

Statistical optimization of industrial textile wastewater treatment by electrochemical methods

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Abstract In this work, the Box–Behnken experimental design and the surface response methodology were applied for the optimization of the operational conditions of the electro-catalytic degradation of wastewaters, resulting from a local textile industry. The experiments were carried out in a laboratory scale batch cell reactor, with monopolar configuration, and electrodes made of boron-doped diamond (anode) and titanium (cathode). The multifactorial experimental design included the following variables: current density (i : 5–10 mA/cm²), pH (3–7), and submerged cathode area (CA: 8–24 cm²). To determine the process efficiency, the degradation percentage of: the chemical oxygen demand (%DCOD), the total organic carbon (%DTOC) and the color (%DC) were defined as response variables. The following optimal conditions for the electro-oxidation (EO) process were obtained: $i = 10$ mA/cm²,

pH = 3 and CA = 16 cm², reaching ca. 92 % of DC, 37 % of DCOD and 31 % of DTOC. The electro-Fenton (EF) and photo-electro-Fenton (PEF) processes were also evaluated at EO optimal conditions. For the EF process, with addition of iron (0.3 mM), the %DC, %DCOD and %DTOC was enhanced to 95, 52 and 45 %, respectively. For the PEF process (UV = 365 nm), it was possible to reach 98 %DC, 56 %DCOD and 48 %DTOC.

Keywords Electro-oxidation · Statistical optimization · Boron-doped diamond · Textile effluents · Electro-Fenton · Photo-electro-Fenton

1 Introduction

In the recent years, the rising demand for textile products has created a dramatic increase in the amount of wastewater effluents coming from this industrial area. It made the textile industry one of the most polluting sectors due to its high discharge volume (125–170 L/kg of product) and wastewater composition [1]. These effluents are characterized with high concentration of dyes, high chemical oxygen demand (COD), variable pH (2–12) and the presence of surfactants, suspended solids, organic matter and non-biodegradable compounds, resistant to destruction by physicochemical treatments. Among the synthetic dyes, widely used in textile industry, the azo ones represent ca. 70 % of the global dye production and 50,000 metric tons of these chemicals are released to the environment every year [2]. They consist of one or more azo bond ($-N=N-$) as chromophore group, associated with aromatic structures containing functional groups such as OH^- and HSO_3^- [3]. Azo dyes are toxic for aquatic microorganisms as well as mutagenic and carcinogenic to humans. Their resistance to

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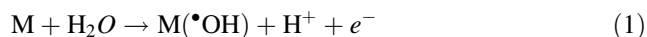
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natural oxidation and reduction processes, light exposure and biodegradation makes the conventional aerobic wastewater treatments not efficient for their degradation [4]. Therefore, the development and implementation of powerful oxidation processes for their treatment is needed. Different physical, chemical and biological treatment technologies have been proposed for azo dyes removal from wastewater [5]. Among them, advanced oxidation processes (AOPs), involving production of hydroxyl radical ($\cdot\text{OH}$), have been identified as highly efficient [6–9]. Here, the hydroxyl radical ($\cdot\text{OH}$), a strong oxidizing agent, reacts rapidly and non-selectively with most of organic contaminants, leading to the formation of dehydrogenated or hydroxylated derivatives, until their final mineralization into CO_2 , H_2O and inorganic ions [10, 11].

Recently, the electrochemical variants of AOPs—EAOPs such as electrochemical oxidation (electro-oxidation, EO) [12], electro-Fenton (EF) [6, 13, 14], and photo-electro-Fenton (PEF) [6] have called a lot of attention due to its environmental compatibility, high efficiency, versatility, flexibility of automation, and safety. The EO, the most popular EAOP, consists of pollutant oxidation by direct electron transfer to the anode (M) and/or mediated oxidation with heterogeneous $\text{M}(\cdot\text{OH})$, formed from water discharge at the anode surface at high current, as follows [15]:



According to the literature [16], the best anode for EO is a non-active boron-doped diamond (BDD) thin-film electrode, due to its inert surface with low adsorption, corrosion stability, and extremely high O_2 -evolution overvoltage. Recently, BDD electrodes have been applied for the degradation of organic pollutants such as textile dyes and herbicides [17]. The electrolysis of water to form the $\cdot\text{OH}$ radical, once the electric current pass through the BDD electrode, is presented in Eq. (2) [18].



The EO can be intensified by the addition of an iron salt and UV radiation to carry out the EF and PEF processes, respectively [6]. The EF process consists of H_2O_2 formation by the two-electron reduction of O_2 at a cathode surface, according to the following equation:



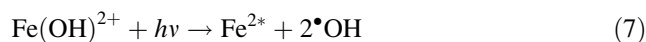
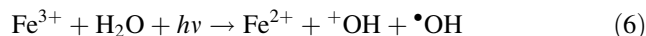
The low oxidation ability of H_2O_2 can be enhanced by adding Fe^{2+} ion as catalyst to the acidic solution to yield Fe^{3+} ion and $\cdot\text{OH}$ via Fenton's reaction:



An advantage of EF comparing to the classical Fenton treatment is the quick regeneration of Fe^{2+} ion, by the reduction of Fe^{3+} ion at the cathode:



Finally, in PEF process, the solution treated by EF is irradiated with an UV radiation, enhancing the mineralization process by faster Fe^{2+} regeneration (Eq. 6) and $\cdot\text{OH}$ production by $\text{Fe}(\text{OH})^{2+}$ photoreduction (Eq. 7), which is the predominant Fe^{3+} species at pH close to 3.



This work deals with the implementation of an effective method for the decolorization and mineralization of wastewater, characterized with high concentration of dyes and high organic matter content, resulting from a textile industry located in the suburbs of Medellin (Colombia). Therefore, three different EAOPs were proposed and evaluated: EO, EF and PEF. Considering that various factors such as pH, current density, conductivity, type of electrode (anode and cathode), electrode gap, time, etc. can affect the efficiency of electrochemical process, its optimization was performed using the response surface methodology (RSM). This statistical technique allows establishing the relationships between several independent variables and one or more dependent ones, minimizing the amount of experiments to be performed. The optimization by the RSM involves the following steps: (1) the implementation of the statistically designed experiments; (2) the estimation of the coefficients of a mathematical model using regression analysis technique; (3) the prediction of the response; and (4) the verification of the adequacy of the model. Among the available statistical design methods, a multi-level Box–Behnken experimental design (BBD) was chosen and implemented for the purpose of response optimization, as presented elsewhere [4, 19]. Recently, few authors have applied statistical methods to investigate systematically the combination of parameters that provides optimal conditions for decolorization and mineralization of methyl orange [3] and Acid Yellow 36 [2, 6, 13, 14] azo dyes. However, as far as we know, no similar study was performed for the industrial wastewater sample being a mixture of different dyes.

Therefore, at first, the optimization of operational conditions of EO was performed. Next, at the optimized conditions, the EF and PEF processes were evaluated. Finally, a kinetic study was settled.

2 Materials and methods

2.1 Wastewater samples

The (red color) samples were taken directly from the wastewater stream of the textile industrial plant, dedicated to the jeans manufacture. Before analysis and treatment in

Table 1 The physicochemical characterization of the industrial wastewater stream resulting from the textile industry

Parameter	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Turbidity (NTU)	COD (mg/L)	TOC (mg/L)	λ_{max}	BOD ₅ (mg/L)	BOD ₅ / COD	TSS* (mg/L)
Value	12.65	8,530	214	1,698	397	520	205.83	0.1212	438.57

* Total suspended solids

the laboratory, they were kept refrigerated in order to avoid compounds degradation during their storage and transportation, following the standard procedures [20]. Table 1 presents its subsequent main characteristics. One can see that its high conductivity, produced by the presence of different salts used in the manufacturing process, can facilitate the application of electrochemical technologies.

It is well known that the BOD₅/COD ratio of wastewater is used to express its biodegradability. When the BOD₅/COD ratio is higher than 0.35, the wastewater is considered as biodegradable. In this study, the initial BOD₅/COD ratio of the wastewater equaled to ca. 0.12, indicating that the analyzed effluent is not biodegradable.

2.2 Reagents

All reagents of analytic grade, provided by different companies, were used without further purification. Ferrous chloride(II) tetra-hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was used as source of Fe^{+2} (0.3 mM) for the EF and PEF experiments. The corresponding reagent solutions were prepared using ultra-pure water (Milli-Q system; 18.0 M Ω cm resistivity). Their pH was adjusted using pure sulfuric acid (99.1 %).

2.3 Analytic methods

The samples taken each time were analyzed by a UV–Vis double-beam spectrophotometer (Spectronic Genesys 2PC)

in the range of 200–700 nm. Standard methods [21] were used for the quantitative analysis of COD, TOC, and biological oxygen demand (BOD₅). The COD analyses were performed following the closed reflux method with colorimetric measurements (method 5220D); the TOC measurements were carried out with a Shimadzu analyzer (model TOC-5000A), following the method 5310D; and BOD₅ measurements were performed following the respirometric method (5210B). The turbidity was determined with an Orbeco-Hellige Turbidimeter (Model 966-01) following the 2130B standard method. Finally, for total suspended solids measurements the 2540B standard method was employed.

2.4 Electrolytic system

A plexiglass batch jacketed cell (0.12 L) was used for all experiments. It consists of two vertical, rectangular, plate electrodes: one a BDD thin-film electrode with a total area of 4 cm², the anode (0.5 mm thickness on silicone substrate, supplied by USA Center for Coatings and Laser Applications), and another, made of titanium (Ti), the cathode, having an area of 23.3 cm² (0.14 cm thickness). The electrodes were disposed vertically in the cell, with a 1 cm gap between them and connected in a monopolar arrangement. Voltage was regulated with a BK-Precision (0–30 V, 0–5 A) source. The reaction mixture of 95 mL was stirred at 240 rpm, and the total reaction time was of

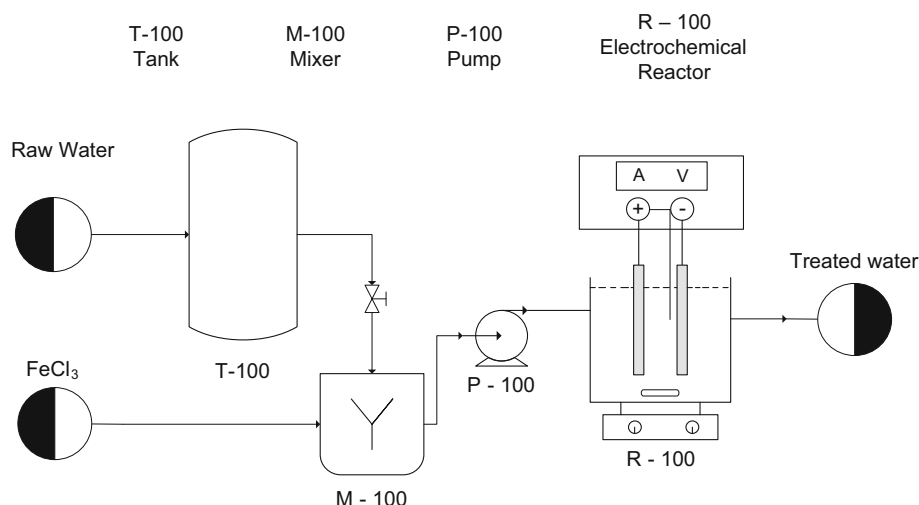
**Fig. 1** Setup of the electro-oxidation process

Table 2 The operating parameters that can affect the efficiency of the wastewater treatment using electrochemical processes

Variable	Method		
	Electro-oxidation	Electro-Fenton	Photo-electro-Fenton
pH	X	X	X
Initial concentration of pollutant	X	X	X
Type of buffer used for pH adjustment	X		
Temperature	X	X	X
Electrolysis time	X	X	X
Current density	X	X	X
Cathode area	X	X	X
Amount and type of the catalyst			X
Reactor design			X
Irradiation wavelength			X
Radiant flux			X
Effect of ionic species (v.g., Ferrous ion, hydrogen peroxide)	X	X	X

Prepared from information in [21] and references therein

35 min. Test temperature was controlled at 28 °C by a Polyscience 712 thermostat connected to the jacket. The set-up of the electro-oxidation process is shown in Fig. 1. For the PEF process, the UV lamp F6T5 Hg 365 was used. The efficiency of the treatment process was calculated as color and COD degradation percentages (%DC and %DCOD, respectively).

2.5 Statistical model and experimental design

The RSM was implemented to establish the effect of different operating factors on the efficiency of electro-catalytic degradation of wastewater, resulting from the local textile plant dedicated to the jeans manufacture. A multifactorial BBD was defined in order to establish the interactive effects of process variables and to optimize operation conditions that maximize the color and organic matter degradation.

Table 2, prepared basing on the exhaustive and critical analysis of the data published in the open literature, summarizes the operating parameters that can affect the efficiency of the wastewater treatment using electrochemical processes, specifically: EO, EF and PEF. One can see a group of variables (pH, initial concentration of pollutant, temperature, electrolysis time, current density, and cathode area) that are commune and relevant to all the analyzed processes (Table 2, marked in gray). Thus, in this work, the following criteria for variables selection were considered: (1) The characteristics of the wastewater; Considering that the studied wastewater sample was originated from a specific textile industrial plant, at first, some of its parameters, specifically temperature, conductivity and initial pollutant concentration were kept as original and were not included into the experimental design as variables. (2) The

Table 3 Factors and level of experimental design

Variable	Coded factors X		
	−1 Level 1	0 Level 2	1 Level 3
A: Current density (i, mA/cm ²)	5	7.5	10
B: pH	3	5	7
C: Cathode area (CA, cm ²)	8	16	24

operational parameters affecting electrochemical process; next, from the rest of operational conditions influencing potentially all studied processes (Table 2), the pH, current density and cathode area were chosen as variables for the optimization of EO. Finally, at optimized EO conditions, the effect of electrolysis time and the presence of ionic species (Fe²⁺) were studied for EO, EF and PEF.

Thus, the following variables were selected for RSM: current density (i: 5–10 mA/cm²), pH (3–7) and submerged cathode area (CA: 8–24 cm²).

The experiments were programmed using Statgraphics 5.1 (Statistical Graphics Corp 1999–2004). Thus, 15 tests with replica were randomly made in order to avoid any systematic error. From preliminary experiments (not presented here), three different levels (values) were chosen for each of three variables. The independent variables and their levels, summarized in Table 3, were coded according to the Eq. (8).

$$X_i = \frac{(x_i - x_{pc})}{\Delta x} \quad (8)$$

where: X_i is the coded level, x_i is the uncoded value, x_{pc} corresponds to the uncoded value at the central point, and Δx_i is the change value between [22].

The parameters chosen as the response variables, %DC and %DCOD, were calculated according to the following equation:

$$\%DC = \frac{(C_0 - C)}{C_0} * 100 \quad (9)$$

For the RSM, the experimental results were adjusted to a second order polynomial model (Eq. 10):

$$Y_i = \beta_0 + \sum_1^3 \beta_i X_i + \sum_1^3 \beta_{ii} X_i^2 + \sum_1^3 \sum_1^3 \beta_{ij} X_i X_j \quad (10)$$

where; β_0 , β_i , β_{ii} , β_{ij} , are regression coefficient for intercept term, lineal, square and interaction respectively and X_i and X_j are independent variables. The quality of this model and its prediction capacity were judged from the variation coefficient, R^2 . Determination of the significant main and interaction effects of factors influencing the dye and organic matter degradation was followed by analysis of variance (ANOVA). Therefore, the statistical analysis was based on the ANOVA, Pareto diagram, Box–Behnken response surface plots and variation coefficients.

3 Results and discussion

3.1 Optimization of EO process

To examine the combined effect of three independent process parameters (i, pH, CA) on the %DC and %DCOD, 15 experiments were performed. The experimental design is given in Table 4, together with the corresponding experimental and model predicted data.

Regression analysis was performed to fit the response variables (%DC and %DCOD). The developed second order polynomial equations, adjusted at 95 % confidence level, represent response variables as functions of current density (i), pH y submerged cathode area (CA). An empirical relationship between the each response and the input test variables, in coded units, can be expressed by the following equations:

$$\begin{aligned} \%DC = & 37.5312 + 16.1 * i - 13.5833 * pH - 0.885417 \\ & * CA - 0.606667 * i^2 - 0.35 * i * pH \\ & + 0.05 * i * CA + 1.30208 * pH^2 \\ & - 0.125 * pH * CA + 0.030599 * CA^2 \end{aligned} \quad (11)$$

$$\begin{aligned} \%DCOD = & 16.75 + 8.05 * i - 10.8125 * pH - 0.515625 \\ & * CA - 0.36 * i^2 - 0.1 * i * pH \\ & + 0.0875 * i * CA + 0.9375 * pH^2 \\ & - 0.046875 * pH * CA \end{aligned} \quad (12)$$

Equations (11 and 12) describe how %DC and %DCOD are affected by the individual variables and/or their double

Table 4 Experimental and model predicted results of the %DC and the %DCOD, according to the Box–Behnken experimental design

Variable			Efficiency results			
A: i (mA/cm ²)	B: pH	C: CA (cm ²)	%DC		%DCOD	
			Y _{exp}	Y _{pred}	Y _{exp}	Y _{pred}
10	7	16	69	70.17	24	24.53
7.5	5	16	65	65.34	21	21.0
7.5	3	24	86	83.53	33	30.06
7.5	5	16	65	65.34	21	21.0
10	5	8	82	79.05	30	26.78
7.5	7	8	63	65.41	18	19.94
5	5	24	43	46.45	4	7.47
5	5	8	50	50.41	12	12.53
7.5	7	24	59	59.05	18	17.50
7.5	5	16	66	65.34	21	21.00
5	7	16	46	43.14	11	8.03
5	3	16	61	60.40	20	18.72
10	3	16	91	93.86	30.5	31.47
10	5	24	79	78.30	29	28.47
7.5	3	8	82	81.88	30	31.00

interactions. The color removal efficiency was linear and also quadratic with respect to current density, pH y submerged cathode area. However, the organic matter degradation efficiency was linear with respect to current density, pH y submerged cathode area and quadratic with respect to current density and pH. Moreover, the following interactions: current density–pH, current density–cathode area and pH–cathode area can affect both % DC and %DCOD.

The ANOVA was employed to determine the most significant main and interaction effects of factors influencing the %DC and %DCOD. The ANOVA results are presented in Table 5. The ANOVA consists of classifying and cross-classifying statistical results. Fisher *F*-test, defined as the ratio of respective mean-square effect and mean-square error, was used to evaluate the presence of a significant difference from control response and to calculate standard errors. The bigger the magnitude of *F* value, more significant is the corresponding coefficient. The *P* values were used to identify experimental parameters that have a statistically significant influence on particular response. If *P* value is lower than 0.05, it is statistically significant with the 95 % confidence level [21]. According to ANOVA results, one can see that all terms in the regression models are not equally important. For both %DC and %DCOD, only two of them (current density: A and pH: B) presented *P* values lower than 0.05 (Table 5 A and B), indicating that only they have a truthfully effect on the %DC and %DCOD, with a confidence interval of 95 %.

Table 5 The ANOVA for the %DC (A) and %DCOD (B), as a function of current density, pH, and cathode area

Factor	Sum of squares	Degrees of freedom	Mean square	F-relation	P value
(A)					
A: Current density	1,830.1	1	1,830.1	115.95	0.0001
B: pH	666.1	1	666.1	42.2	0.0013
C: Cathode area	0.0	1	0.0	0	1
AA	23.85	1	23.85	1.51	0.2736
AB	12.3	1	12.3	0.78	0.4187
AC	4.0	1	4.0	0.25	0.6361
BB	57.85	1	57.85	3.67	0.1137
BC	81.0	1	81.0	5.1	0.0729
CC	1.85	1	1.85	0.12	0.7458
Total error	78.9	5	15.78		
Total error (Fixed)	2,761.7	14			
R ² (%)	98.85				
R ² _{Adj} (%)	92				
(B)					
A: Current density	630.125	1	630.125	60.30	0.0006
B: pH	276.125	1	276.125	26.42	0.0036
C: Cathode area	4.5	1	4.5	0.43	0.5407
AA	18.6923	1	18.6923	1.79	0.2387
AB	1.0	1	1.0	0.1	0.7695
AC	12.25	1	12.25	1.17	0.3284
BB	51.9231	1	51.9231	4.97	0.0763
BC	2.25	1	2.25	0.22	0.6621
CC	0.585	1	0.585	0.042	0.9858
Total error	52.25	5	10.45		
Total error (Fixed)	1,054.4	14			
R ² (%)	95.05				
R ² _{Adj} (%)	89.1248				

The quality of the developed models was evaluated basing on the variation coefficients (R^2). The closer the R^2 value to unity, more accurate the response could be predicted by the model. The R^2 values for Eqs. (11) and (12) were found to be 0.9885 and 0.9505, respectively. It indicates that 98.85 % of the total variation in the color removal efficiency and 95.05 % of the total variation in the organic matter degradation was attributed to the studied experimental variables. The adjusted determination coefficients ($R^2_{Adj} = 0.92$ and 0.89) showed that 92 and 89 % of the variability observed in data can be explained by the models built for decolorization and organic matter degradation efficiency, respectively, leaving between 8 and 11 % of variability owing to random error. Consequently, the linear regression models, given by Eqs. (11) and (12), can be used to predict successfully the %DC and %DCOD efficiencies, to create and explore the response surface and to find out the optimal conditions of the decolorization and degradation process.

The Pareto analysis (Fig. 2) was used to identify factors that have the greatest cumulative effect on the %DC and %DCOD, and thus to screen out the less significant ones. A Pareto diagram is a series of bars whose heights reflect the frequency or impact of each factor. The bars are arranged in descending order of heights from left to right. Therefore, the factors represented by the tall bars are relatively more significant. Here, the Pareto analysis was also carried out to determine the percentage effect of each factor according to the following equation [22]:

$$P_i = \left[\frac{b_i^2}{\sum b_i^2} \right] \times 100 \quad (i \neq 0) \quad (13)$$

Thus, statistically important factors correspond to all those which values overpass the inner vertical line (Fig. 2). The vertical line corresponds to the t value in the t -student distribution, with a 95 % confidence and for 14 degrees of freedom. Next, this value is compared to the values of each effect and interaction of analyzed factor. The comparison

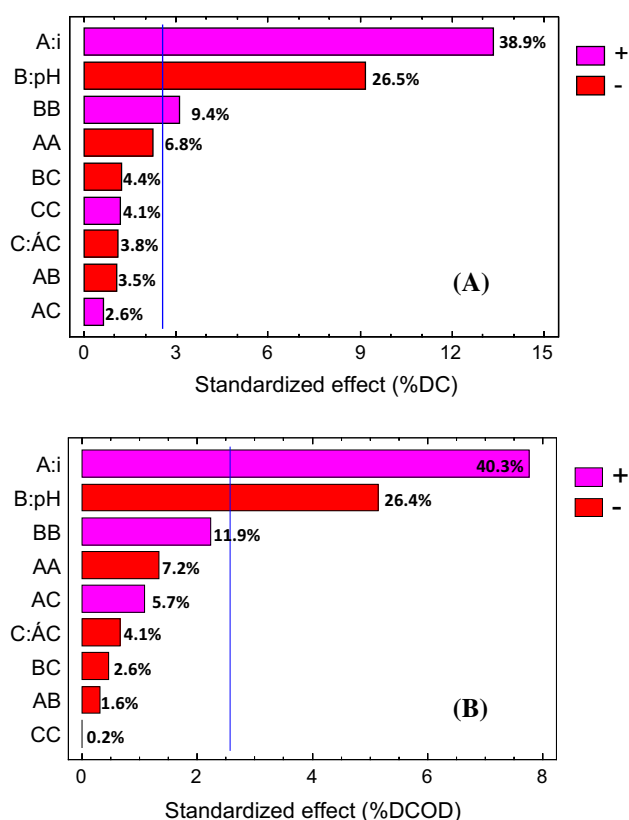
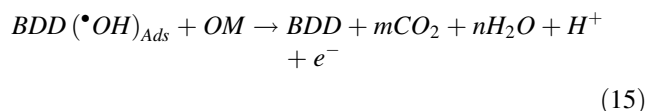
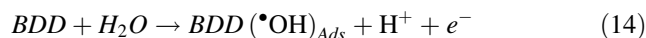


Fig. 2 Pareto diagrams for the %DC (a) and %DCOD (b)

defines the statistical significance of each factor in the analysed process. Therefore, the following factors have an influence on the decolorization process (Fig. 2a): *i* (A), pH (B) and their interactions: B–B. It could be concluded that the %DC is directly proportional (+) to the current density (A), and pH–pH interaction (BB) and inversely proportional (–) to the pH (B). Moreover, the organic matter degradation will be affected by (Fig. 2b): *i* (A) and pH (B). The %DCOD is directly proportional (+) to the current density (A) and inversely proportional (–) to the pH (B).

The effect of interaction between current density and pH on %DC and %DCOD is shown in two contour plots (Fig. 3). The efficiency of decolorization (Fig. 3a) and organic matter degradation (Fig. 3b) significantly increases with the increase in *i* and the decrease in pH value. The enhancement in decolorization/degradation efficiency, obtained under increasing *i*, can be associated to the acceleration of reaction (1), on the anodic surface, which regulates the amount of produced oxidant BDD ($\bullet\text{OH}$). Therefore, larger quantities of BDD ($\bullet\text{OH}$) are generated (Eq. 14), more rapidly the conjugated chromophore system of organic matter (OM) can be destroyed, according to the Eq. (15) [23]:



On the other hand, the increase in decolorization/degradation efficiency, obtained under decreasing pH, can be related to the electrogeneration of H_2O_2 in acid medium, according to the reaction (3). Moreover, it is well known that H_2O_2 is unstable in alkaline solution and consequently it loses its oxidizing potential. Therefore, the $\bullet\text{OH}$ adsorbed at the BDD anode, produced according to the Eq. (2), remains the main oxidizing agent in the EO process.

In conclusion, the following optimal conditions for decolorization/degradation of textile industrial wastewater using EO process were found: pH = 3, *i* = 10 mA/cm² and CA = 16 cm². The signs ‘+’ indicate the optimum values of *i* and pH that maximize the %DC and %DCOD (Fig. 3a, b, respectively).

Next, at optimized conditions, a kinetic analysis was developed by monitoring the evolution of %DC, %DCOD and %DTOC, as a function of time (Fig. 4). One can see that after 35 min of reaction, the 94 % of color degradation was accomplished. However, only 37 % of DCOD and 31 % of DTOC were obtained, showing that the EO does not let to achieve the total mineralization of azo dye, and therefore the reaction (15) can be considered as incomplete. This poor efficiency of the surface can be attributed to the formation of secondary products of lower molecular weight, such as carboxylic acids, coming from the colorant oxidation [2]. This observation is in accordance with the results reported by some authors, who stated that in the potential region before oxygen evolution over BDD electrode, there is no electrocatalytic activity for the oxidation of carboxylic acids, and the oxidation of aromatic compounds results in the deactivation of BDD surface [24].

The results given in Fig. 4 were further analyzed using kinetic equations related to the different reaction orders. Good linear plots were only obtained when kinetics of EO process was fitted using pseudo-first-order reaction. The evolution of %DC, %DCOD and %DTOC followed the subsequent equation:

$$\ln \frac{C}{C_0} = k \cdot t \quad (16)$$

where *k* is the apparent first-order reaction rate constant, *t* is the reaction time, and *C*₀ and *C* are the initial and final response values (%DC, %DCOD and %DTOC), respectively. The following kinetic constants were achieved: *k*_{%DC} = 0.0237 min^{–1}, *k*_{%DCOD} = 0.0059 min^{–1} and *k*_{%DTOC} = 0.0048 min^{–1} with *R*² > 0.99 in all cases.

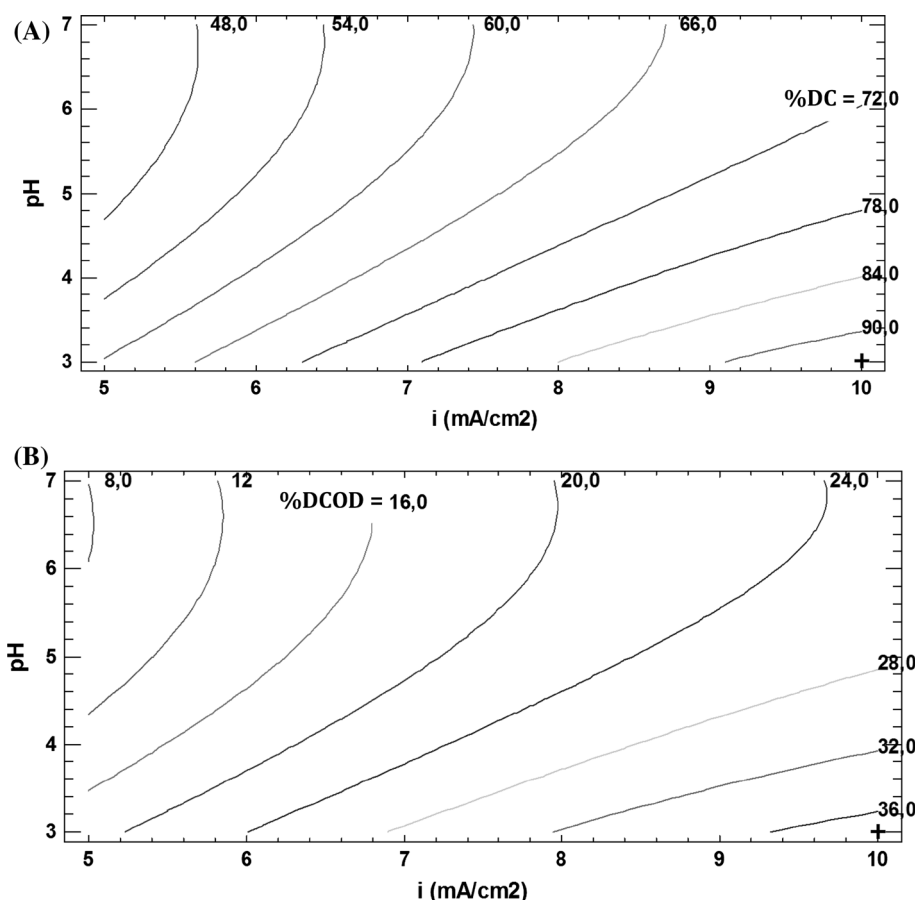


Fig. 3 The contour plots for the interactive effects of i and pH on: %DC (a) and %DCOD (b). Reaction time = 35 min; Temperature = 28 °C; Cathode area = 16 cm². The sign '+' indicates the optimum values of i and pH

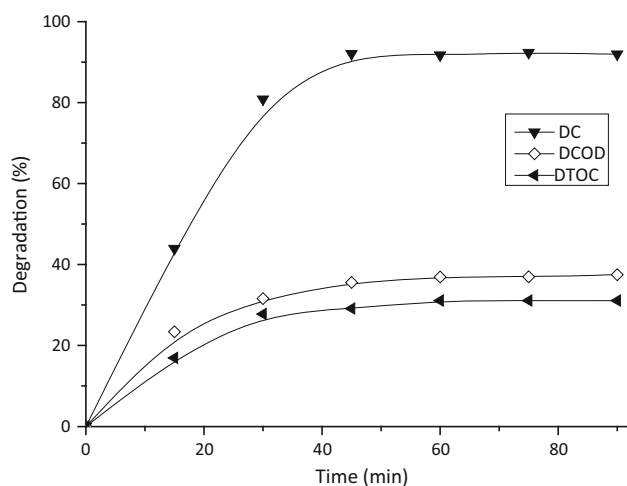


Fig. 4 The evolution of the %DC, %DCOD and %DTC of the wastewater treated using EO process: pH = 3, current intensity = 10 mA/cm² and cathode area = 16 cm²

3.2 The intensification of electro-oxidation process

The efficiency of the EO process was intensified by the addition of 0.3 mM of Fe²⁺ to the reactive system under the optimized experimental conditions. In the presence of Fe²⁺ (EF process), the significant increase in %DCOD and %DTC was observed (Fig. 5a, b, respectively). The addition of Fe²⁺, as catalyst, to the acidic pollutant solution enhances the low oxidation ability of H₂O₂ to yield Fe³⁺ and ·OH via Fenton's reaction (Eq. 4). Moreover, the quick regeneration of Fe²⁺ ion by the reduction of Fe³⁺ at the cathode rises degradation efficiency (Eq. 5). As a result, the EF process let to obtain %DCOD = 52 and %DTC = 45. Consequently, the obtained results were also fitted using pseudo-first-order kinetics, according to the Eq. (16). The following kinetic constants were achieved: $k_{\%DCOD} = 0.0073 \text{ min}^{-1}$ ($R^2 = 0.993$) and $k_{\%DTC} = 0.0083 \text{ min}^{-1}$ ($R^2 = 0.995$).

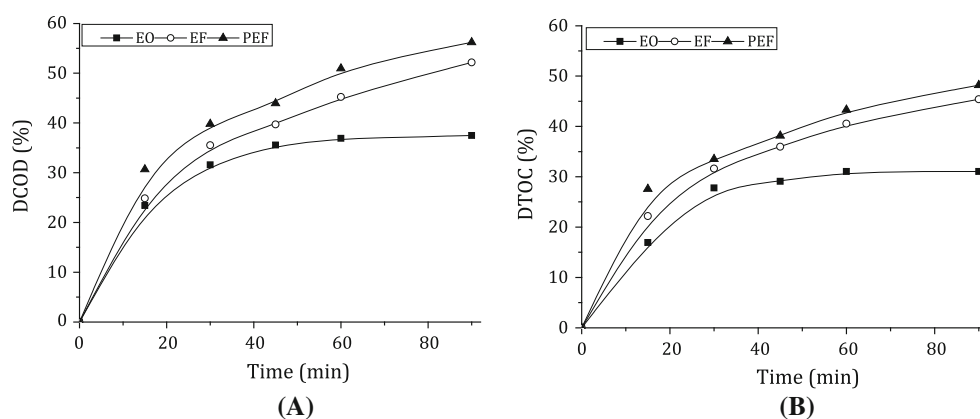


Fig. 5 The evolution of the %DCOD (a) and %DTOC (b) of the wastewater treated using EO, EF and PEF processes. Reaction conditions: $i = 10 \text{ mA/cm}^2$, pH 3, CA = 16 cm^2 , Fe^{2+} concentration = 0.3 mM (for EF and PEF experiments) and UV = 365 nm (for PEF process)

Further increase in the %DCOD and %DTOC up to 56 and 48, respectively was obtained using PEF process, the combination between EF and UV radiation (365 nm), performed at optimized EO conditions. Here, the increase in process efficiency was achieved by faster Fe^{2+} regeneration (Eq. 6) and $\cdot\text{OH}$ formation by $\text{Fe}(\text{OH})^{2+}$ photoreduction (Eq. 7) in acidic solution. Finally, the data fitting using pseudo-first-order kinetics (Eq. 16) let to maximize the kinetic constants in the following way: $k_{\% \text{DCOD}} = 0.0093 \text{ min}^{-1}$ ($R^2 = 0.991$) and $k_{\% \text{DTOC}} = 0.0106 \text{ min}^{-1}$ ($R^2 = 0.989$).

The decrease in colorant concentration during PEF process was followed spectrophotometrically, monitoring the intensity of its absorbance (Fig. 6). One can see that before treatment (time 0 min), its UV–Vis spectrum consisted of two main characteristic absorption bands: one in the visible region ($400\text{--}700 \text{ nm}$) with the maximum at 520 nm , responsible for wastewater color; and the other one, in the UV region ($200\text{--}400 \text{ nm}$), with two characteristic maxima: at 226 nm and 286 nm , corresponding to the presence of aromatic and organic compounds in the wastewater sample. After 15 min of PEF process, the absorption band observed in the visible region was reduced drastically. However, the band observed in the UV region increased its intensity. This due to the rupture of the dye chromophore bond, leading to the formation of shorter molecular chain compounds. Moreover, the H_2O_2 appearance, due to water hydrolysis is registered, as absorbance band at 220 nm . After 90 min of reaction, the absence of band in visible region confirms the total decolorization of wastewater. However, total degradation of the sample was not achieved, as confirmed by the presence of characteristic bands in UV region.

4 Energy consumption during PEP

To determine the efficacy of the PEP process, the energy consumption (EC) during the electrochemical processing

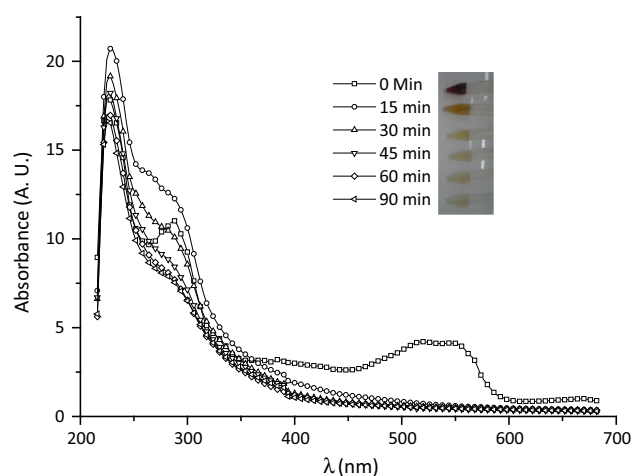


Fig. 6 The UV–Vis spectra of the textile industrial wastewater degradation by PEF at different electrolysis times for the following experimental conditions: $i = 10 \text{ mA/cm}^2$, pH 3, CA = 16 cm^2 , Fe^{2+} concentration = 0.3 mM and UV radiation = 365 nm

of the textile industrial wastewater was determined. Thus, the power (P in kW/h) consumed was estimated from:

$$P = \frac{E_{\text{cel}} I t}{1000} \quad (17)$$

where: E_{cel} is the measured cell potential (V), I is the current applied (A), and t is the time of electrolysis (h). The EC related to the power consumed per g of TOC removed was calculated from:

$$EC = \frac{P}{m} \quad (18)$$

The E_{cel} varied between 5.7 and 6 V, the I used was of 20 mA, and the TOC removed was of 48 % after 1.5 h. Thus, the energy consumption was estimated in 9.94 kW-h/Kg TOC (the price per kW-h in the industrial area varies between 0.16 and 0.21 \$US).

5 Conclusions

This work evidences the applicability of electro-oxidation processes and its coupling with Fenton reactions for the treatment of industrial textile wastewaters. A Box–Behnken experimental design was successfully employed for the optimization of the operational conditions for the treatment of wastewater resulting from a local textile industry. Color, COD, and TOC degradation efficiency were evaluated in electro-oxidation (EO), electro-Fenton (EF), and photo-electro-Fenton (PEF) processes. Regression analysis showed a high coefficient of determination value ($R^2 = 0.94$), ensuring a satisfactory adjustment of the second-order regression model with the experimental data. The optimum operational conditions for the EO process were: pH = 3, current density = 10 mA/cm² and submerged cathode area = 16 cm². At this condition, the following degradation efficiencies were obtained: 92 %DC, 37 %DCOD, and 31 %DTOC. The statistical analysis revealed that the variables with the highest relevance were the current density followed by pH. The EO processes was intensified with the addition of Fe²⁺ = 0.3 mM (EF). The degradation rate of COD and TOC was enhanced, reaching 95 %DC, 52 %DCOD, and 45 %DTOC. The PEF process (using Fe²⁺ = 0.3 mM and UV = 365 nm) generated 98 %DC, 56 %DCOD and 48 %DTOC.

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