineralization.

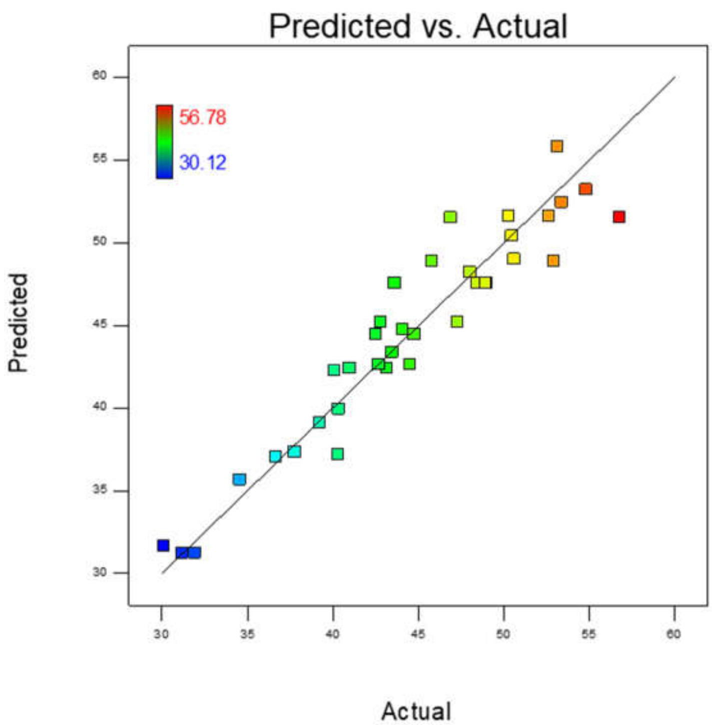

Figure S3. Predicted vs. actual values plot for total nitrogen removal.

"Residuals vs. Run" plots that evaluated decolorization (Figure S4), mineralization (Figure S5) and TN removal (Figure S6) showed that run numbers are randomly distributed around the central line, indicating the random process of the experiments.

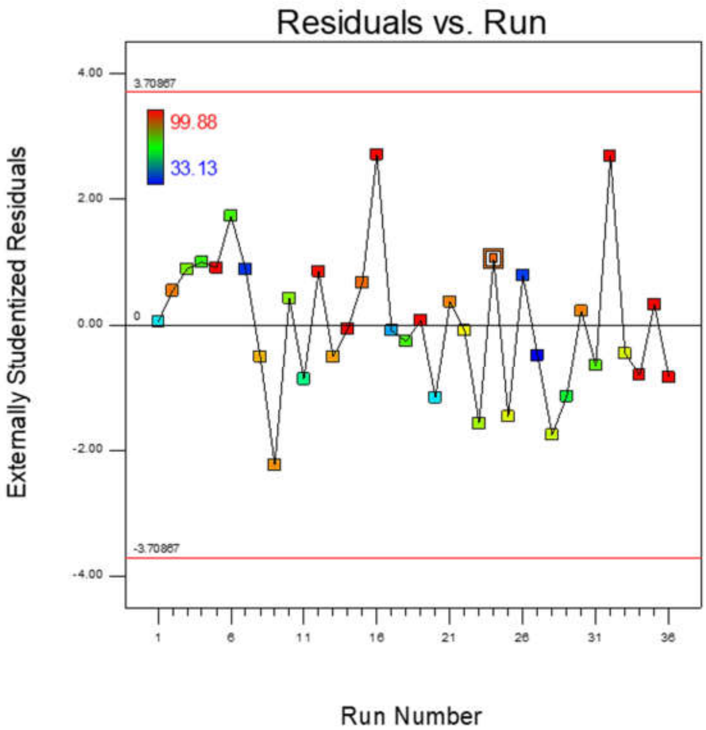

Figure S4. Residual plot for the assessment of appropriateness of the decolorization model.

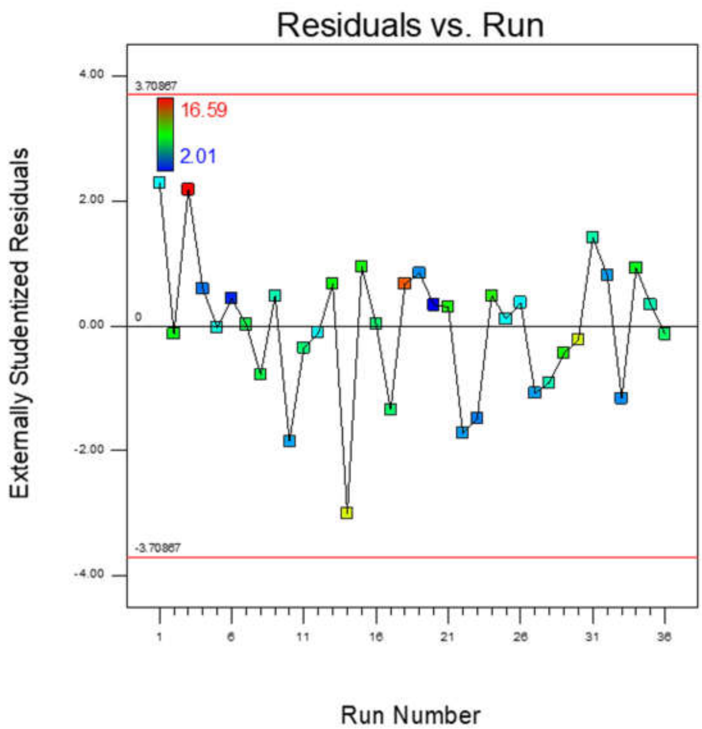

Figure S5. Residual plot for the assessment of appropriateness of the mineralization model.

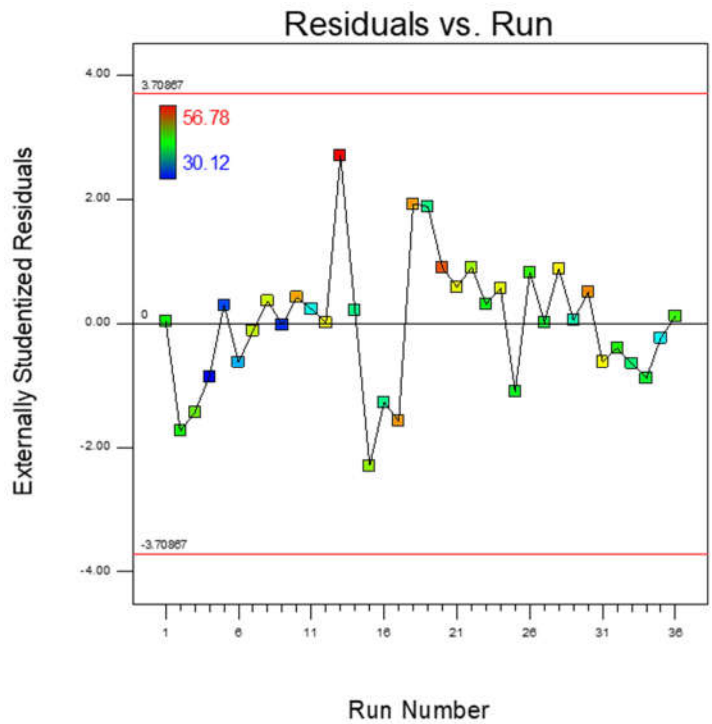

Figure S6. Residual plot for the assessment of appropriateness of the TN removal model.

"Residuals vs. Predicted" plots that evaluated decolorization (Figure S7), mineralization (Figure S8) and TN removal (Figure S9) showed random behavior and the formation of an approximately horizontal band around the residual = 0 line. This plot is also used to examine outliers. Outliers are runs with residuals outside the red lines on the plot. An outlier is an observation that is not fit well by the model.

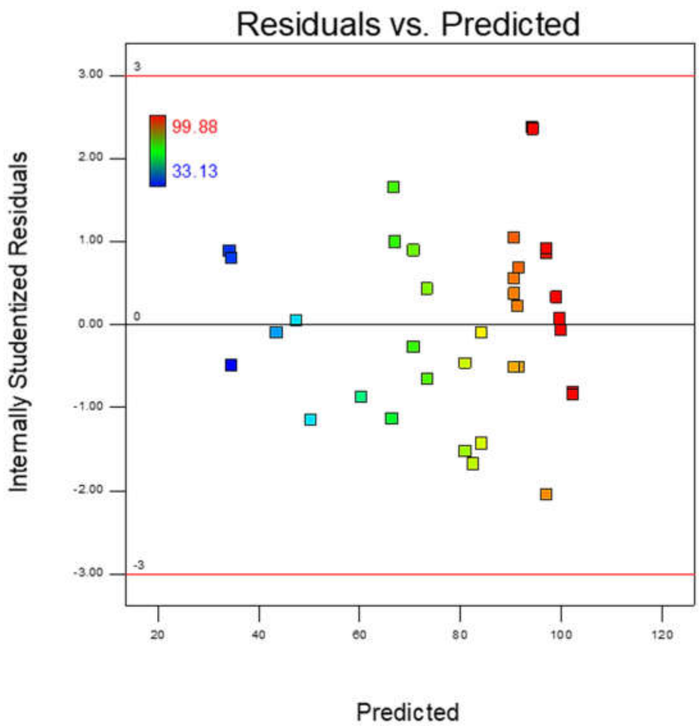

Figure S7. Studentized residuals vs. predicted response plot for the decolorization model.

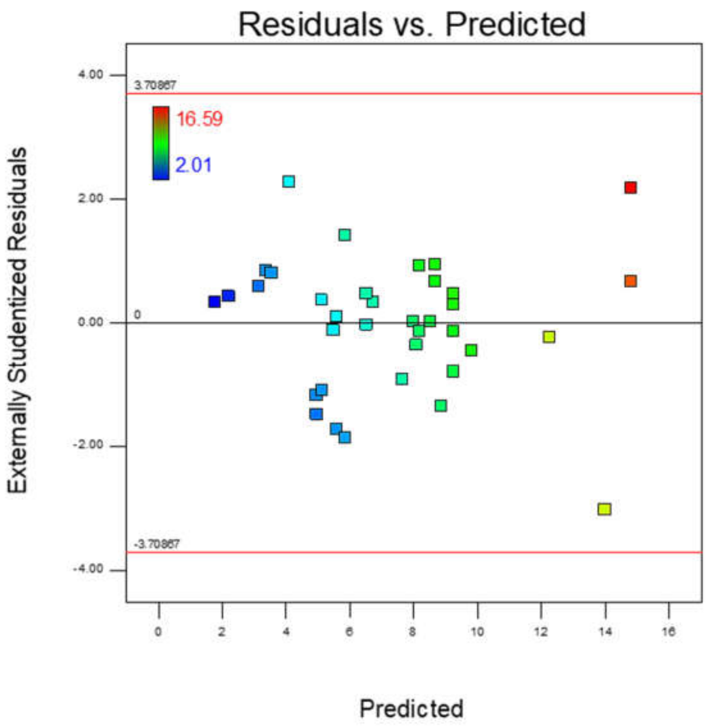

Figure S8. Studentized residuals vs. predicted response plot for the mineralization model.

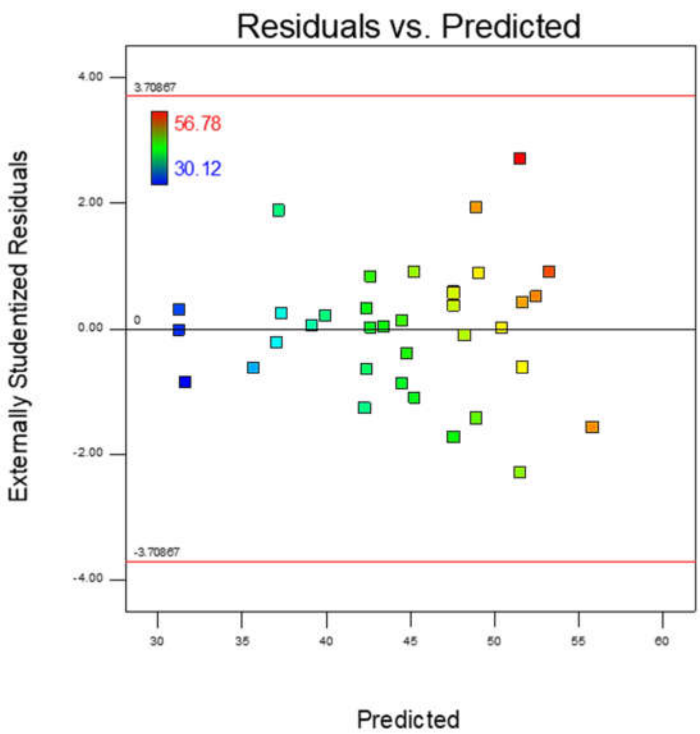

Figure S9. Studentized residuals vs. predicted response plot for the TN removal model.

2. Post-oxidation cobalt adsorption

Considering that cobalt ions (Co^{2+}) can interact with bicarbonate ions (HCO_3^-), the distribution of species, depending on the pH of the solution, is shown in Figure S10. For an aqueous solution with 9.00 μM Co^{2+} and 2.00 mM $NaHCO_3$, the predominant species in the pH range 1.0 to 6.0 is Co^{2+}, while at pH values greater than 6.0, is $CoHCO_3^+$, $CoCO_3$(s) and

$Co(OH)_2(s)$. Under reaction conditions of the Co^{2+}–BAP system, where pH varies between 8.4–8.7, $CoCO_3$ does not precipitate since the solubility product constant (Kps) is very low, as it is the Co^{2+} concentration. At pH between 5.0 and 7.0, the $CoHCO_3^+$ complex can be formed [69].

[69] Mnasri-Ghnimi, S.; Frini-Srasra, N. Removal of heavy metals from aqueous solutions by adsorption using single and mixed pillared clays. *Appl. Clay Sci.* **2019**, *179*, 105151.

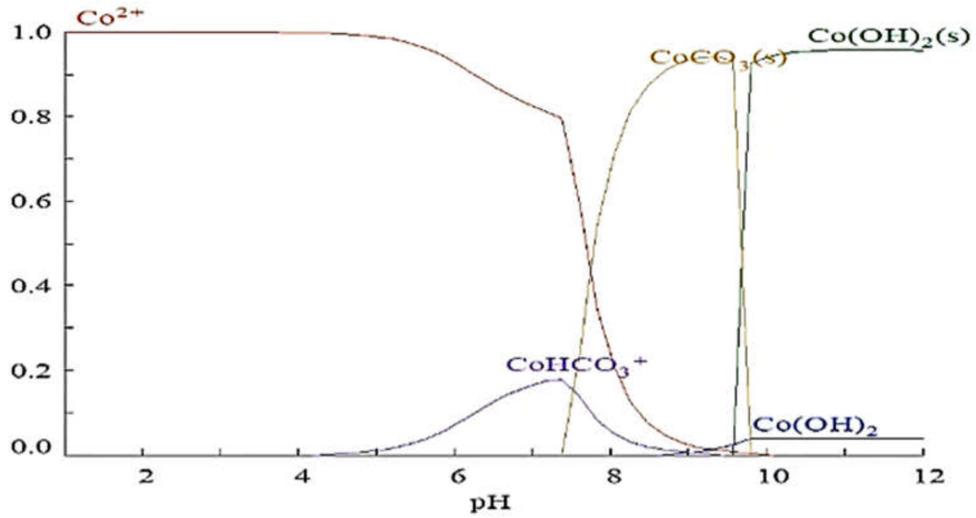

Figure S10. Diagram of cobalt species at a concentration of Co^{2+} 9.00 µM and $NaHCO_3$ 2.00 mM.

The pH of the solution is a variable to be considered in heavy metal adsorption tests due to its influence on the dissociation of metals, the formation of complexes and the modification of the surface charge of the adsorbent. The effect of pH on the removal of Co^{2+} is shown in Figure S11, where it can be observed that, by increasing the pH from 6.0 to 7.0, the removal of cobalt augmented from 22.34 to 56.74%. At a pH between 7.0 and 8.5, the removal remained constant at 56.54%. At a pH 7.0, Na^+ cations present in the interlayer space of Na-Bent clay are exchanged with Co^{2+} and $CoHCO_3^+$, where Co^{2+} was the species found in the highest proportion. It is important to clarify that $2Na^+$ ions are exchanged for a Co^{2+} cation, while the $CoHCO_3^+$ species is exchanged for a Na^+ ion, in order to preserve electroneutrality in the clay.

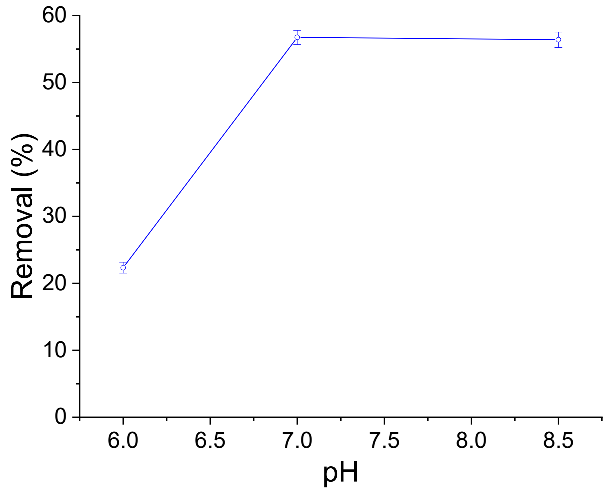

Figure S11. Effect of pH on the removal of Co^{2+} in an aqueous solution at 25 °C. Adsorption conditions: Post-oxidation solution volume = 200 mL, [Co^{2+}] = 9.00 μM, adsorbent mass = 50 mg Na–Bent, stirring speed = 300 rpm, contact time = 2 h, pH adjustment with 0.5 M HCl.

The effect of contact time on Co^{2+} adsorption using Na–Bent is shown in Figure S12. The removal of cobalt after 15 min of contact time is high (42.01%). Between 30 and 60 min it increased slightly, from 43.02 to 55.81%, and between 60 and 120 min it stabilized around 56.54. Therefore, a contact time of 120 min guaranteed equilibrium conditions for Co^{2+} adsorption using Na–Bent as the adsorbent material.

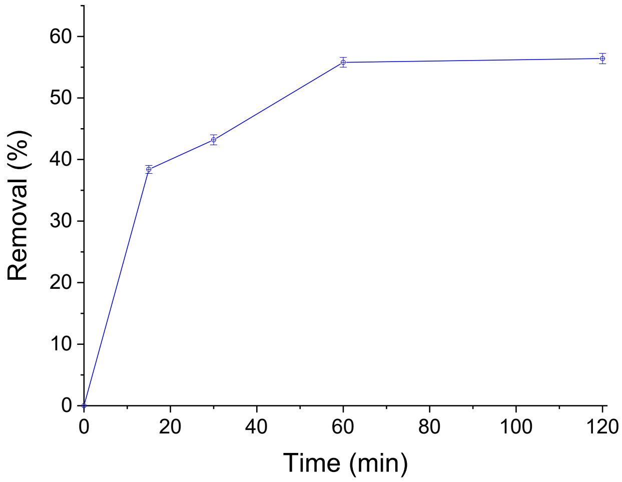

Figure S12. Effect of contact time on the removal of Co^{2+} in an aqueous solution at 25 °C. Adsorption conditions: Post-oxidation solution volume = 200 mL, [Co^{2+}] = 9.00 μM, adsorbent mass = 50 mg Na–Bent, stirring speed = 300 rpm, pH = 8.5.