Sequential Congo Red Elimination by UASB Coupled to Electrochemical Systems

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Abstract: Response surface methodology was investigated to determine the operational parameters on the degradation of Congo red dye (CR) and chemical oxygen demand (COD) in two electrochemical systems evaluated individually on effluent pretreated by an up-flow anaerobic sludge blanket (UASB) reactor. The UASB reactor was fed with 100 mg L−1 of CR and was operated for 12 weeks at different hydraulic residence times (HRTs) of 12 h, 10 h, and 8 h. Once stabilized at an HRT of 8 h, the effluent was collected, homogenized, and independently treated by electrooxidation (EO) and electrocoagulation (EC) cells. On both electrochemical systems, two electrode pairs were used; solid for EC (Fe and stainless-steel) and mesh electrodes for EO (Ti/PbO2 and Ti), and the effect of intensity (A), recirculation flow rate (mL min−1), and experimental time (min) was optimized on response variables. The maximum efficiencies of sequential systems for COD degradation and CR decolorization were 92.78% and 99.84% by EO, respectively. Results indicate that the coupled systems can be used in textile industry wastewater treatment for the removal of dyes and the decolorized by-products.

Keywords: azo dye; electrooxidation; electrocoagulation; Congo red; UASB; wastewater

1. Introduction

The textile industry generates significant environmental pollution due to the excessive amount and diversity of colorants and color auxiliaries used during dyeing processes. In recent years, clothing demand and the use of azo-type dyes, which represent around 60–70% of the total dye used industrially, have increased [1]. The presence of small amounts of dyes in aquatic systems reduces light penetration, which inhibits photosynthesis, affecting gas solubility and, consequently, trophic chain [2,3]. Azo dyes are synthetic, highly toxic, and present resistance to degradation by oxidizing agents, photodegradation, and biological systems [4,5]. In addition, the textile industry consumes high amounts of water, and in places with scarce drinking water, textile effluents are generally recycled to reduce requirements, which increases the risk of exposure to these compounds [6]. Congo red (CR) is a synthetic benzidine-based anionic diazo dye widely used by the textile, paper, and...
plastic industries due to its high fixation in cotton. It is used in measurement as a natural dye and as an indicator. CR is difficult to biodegrade, and it is metabolized to benzidine, a human carcinogen that is an irritant to eyes and skin and can cause allergic reactions [7,8]. Biological, chemical, electrochemical, and physical systems have been evaluated in different studies [9]. Adsorption methods have been the most studied, using several materials [2,3,7,8,10–13]. However, high doses of adsorbents may be required [9,14,15], regeneration of the adsorbent is difficult and expensive, additional treatment methods for the mineralization of dyes are necessary, and is not applicable to a wide variety of dyes [16,17]. The application of aerobic systems does not allow the effective degradation of azo dyes by their electrophilic nature [18]. However, under anaerobic conditions, azo dyes are susceptible to duffer reductive biotransformation using up-flow anaerobic sludge blanket (UASB) reactors [19–21] and other systems [22]. The UASB reactors have the economic advantage of not requiring oxygen; they generate low biomass and can withstand high loads of organic matter compared to other systems [23]. Under anaerobic conditions, azo dyes are reduced to aromatic amines [20,21,23,24], which presents the need to use a posterior system for the complete oxidation/elimination of these toxic compounds.

For the complete removal of azo dyes, biological sequential anaerobic-aerobic treatment has been used. However, aromatic amines have substituents with nitro and sulfonic groups; these are highly recalcitrant for aerobic bacteria, which does not allow the efficient mineralization of these compounds in a biological aerobic post-treatment [22]. Nonetheless, the coupled system by electrochemical-biological methods, with the theoretical principle to convert the dye molecules to readily biodegradable compounds by electrochemical treatment [25,26], cannot be used with high loads of organic matter because of the competition with the dyes. Furthermore, the application of the electrochemical process may promote the mineralization of azo dyes to more toxic compounds, which limits efficient removal in the biological system.

The aromatic amines and color remnant from UASB reactors and the other anaerobic systems can be removed using electrochemical systems, in which electrooxidation contributes to the mineralization of contaminants and allows entrainment by electrocoagulation [27]. During the electrooxidation process, OH$^-$ radicals (highly oxidizing agents) are generated on the anode surface and are responsible for carrying out more than 90% of the oxidation (direct), until CO$_2$ and H$_2$O [28,29]. The material of the anode is an essential factor in the generation of OH$^-$ radicals. Diamond doped boron (BDD) is the anode with the highest reported efficiency. However, it has the disadvantage of having a very elevated cost. PbO$_2$ coated anodes have a removal rate close to BDD, are of low cost, and can be used for the efficient oxidation of azo dyes and aromatics amines. On the other hand, in the electrocoagulation process by applying electrical current, adsorbents (Fe(OH)$_3$, Fe(OH)$_2^+$, Fe(OH)$_2^+$ and Fe$_2$(OH)$_2^{4+}$ [30]) are generated on the Fe anode. For this type of dye, Fe has a higher affinity. The adsorbents generated will trap amines and other contaminants that could not be eliminated in the preliminary stage. Some studies of UASB reactors coupled to electrochemical systems have achieved decolorization of color above 92% and of COD ~67–90% on different wastewater effluents [31–33]. The objective of this work was to decolorize the CR dye by a sequential system using a conventional UASB reactor as a biological treatment to remove the organic matter and promote the reduction of the dye, coupled with two electrochemical treatments (electrooxidation and electrocoagulation), operated individually, as post treatment.

2. Materials and Methods

2.1. Experimental Unit and Operation Conditions

Biological treatment was conducted in a 900 mL cylindrical UASB reactor made of Plexiglas material (Figure 1). The bioreactor was inoculated with 340 g of anaerobic sludge, equivalent to 23.3 g volatile suspended solids (VSS) L$^{-1}$. The sludge was collected from an industrial UASB reactor installed in a brewery. The bioreactor was fed with a solution composed of 153.85 mg L$^{-1}$ of CR (65% Sigma Aldrich) and 1 g L$^{-1}$ of
sodium acetate (99% purity Faga Lab) as a carbon and energy source. In addition, the solution was prepared according to the basal medium described by Alvarez and Cervantes [34], with the following composition (g L⁻¹, ≥99.0% Sigma Aldrich): NaHCO₃, 1.68; NH₄Cl, 0.3; KH₂PO₄, 0.2; MgCl₂·6H₂O, 0.03; CaCl₂, 0.1; and 1 mL L⁻¹ of trace elements solution. Trace elements solution contained (mg L⁻¹): FeCl₂·4H₂O, 2000; H₃BO₃, 50; ZnCl₂, 50; CuCl₂·2H₂O, 38; MnCl₂·4H₂O, 500; (NH₄)₆Mo₇O₂₄·4H₂O, 50; AlCl₃·6H₂O, 90; CoCl₂·6H₂O, 2000; NiCl₂·6H₂O, 92; Na₂SeO₃·5H₂O, 162; EDTA, 1000; and 1 mL L⁻¹ of HCl, 36% (≥99.0% Sigma Aldrich). The solution was adjusted to pH 7. Three hydraulic residence times (HRTs) of 12 h, 10 h, and 8 h were evaluated during 12 weeks of the total operation. Once the anaerobic system had stabilized at an HRT of 8 h, its effluent was periodically collected in containers of 1.5 L and was frozen at 4 ℃ in the dark. For subsequent treatment in electrochemical systems, a frozen container was taken for each experiment, and it was gradually thawed in the dark, homogenized, and evaluated under the parameters established in the experimental design.

![Continuous Anaerobic Treatment](image)

**Figure 1.** Scheme of systems used for CR elimination. The left anaerobic reactor operated continuously and in the proper flow direction in the electrochemical cells operated in batch.

The electrochemical systems (electrocoagulation (EC) of 0.9 L and electrooxidation (EO) of 1.12 L) were operated with dynamic flow interaction. That is, the liquid followed a flow direction from top to bottom and from bottom to top in 5 different sections, parallel to the electrodes and separated by walls of acrylic (Figure 1). This operation method allowed for increasing the homogenization in the system. On the other hand, two pairs of electrodes were used. For EC, anode and cathode solids of Fe and stainless steel, with an electrochemically active surface area of 110 cm², were used. In EO, mesh electrodes were used, Ti/PbO₂ anodes and Ti cathodes, with an electrochemically active surface area of 366 cm² and 320 cm², respectively. The power was supplied with Single-Phase BK Precision® equipment. The color and chemical oxygen demand (COD) in the influents and effluents of the biological and ECH systems was monitored to establish the treatment efficiency.
2.2. Analytical Details

Samples were collected from the influent and the effluent of the UASB reactor during 12 weeks of operation. In addition, in the electrochemical systems, samples from the influent and effluent of each experiment, according to the experimental matrix conditions (Table 1), were collected and preserved for posterior analysis. Dye concentration was evaluated in a UV spectrophotometer (Thermo Fisher Scientific, UV GENESYS 10S, Waltham, MA, USA) at 495 nm. The chemical oxygen demand (COD) was determined using the colorimetric method [35]. CR and COD removal were calculated using Equations (1) and (2), respectively.

\[
\text{CR removal (\%)} = \left(\frac{[\text{CR}]_0 - [\text{CR}]_f}{[\text{CR}]_0}\right) \times 100
\]

(1)

\[
\text{COD removal (\%)} = \left(\frac{[\text{COD}]_0 - [\text{COD}]_f}{[\text{COD}]_0}\right) \times 100
\]

(2)

where [CR]_0 is the initial concentration of CR (mg L\(^{-1}\)), [CR]_f is the final concentration of CR (mg L\(^{-1}\)), CR removal is Congo red decolorization (%), [COD]_0 is the initial concentration of COD (mg L\(^{-1}\)), [COD]_f is the final concentration of COD (mg L\(^{-1}\)), and COD removal is the chemical oxygen demand removal (%).

Table 1. Experimental matrix and values of independent factors.

| Coded Variables | Factors (U\(_i\)) | Experimental Domain | U\(_{i,0}\) | \(\Delta U_i\) |
|-----------------|-------------------|---------------------|----------|-------------|
| Electrooxidation|                   |                     |          |             |
| \(X_1\)         | U\(_1\): Intensity (I; A) | 1 2 1.5 0.5 |          |             |
| \(X_2\)         | U\(_2\): Recirculation Flow Rate (RFR; mL min\(^{-1}\)) | 10 30 20 10 |          |             |
| \(X_3\)         | U\(_3\): Experimental Time (ET; min) | 60 140 100 40 |          |             |
| Electrocoagulation|                   |                     |          |             |
| \(X_1\)         | U\(_1\): Intensity (I; A) | 1 2 1.5 0.5 |          |             |
| \(X_2\)         | U\(_2\): Recirculation Flow Rate (RFR; mL min\(^{-1}\)) | 10 30 20 10 |          |             |
| \(X_3\)         | U\(_3\): Experimental Time (ET; min) | 10 25 17.5 7.5 |          |             |

2.3. Experimental Design for Electrochemical Systems

CR and COD degradation on the electrochemical systems was performed using response surface methodology (RSM). Intensity (\(X_1\), A), recirculation flow rate (\(X_2\), mL min\(^{-1}\)), and experimental time (\(X_3\), min) were the independent variables evaluated. Five levels and a total of 20 treatments comprised eight runs for factorial design, six replicates at the center point, and six runs for high and low extreme levels (Table 2). CR (\(Y_1\)) decolorization and COD (\(Y_2\)) removal in % were the two investigated responses variables. Design Expert\textsuperscript{\reg} 7 (version 7.0.0) was used to generate the model and to perform the analysis variance (ANOVA). The experimental matrix and values of each independent factor are represented in Table 1. The following second-order equation gives the predicted response in all experimental fields [28,36] (Equation (3)).

\[
Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=2}^{k} b_{ij} X_i X_j
\]

(3)

where \(Y\) is the experimental response; \(b_0\) is the average of the experimental response; Coefficients \(b_i\), \(b_{ii}\), and \(b_{ij}\) are the linear, quadratic, and interaction effects between \(i\) and \(j\) factors for the response \(Y\), respectively.
Table 2. Experimental levels and factorial $2^2$ and central composite matrix for EO and EC.

| Experiment | $X_1$ (I (A)) | $X_2$ RFR (mL min$^{-1}$) | $X_3$ ET (min) | $Y_1$ CR R (%) | $Y_2$ COD R (%) | Experiment | $X_1$ (I (A)) | $X_2$ RFR (mL min$^{-1}$) | $X_3$ ET (min) | $Y_1$ CR D (%) | $Y_2$ COD R (%) |
|------------|--------------|--------------------------|---------------|----------------|----------------|------------|--------------|----------------|---------------|----------------|----------------|
| 1          | 1            | 10                       | 60            | 10.87          | 42.62          | 1          | 10           | 10            | 33.33         | 28.95          |
| 2          | 1            | 10                       | 140           | 63.11          | 60.65          | 1          | 10           | 25            | 37.12         | 43.43          |
| 3          | 1            | 30                       | 60            | 11.28          | 45.45          | 1          | 30           | 10            | 35.12         | 30.01          |
| 4          | 1            | 30                       | 140           | 67.14          | 63.93          | 1          | 30           | 25            | 38.12         | 44.7           |
| 5          | 2            | 10                       | 60            | 48.28          | 47.54          | 2          | 10           | 10            | 50.9          | 33.97          |
| 6          | 2            | 10                       | 140           | 84             | 83.77          | 2          | 10           | 25            | 52.9          | 52.3           |
| 7          | 2            | 30                       | 60            | 55.42          | 54.09          | 2          | 30           | 10            | 49.91         | 34.91          |
| 8          | 2            | 30                       | 140           | 87.42          | 90.16          | 2          | 30           | 25            | 51.21         | 52.67          |
| 9          | 1.5          | 20                       | 100           | 47.28          | 49.9           | 1.5        | 20           | 17.5          | 38.42         | 47.34          |
| 10         | 1.5          | 20                       | 100           | 52.85          | 52.45          | 1.5        | 20           | 17.5          | 37.87         | 48.72          |
| 11         | 1.5          | 20                       | 100           | 53.63          | 51.23          | 1.5        | 20           | 17.5          | 39.12         | 48.99          |
| 12         | 1.5          | 20                       | 100           | 53.26          | 51.5           | 1.5        | 20           | 17.5          | 38.23         | 47.34          |
| 13         | 1.5          | 20                       | 100           | 47.17          | 49.44          | 1.5        | 20           | 17.5          | 36.65         | 46.57          |
| 14         | 1.5          | 20                       | 100           | 49.51          | 48.97          | 1.5        | 20           | 17.5          | 38.32         | 47.57          |
| 15         | 1.5          | 20                       | 167.27        | 85.85          | 99             | 1.5        | 20           | 4.887         | 12.12         | 16.42          |
| 16         | 1.5          | 20                       | 32.72         | 15.23          | 29.98          | 1.5        | 20           | 30.11         | 52.12         | 53.49          |
| 17         | 1.5          | 3.18                     | 100           | 45.1           | 46.84          | 1.5        | 3.18         | 17.5          | 36.45         | 46.53          |
| 18         | 1.5          | 36.81                    | 100           | 48.12          | 47.11          | 1.5        | 36.81        | 17.5          | 41.93         | 49.45          |
| 19         | 0.65         | 20                       | 100           | 17.83          | 26.47          | 0.65       | 20           | 17.5          | 10.72         | 13.21          |
| 20         | 2.34         | 20                       | 100           | 91.25          | 99             | 2.34       | 20           | 17.5          | 53.61         | 54.32          |

3. Results and Discussion

3.1. Biological Treatment: Upflow Anaerobic Sludge Blanket

Biological treatment for CR decolorization and COD removal was evaluated over 84 d (12 weeks) at different HRTs. The initial decolorization efficiency for CR was 80% and removal for COD 72%, which gradually increased until reaching ≥96.6% and ≥84.2%, respectively. The concentrations at the effluent of the UASB reactor were 3.4 mg L$^{-1}$ of CR (from 100 mg L$^{-1}$ of initial dye) and 158 mg L$^{-1}$ of COD (from 1000 mg L$^{-1}$ of initial COD), after three weeks of operation with an HRT of 12 h (Figure 2). Similar removal efficiency values were observed in the following stages despite the change in the TRH to 10 h and 8 h, suggesting that the anaerobic sludge was already acclimated to the presence of the azo compound [37]. Under anaerobic conditions, azo compounds are susceptible to suffering reductive biotransformation by the cleavage of azo linkages, producing generally colorless but potentially dangerous aromatic amines. The reduction mechanism of azo dyes is mainly attributable to the capacity of anaerobic microorganisms to produce redox-active molecules (e.g., favines and hydroquinones) capable of transferring reducing equivalents to promote the reduction [6]. The reduction mechanism for CR suggests that three products were obtained: benzidine and two aromatic amines (with the same structure). The reduction is a two-stage process, in which the rate of benzidine production is slower than the decolorization rate, which indicates that one azo bond is broken first, promoting the decolorization, followed by a slower breaking of the second azo bond for benzidine production [38]. According to the results, CR was easily reduced by the anaerobic sludge according to the extent indicated (Figure 2). Previous studies indicate that tri-azo structures, as presented in the CR structure, are more recalcitrant compared to mono- and di-azo structures [39]. Nonetheless, the reduction of different azo dyes may occur differently, according to the toxicity extent, recalcitrance, and resistance to removal, regardless of the number of azo bonds [40]. In addition, the production of aromatic amines by the reduction in anaerobic systems treating azo compounds may result in highly toxic effluent, which makes necessary a subsequent treatment to eliminate them. Some processes, such as oxidation or adsorption systems can be applied [24,37,41].
Figure 2. COD removal and CR decolorization (%) in the UASB reactor, after 12 weeks (84 days) of operation at different hydraulic residence times: 12 h, 10 h, and 8 h.

3.2. Post-Treatment Optimization: Electrochemical Systems

3.2.1. Congo Red and Chemical Oxygen Demand Degradation in Electrooxidation Process

Three variables were evaluated: intensity (X1, I), recirculation flow rate (X2, RFR), and experimental time (X3, ET) on congo red CR decolorization and chemical oxygen demand (COD) removal by the electrooxidation (EO) process using a response surface with a total of 20 experiments and five levels. Table 2 shows the experimental results obtained. The highest removal efficiencies were found at the higher I levels tested (2.34 A), at 20 mL min\(^{-1}\) RFR and 100 min ET, achieving values of 91.25% for CR and 99% for COD. The lowest removal efficiencies were obtained for I = 1 A and 0.65 A, RFR = 10 mL min\(^{-1}\) and 20 mL min\(^{-1}\), and ET = 60 min and 100 min for CR (10.8%) and COD (26.4 7%), respectively. Second-order polynomial equations are given by Equations (3) and (4) for CR and COD degradation, respectively:

\[
Y_1 = 50.52 + 18.03X_1 + 21.57X_3 - 5.05X_1X_3
\]

\[
Y_2 = 50.50 + 13.54X_1 + 16.47X_3 + 4.47X_1X_3 + 4.83X_1^2 + 5.45X_3^2
\]

Coefficients were calculated by the difference of half the arithmetic average of the highest and lowest level of results obtained. Positive coefficients have a positive effect on the response, and negative have the opposite effect [28,36]. \(b_9 = 50.52\) and 50.50 in Equations (4) and (5) are the average of the responses obtained in all experiments for CR and COD removal. \(b_1 = +18.03\) and +13.54 indicate that CR and COD degradation increase 36.06% (2 × 18.03) and 27.08% (2 × 13.54) when I increases from 1 A to 2 A. \(b_2 = +1.47\) and +1.43 means that CR decolorization and COD removal increase 2.94% (2 × 1.47) and 2.86% (2 × 1.43) when RFR increases from 10 mL min\(^{-1}\) to 30 mL min\(^{-1}\). \(b_3 = +21.57\) and +16.47 show that CR and COD degradation increase 43.14% (2 × 21.57) and 32.94% (2 × 16.47) when ET increases from 60 min to 140 min.

The effect of I, RFR, and ET on CR and COD removal is shown in response surface plots (Figure 3). As observed, the decolorization of CR and removal of COD can reach 91.25% and 99% if response variables \((X_1, X_2,\) and \(X_3)\) are increased. For CR R and COD R, the \(p\)-value model is <0.0001 and 0.0008; this indicates that the model is significant (Table 3). For CR decolorization, the \(p\)-value for \(X_2\) and \(X_3\) is <0.0001 (significant, \(p < 0.05\) with an \(F\)-value of 192.48 and 275.59) and for \(X_2\) is 0.2783 (not significant). Similar results are seen for COD removal; \(p\)-value for \(X_1\) and \(X_3\) is 0.0003 and <0.0001 (significant, \(p < 0.05\),
with an F-value of 30.26 and 44.76) and for \( X_2 \) is 0.5746 (not significant). Low dispersion is observed on data in Table 3, with a coefficient correlation value of \( R^2 = 0.9735 \) (for CR decolorization) and \( R^2 = 0.8961 \) (for COD removal), which means that only 2.65% and 10.39% of variation do not belong to the models.

![Figure 3](image-url)  
Figure 3. Effect of independent variables (I, X1; RFR, X2, and ET, X3) on response variables (CR decolorization and COD removal) during electrooxidation process (EO): (A) ET and I on CR decolorization; (B) RFR and I on CR decolorization; (C) ET and RFR on CR decolorization; (D) ET and I on COD removal; (E) RFR and I on COD removal; (F) RFR and ET on COD removal.

| Source | Analysis of Variance |
|--------|----------------------|
|        | Sum of Square | d.f. | Mean of Square | F-Value | Pr > F |
| CR R   | Electrooxidation    |                   |
| Model  | 11,030.79       | 9    | 1838.47        | 79.73   | <0.0001 |
|        | X1-I            | 4438.29 | 1 | 4438.29 | 192.48 | <0.0001 |
|        | X2-RFR          | 29.52  | 1    | 29.52   | 1.28   | 0.2783 |
|        | X3-ET           | 6354.48 | 1 | 6354.48 | 275.59 | <0.0001 |
|        | X1X2            | 4.68   | 1    | 4.68    | 0.21   | 0.6576 |
|        | X1X3            | 203.82 | 1    | 203.82  | 9.08   | 0.0130 |
|        | X2X3            | 0.001  | 1    | 0.001   | 0.00005 | 0.9942 |
|        | X1^2            | 57.35  | 1    | 57.35   | 2.56   | 0.1410 |
|        | X2^2            | 9.43   | 1    | 9.43    | 0.42   | 0.5314 |
|        | X3^2            | 4.86   | 1    | 4.86    | 0.22   | 0.6517 |
| COD R  | Model           | 7135.92 | 9 | 792.88 | 9.58 | 0.0008 |
|        | X1-I            | 2503.10 | 1 | 2503.10 | 30.26 | 0.0003 |
|        | X2-RFR          | 27.85  | 1    | 27.85   | 0.34   | 0.5746 |
|        | X3-ET           | 3703.22 | 1 | 3703.22 | 44.76 | <0.0001 |
|        | X1X2            | 5.83   | 1    | 5.83    | 0.070  | 0.7960 |
Table 3. Cont.

| Source | Analysis of Variance |
|--------|----------------------|
|        | Sum of Square | d.f.  | Mean of Square | F-Value | Pr > F |
| $X_1X_3$ | 160.12 | 1 | 160.12 | 1.94 | 0.1943 |
| $X_2X_3$ | 0.011 | 1 | 0.011 | 0.0001 | 0.9912 |
| $X_1^2$ | 335.58 | 1 | 335.8 | 4.06 | 0.0717 |
| $X_3^2$ | 8.03 | 1 | 8.03 | 0.097 | 0.7618 |
| $X_2^2$ | 427.43 | 1 | 427.43 | 5.17 | 0.0463 |

Electrocoagulation

| CR D | Model | 2401.06 | 9 | 266.78 | 8.81 | 0.0011 |
| X_1 | 673.40 | 1 | 673.40 | 22.23 | 0.0008 |
| X_2-RFR | 5.35 | 1 | 5.35 | 0.18 | 0.6831 |
| X_3-ET | 1192.28 | 1 | 1192.28 | 39.35 | <0.0001 |
| X_1X_2 | 0.13 | 1 | 0.13 | 0.004 | 0.9491 |
| X_1X_3 | 5.99 | 1 | 5.99 | 0.20 | 0.6662 |
| X_2X_3 | 0.016 | 1 | 0.016 | 0.0005 | 0.9820 |
| X_3 | 301.86 | 1 | 301.86 | 9.96 | 0.0102 |
| X_2 | 2.95 | 1 | 2.95 | 0.007 | 0.7613 |
| X_3^2 | 248.91 | 1 | 248.91 | 8.22 | 0.0168 |

| COD R | Model | 1835.69 | 9 | 203.97 | 2.72 | 0.0673 |
| X_1 | 1302.31 | 1 | 1302.31 | 17.39 | 0.0019 |
| X_2-RFR | 6.37 | 1 | 6.37 | 0.085 | 0.7766 |
| X_3-ET | 438.23 | 1 | 438.23 | 5.85 | 0.0361 |
| X_1X_2 | 3.74 | 1 | 3.74 | 0.050 | 0.8277 |
| X_1X_3 | 1.52 | 1 | 1.52 | 0.020 | 0.8895 |
| X_2X_3 | 0.28 | 1 | 0.28 | 0.004 | 0.9527 |
| X_3 | 79.46 | 1 | 79.46 | 1.06 | 0.3273 |
| X_2^2 | 0.33 | 1 | 0.33 | 0.004 | 0.9483 |

R² = 0.9735 for CR D in EO. R² = 0.8961 for COD R in EO. R² = 0.8880 for CR D in EC. R² = 0.8917 for COD R in EC. a Degree of freedom.

The contribution of independent variables to response variables is expressed as a percentage and is shown in Figure 4. The highest contribution to the response variable is 64.51% and 67.7% for $X_3$ and 31.43% and 22.63% for $X_1$ on CR decolorization and COD removal. The remainder is attributed to $X_2$ and interaction between variables. This high contribution in $X_1$ and $X_3$ is because they control hydroxyl radical (OH⁻) production in the surface anode and the other oxidants indirectly generated, such as HClO, H₂SO₄, and H₂O₂ [28,29,42–44].

To establish optimal conditions in response variables, energy consumption (I) and operating time (ET) were minimized, assigning an importance of 3 out of 5 for $X_1$ and $X_3$ (variables with the greatest effect in this study). Likewise, COD removal and CR decolorization were maximized, giving them an importance of 4 out of 5 and 5 out of 5, respectively. Optimization conditions obtained were $I = 1.96 \text{ A}$, $\text{RFR} = 23.51 \text{ mL min}^{-1}$, and $\text{ET} = 110.80 \text{ min}$ to obtain a degradation of 74.12% and 73.74% of CR and COD. These conditions show that high removals can be obtained by reducing the operating conditions of the variables studied ($X_1$, $X_2$, and $X_3$).

3.2.2. CR Decolorization and COD Removal in EC Process

For EC, the range for $X_3$ was reduced to 10–25 min (Table 1); this is because the EC process is faster than EO [29]. Preliminary experiments were the basis for taking $X_3$ values. Table 2 shows the experimental results obtained. Best degradations were found at the higher I levels tested (2.34 A), at 20 mL min⁻¹ RFR and 17.5 min ET with a CR decolorization...
and COD removal of 53.61% and 54.32%. Second-order polynomial and lineal equations are given by Equations (6) and (7) for CR and COD degradation, respectively:

\[
Y_1 = 47.70 + 7.02X_1 + 9.34X_3 - 4.58X_1^2 - 4.16X_3^2
\]  
(6)

\[
Y_2 = 37.80 + 9.77X_1 + 5.66X_3
\]  
(7)

Coefficients were calculated by the difference of half the arithmetic average of the highest and lowest level of the results obtained. Positive coefficients have a positive effect on the response, and negative have the opposite effect [28,36]. \( b_0 = 47.70 \) and 37.80 in Equations (6) and (7) are the averages of the responses obtained in all experiments for CR decolorization and COD removal.

The effects of I, RFR, and ET on CR decolorization and COD removal are shown in response surface plots (Figure 5). As observed, the degradation of CR and COD can reach 53.61% and 54.32% if response variables \( (X_1, X_2, \) and \( X_3 \) are increased. For CR and COD degradation, the \( p \)-value model is 0.0011 and 0.0003; this indicates the model is significant (significant, \( p < 0.05 \)). For CR decolorization, the \( p \)-value for \( X_1 \) and \( X_3 \) is 0.0008 and for \( X_2 \) is 0.6831 (not significant). Similar results are found for COD removal, where \( X_2 \) is 0.7318. Low dispersion is observed on data in Table 3, with a coefficient correlation value of \( R^2 = 0.8880 \) and \( R^2 = 0.8961 \) for CR and COD degradation, respectively.

The variables with the highest contribution in CR decolorization and COD removal were \( X_1 \) with 96.25% and 14.21% and \( X_3 \) with 2.61% and 84.54% (Figure 5). This is because, at high current intensity, the coagulant production increases, and pollutant entrapment takes place [45–47]. Likewise, using iron anodes, we can have coagulant species of \( \text{Fe(OH)}_3 \), \( \text{Fe(OH)}_2^+ \), \( \text{Fe(OH)}_2^- \), and \( \text{Fe}_2(\text{OH})_2^{4+} \) [30]. On the other hand, optimization was to minimize energy consumption (I) and operating time (ET), assigning an importance of 3 out of 5 to I, RFR, and ET = 17.5 min, with a CR decolorization and COD removal of 53.61% and 54.32% if response variables \( (X_1, X_2, \) and \( X_3 \) are increased. For CR and COD degradation, the \( p \)-value model is 0.0011 and 0.0003; this indicates the model is significant (significant, \( p < 0.05 \)). For CR decolorization, the \( p \)-value for \( X_1 \) and \( X_3 \) is 0.0008 and for \( X_2 \) is 0.6831 (not significant). Similar results are found for COD removal, where \( X_2 \) is 0.7318. Low dispersion is observed on data in Table 3, with a coefficient correlation value of \( R^2 = 0.8880 \) and \( R^2 = 0.8961 \) for CR and COD degradation, respectively.

The low yield eliminations in EC are due to the short experimental time used (it was chosen according to the preliminary kinetics). Efficiencies can be increased by increasing the current intensity and the experimental time as these were the variables with the greatest influence and contribution to the response variables [30,47].

Figure 4. Contribution percentage of each variable and the interaction \( (X_1, X_2, X_3, X_1X_2, X_1X_3, X_2X_3) \) in both electrochemical systems.
Effect of independent variables (I, X1; RFR, X2, and ET, X3) on response variables (CR decolorization and COD removal) during electrocoagulation process (EC): (A) ET and I on CR decolorization; (B) RFR and I on CR decolorization; (C) ET and RFR on CR decolorization; (D) ET and I on COD removal; (E) RFR and I on COD removal; and (F) RFR and ET on COD removal.

3.3. CR and COD Degradation by Coupled Biological-ECH Systems

Total degradations for the UASB reactor coupled to EO were 99.71% for CR decolorization and 99.84% for COD removal, obtaining final concentrations of 0.29 mg L$^{-1}$ of CR and 1.58 mg L$^{-1}$ of COD. For the UASB + EC, the maximum degradations for CR and COD were 98.43% and 92.78%. Previously, Aravind et al. [48] coupled the electrooxidation process to the photodegradation and biological system, achieving eliminations of 92% and 90% for color and COD degradation, respectively. Venkatesh et al. [26] used ozonation coupled to the UASB reactor for Reactive Black 5 and found a removal of 90% for COD and 94% for dye decolorization. Likewise, Buzzini et al. [31] used an inverse treatment coupling electrocoagulation to UASB, reaching 98% color and 67% COD degradation. Yetilmezsoy et al. [32] decolorized and removed the organic matter from poultry manure wastewater pretreated by a UASB and using EC as a post-treatment. They achieved degradations in the coupled system of 90% of COD and 92% of residual color. Likewise, Makwana and Ahmed [33] treated urban wastewater using a UASB coupled to an EC system, reaching removals of 71.3% for COD and 96.8% for color. The literature addresses the inverted process (electrochemical-biological); however, the by-products of these contaminants are more toxic than the original pollutant, and this limits the complete mineralization in the biological (secondary) treatment. In addition to the high degradation capacity of electrochemical systems as post-treatment, they have the advantage of occupying small spaces and do not require the addition of chemical agents [49]. In this study, anaerobic-electrochemical treatment is approached due to the azo dyes being reduced in the biological system forming the aromatic amines: benzidine and two aromatic amines (with the same structure). These amines are oxidized and desulphonated by the secondary treatment (electrooxidation) or by trapping in an adsorbent (electrocoagulation). During the electro-oxidation process, 8-Amino naphthalene diazine 3-sulfonic acid will oxidize and form metabolites (3-Hydroperoxy 8-nitrosanaphthol) [50], which will continue to oxidize until completely mineralized [51]. On EC, using iron anodes, coagulant species of Fe(OH)$_3$, Fe(OH)$_2^+$, Fe(OH)$_2^+$, and Fe$_2$(OH)$_4^{2+}$ [30] are formed. These compounds trap in their matrix the amines and metabolites formed in the anaerobic system as well as the remaining color.
The advantage of using electrooxidation for organic pollutant degradation is that complete mineralization of these compounds can be achieved up until CO\textsubscript{2} and H\textsubscript{2}O, directly by the OH\textsuperscript{−} radicals generated in the anode and by other oxidants generated in the process (such as HClO, H\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, H\textsubscript{2}O\textsubscript{2}, etc.) [28,29,51]. Likewise, methane generated in a biological treatment [40] can fully or partially supply the system demand. EO, compared to EC, has the disadvantage that the reaction process requires more time; however, in EC, the electrodes are sacrificial; that is, they are worn during each operation. On the other hand, the EC system requires less operation time, which makes it more economical. However, if an anaerobic biological system is used as a preliminary treatment (as in this study), a large part of the energy requirement can be supplied. EC has the disadvantage of generating a coagulant to trap the pollutants. It will require a subsequent treatment to remove them from the treated effluent [29]. The coupled system evaluated in this research allowed analysis of how these electrochemical systems behave when used as post-treatment of an anaerobic system in dye decolorization. In future works, it will be essential to evaluate the methane production (in specific conditions) to know the contribution that a preliminary anaerobic treatment would have in an electrochemical system. Likewise, it is crucial to evaluate the toxicity after applying EO and EC and the degree of mineralization after applying EO.

4. Conclusions

The coupled system evaluated in this study improved contaminant degradation. The biological treatment system (UASB) eliminated a large concentration of CR and COD and contributed to biogas production (anaerobic system), which can be used in electrochemical cell energy requirements. When an azo bond is broken during pretreatment, it generates new pollutants (aromatic amines), which can be degraded and mineralized post-treatment (electrochemical reactors). The maximum efficiencies of sequential systems for COD removal and CR decolorization were 92.78% and 98.43% by EC and \( \geq \)99.84% and \( \geq \)99.71% by EO. The best degradation achieved was in the UASB + EO coupled system, despite the fact that this system requires more experimental time compared to the EC. The most critical variables in both electrochemical systems were I, with a 96.25% contribution in color degradation, and ET, with 84.54% in DQO removal. Likewise, EC requires treatment of subsequent sedimentation to reduce the clots present. According to the results, this coupled system can be applied and scaled to wastewater treatment with high concentrations of colorants.

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