Efficient treatment for textile wastewater through sequential electrocoagulation, electrochemical oxidation and adsorption processes: Optimization and toxicity assessment

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ABSTRACT

In this work, the sequential Electrocoagulation + Electro-oxidation + Activated carbon adsorption (EC + EO + AC) process was studied as an alternative for the treatment of an industrial textile wastewater (TWW) issuing from a manufacturing company located in Medellín (Colombia). The EC's and EO's operational conditions were optimized using a Box-Behnken experimental design, the Response Surface Methodology and a constrained nonlinear optimization algorithm in terms of organic matter degradation efficiency. The best performance for EC (i. e., dye removal = 94%, COD and TOC degradation of 45 and 40%, respectively) was obtained using Fe anode and Boron Doped Diamond (BDD) cathode, with current density, j_{EC}, equals to 5 mA/cm^2, pH = 9.3, 60 RPM and 10 min of electrolysis. After EC treatment, the effluent biodegradability (evaluated as the BOD$_5$/COD ratio) increases from 0.14 to 0.23. Regrettably, EC was not effective for the removal of acute toxicity to *Artemia salina* since the treated effluent remained very toxic (100%). The treatment of EC's effluent by EO enhanced organic pollutant removal. For EC + EO sequential process, EO optimal operational conditions (j_{EO} = 10 mA/cm^2, pH = 3, 240 RPM, BDD as anode and Fe as cathode) allowed reduction of 100% of color, 88% of COD and 79% of TOC after 30 min of electrolysis. Moreover, the BOD$_5$/COD ratio increased from 0.23 to 0.58; however, the treated effluent remained very toxic to the *Artemia salina*. Consequently, an activated carbon adsorption step was included to complete the treatment process. Thus, by coupling the EC + EO + AC process, effluent's acute toxicity decreased completely. From molecular weight distribution analysis, it was concluded that EC + EO was efficient in eliminating low molecular weight (< 5 kDa) compounds. Finally, the operation cost, which includes chemical reagents, electrodes, energy consumption, and sludge disposal, for the EC + EO + AC sequential process was estimated in 3.83 USD /m^3.

1. Introduction

The progressive accumulation of organic compounds in water bodies is mostly due to anthropogenic activities such as chemical technologies for organic synthesis and processing. Textile industries are one of the largest consumers of water, dyes, and chemical products, which are used during the different stages of fabric processing. Industrial textile wastewater (TWW) is a major pollutant that often contains high levels of un-fixed dyes (about 20% wt.) and is characterized by alkaline pH, significant salinity, intensive color, high organic matter load, high ionic strength, poor biodegradability, high dissolved solids content, and high toxicity [1]. Accordingly, governments are imposing more stringent regulations and emission limits, and both industries and academy are requested to seek new methods and technologies capable of effectively removing organic matter (COD, BOD$_5$, TOC), dyes and solid content (total solids and turbidity) and toxicity [2].

Electrochemical technologies, such as Electrocoagulation (EC) and Electro-Oxidation (EO), have received great attention because of their capability to effectively treat wastewater [3]. EC is a versatile method for water and wastewater treatment that relies upon the electrochemical dissolution of sacrificial metal electrodes (usually iron or aluminum) into soluble or insoluble species that enhance coagulation, adsorption and/or the precipitation of soluble or colloidal pollutants. EC differs markedly from conventional chemical coagulation in which the coagulant is added at once. During EC, an active coagulant is progressively formed in situ by the corrosion of the anode due to a

fixed current or cell potential. In the case of iron ion, it can be represented as follows [4]:

$$Fe_s \rightarrow Fe^{+2}_{(aq)} + 2e^- \tag{1}$$

At the cathode, hydroxide ion and H_2 are produced according to the following complementary reaction:

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \tag{2}$$

Next, the Fe^{+2} and OH^- ions react to form various Fe species, including monomeric and polymeric complexes. At appropriate pH value, they destabilize and aggregate suspended particles to convert them into settleable flocs. The important factors influencing the effectiveness of effluent treatment by EC are: type of pollutant, electrode material, current density, pH, and electrolyte concentration and type. EC has been successfully applied to remove a wide variety of pollutants, such as: heavy metals, various anions [5] and organic compounds including dyes [6–8]. Recently, Tünay et al. [9] and Hendaoui et al. [7] reported on the treatability of indigo dyeing effluents by the EC reaching almost complete decolourization, and COD removal up to 90%. EC presents many advantages over other techniques, such as high efficiency at low capital and operational costs, low volume requirement and process control simplicity [10].

EO has also been widely studied for the treatment of dye-containing wastewater. Color removal can be achieved by EO with non-soluble anodes. Several anode materials, like iron, conducting polymers, Boron Doped Diamond (BDD) electrodes etc., at different experimental conditions, have been used successfully in the electro-degradation of dyes [11]. The main advantages of adopting EO technologies to treat pollutants are: (1) the elimination of redox chemicals, avoiding the need of treating spent redox streams; (2) close control of the desired reactions by manipulating applied potential or current; and (3) the increased possibility of onsite treatment [12]. Two major mechanisms are responsible for pollutants removal by EO: (1) direct oxidation at the anodic electrode surface through anodic electron transfer reaction; and/or (2) indirect oxidation by electrochemically generated active chlorine, when chloride is used as supporting electrolyte. Usually, indirect oxidation has a stronger ability for color removal when NaCl is used as supporting electrolyte [13]. The prevailing mechanisms for electrochemical oxidation can be summarized as follows: during electrochemical oxidation, chloride is anodically converted to chlorine/hypochloric acid (Eqs. (3) and (4)); then, chlorine/hypochloric acid, which are strong oxidants that can oxidize dyes to intermediates, leads to color removal (Eq. (5)) [14].

$$Anode: 2Cl^- \rightarrow Cl_2 + 2e^- \tag{3}$$

$$Solution: Cl_2 + H_2O \rightarrow HClO + HCl \tag{4}$$

$$Solution: Dye + HClO \rightarrow oxidized\ dye + 2Cl^- \tag{5}$$
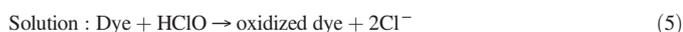
Some research groups have reported on the advantage of coupling EC and EO processes, aiming developing more powerful processes for dye removal [3,15]. The synergistic action of EC-EO process has been successful in the removal of different kind of pollutants [16–18]. In fact, EC process would be used for the decrease of organic load, and suspended solids and EO would be applied for the degradation of color and organic compounds. AC was used to remove the toxicity of chlorine/hypochlorite in the subsequent study. In general, the coupled process is considered as an effective and feasible process for making possible a posttreatment of the effluent in a biological system. In fact, in some cases, the partial oxidation of organic contaminants may result in the formation of intermediates that are more toxic than parent compounds. In response to this drawback, adsorption process is commonly used as a final step in the treatment of polluting by-products that are significantly resistant to biodegradation even at very low concentration levels [19]. Activated carbon (AC) is an efficient adsorbent for removing volatile, semi-volatile and non-volatile chlorinated

organic pollutants, and free chlorine from water due to its unique microporous structure with high surface area, large pore volume and high adsorption efficiency [20,21]. AC may react with free chlorine in two types of chemical reactions [22]: the first type produces oxygen-containing organic compounds on the carbon surface, resulting in a net weight gain (Eqs. (6) and (7)); while the second type (Eqs. (8) and (9)) produces CO_2 as the final product, resulting in a net weight loss:

$$HClO + C^* \rightarrow C^*O + Cl^- + H^+ \tag{6}$$

$$OCl^- + C^* \rightarrow C^*O + Cl^- \tag{7}$$

$$HClO \rightarrow Cl^- + H^+ + [O] \tag{8}$$

$$2[O] + C \rightarrow CO_2\uparrow \tag{9}$$
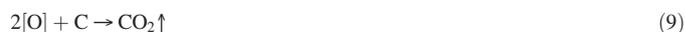
where C^* represents active sites on carbon surface and C^*O corresponds to surface oxides. HClO is a weak acid, with a pKa = 7.6 at 23 °C. Thus, at a pH = 3, HClO dominates; at pH = 8, OCl^- prevails; and at pH = 7.6, the concentrations of each species are approximately equal [22]. The use of AC as final treatment step could significantly reduce the toxicity of the intermediate products generated during the electrochemical process.

In most of the studies reported in the open literature for textile wastewater treatment by electrochemical technologies, authors used synthetic textile wastewater by dissolving dye in distilled water. Zhang et al. [23] used the sequential EC + EO processes to treat a synthetic acid red 2 solution. They found that the decolorization efficiency was high, over 98% after 40 min electrolysis, but with very low COD removal (ca. 33%). However, they did not optimize EC + EO operation conditions nor the effluents' toxicity were reported. In another work, Thiam et al. [16] evaluated the sequential EC + PEF (Photo-Electro-Fenton) process for the decolorization and mineralization of tartrazine synthetic solutions. The EC treatment, at pH = 6.3, during 15 min, followed by treating the supernatant by PEF, at pH = 3 for ca. 300 min, yielded total decolorization and mineralization. Although this is a rigorous study, researchers did not optimize operation conditions nor effluent toxicity was evaluated. On the other hand, the treatment of industrial wastewater samples involves additional challenging tasks. In fact, the electrochemical technologies performance can be hindered by the presence of mixed pollutants and auxiliaries' chemicals used during the textile process, as well as by many other factors such as turbidity, high chloride content, pH, etc. Only few works reported on the use of electrochemical methods for industrial wastewater treatment. Raju et al. [24] reported the treatment of a textile wastewater sample by EC + EO reaching a COD reduction of 88% after 180 min of electrolysis. In another work, Zazou et al [3] evaluated the treatment of a mixture of reactive dyes (mainly methylene blue) by EC coupled to some electrochemical advanced oxidation processes. Among them, the sequential EC + EF (Electro-Fenton) process allowed removing 97% of TOC, 100% turbidity, and 100% color after 120 min of electrolysis. Nevertheless, neither of these two works [3,24] optimized operation conditions to lower costs, nor toxicity studies were carried out. Moreover, to the best of our knowledge, no study combining the application of electrochemical processes and adsorption for the treatment of industrial textile effluents (monitoring not only color, COD and TOC removals but also the evolution of acute toxicity) has been reported. Therefore, in order to gain insight into the performance and applicability of electrochemical methods for TWW treatment, more studies involving industrial effluents are needed. In the present study, an industrial effluent was treated by EC + EO with a subsequent AC step, monitoring the evolution of organic matter and toxicity during the whole process. Operation cost was evaluated in every treatment step. Combining EC + EO + AC is a strategy to reduce organic load and toxicity from TWW; also, it contributes to reducing the amount of chlorine/hypochlorite, hypochlorous acid, and toxic intermediates that need to be removed before discharging wastewater. At first, a complete characterization of the industrial effluent was made in terms of organic matter loading (COD, BOD_5, TOC), biodegradability (BOD_5/COD), toxicity, and solids content. Secondly, the potential of a

sequential EC + EO process was evaluated. A Box-Behnken experimental design (BBD) together with the Response Surface Methodology and a constrained nonlinear optimization algorithm were used to optimize the efficiency of EC + EO sequential process in terms of organic matter degradation. Finally, to reduce the intermediate toxicity of textile wastewater, the EC + EO process' effluent was treated by AC adsorption.

2. Materials and methods

2.1. Materials

Wastewater samples were collected from an equalization tank of a textile industry, located in Medellin-Colombia. This facility focuses on the production of denim jeans and generates an average of 800 m^3/day of effluents as a result of pre-washing, washing, dyeing, and finishing steps where industrial detergents, dyes, and other chemical compounds are released as TWW. It presents a dark blue color due to the mixture of several dyes (v. g., reactive, direct, dispersive, acid, and vat dyes). In order to determine its representative characteristics, the sampling was performed bimonthly for 1 year. Samples were kept at 4 °C to avoid degradation during storage, following standard procedures [25]. All reagents were used as received from suppliers without any further purification. The corresponding aqueous solutions were prepared using ultrapure water (Milli-Q system, Billerica, Massachusetts; conductivity <1 $\mu S.cm^{-1}$). The solution pH was adjusted with sulfuric acid (H_2SO_4; Merck, purity = 98%). MnO_2 (Sigma Aldrich; reagent grade $\geq$ 90%) was also used as explained subsequently.

2.2. Methods

Standard methods [25] were followed for the quantitative analysis of TWW and after-treatment samples: pH (pH-meter LAB-850-Analytics); Conductivity (2510-B, conductivimeter LAB-960 Analytics); Color (A UV-VIS double-beam spectrophotometer equipped with a 1 cm path length quartz cell (Spectronic Genesys 2 PC) to measure the absorbance spectrum in the range of 200–700 nm); Turbidity (2130 B, Orbeco-Hellige turbidimeter (Model 966–01)); Total Solids (2540D); COD (5220D, the closed reflux method with colorimetric determination); TOC (5310D); BOD_5 (5210B, the respirometric method); and generated sludge (the EC effluent was filtered and the solid residue was dried until constant weight).

Generated carboxylic acids were quantified by ion-exclusion HPLC (Agilent 1200, using a Hi-Plex column, 300 mm × 7.8 mm, at 35 °C and setting the photodiode array detector at λ = 210 nm). These measurements were made by injecting 20 μL aliquots into the LC and using a mobile phase of 4 mM H_2SO_4 at 0.6 mL/min. The chromatograms displayed well-defined peaks at retention time values of 7.2 min for oxalic acid, 9.2 min for tartaric acid, 10.9 min for malonic acid, and 14.9 min for formic acid.

Test kit HI-38020 Chlorine was used to determine the concentration of aqueous chlorine. Finally, H_2O_2 concentration was measured by iodometric titration. To avoid the interference of H_2O_2 during COD measurements, the residual H_2O_2 was quenched using MnO_2. Triplicate measurements were performed for all analyses.

2.3. Electrochemical reaction system and procedure

For electrochemical experiments, plexiglass, continuously stirred, batch jacketed reactor (0.12 L) was used. It contained two vertical plate electrodes, connected in a mono-polar arrangement to a DC power source (BK-Precision, 0–30 V, 0–5 A, Yorba Linda, California) operating in galvanostatic mode. The electrode materials and dimensions were: iron (> 98 wt%; 18 mm width, 50 mm height and 0.6 cm thickness) and BDD film deposited on silicon substrate (BDD/Si; film ≈ 3 μm thick; doping level: 700–800 ppm boron; 25 mm width, 50 mm height and 2 mm thickness; Supplier: Fraunhofer, USA). The gap between the electrode pair was set at 1 cm. On the top of the cell, a PT-100 sensor (± 0.01 K) was placed to measure the solution's temperature. For all experiments, the temperature was maintained at 22 °C using a Polyscience 712 thermostat (Niles, Illinois)

connected to the reactor jacket. Before each experiment, the iron electrode was rinsed in a solution of 30 wt% H_2SO_4 and then washed with distilled water. The BDD electrode was dipped into deionized water for 5 min. The electrochemical integrated process started when the DC power supply was switched on. Thus, for the EC process (10 min) the iron electrode was used as the anode and BDD served as the cathode, stirring speed was maintained at 60 rpm and pH = 9.28 (corresponding to the raw wastewater). Indeed, for EC, the iron electrode is more efficient in neutral and alkaline medium, especially between 6 < pH < 9 [26]. The current density was adjusted to the desired j_{EC} value. After the EC process, the solution pH was adjusted to the desired value. Next, to perform the EO process (during 30 additional min), electrode's polarities were switched (i.e., the BDD electrode became the anode), the current density was set to the desired value again and the stirring speed maintained at 240 rpm. The initial solution pH for EO experiments was adjusted with dilute H_2SO_4. At the end of each run, a 5 mL sample was taken and centrifuged at 2000 rpm for 10 min before analysis.

2.4. AC adsorption process

To eliminate active chlorine and other compounds that contribute to toxicity remaining after the sequential (EC + EO) treatment, the effluent was passed through a granular activated carbon (AC) packed bed column (AC from Hong-Yu Inc., Taiwan). The average physical properties of the activated carbon are: surface area (BET) = 1200 m^2/g, iodine number = 1150 mg/g, apparent density = 482 kg/m^3, U.S. Standard Sieve Size (Mesh Size) = 30 and Ash (max) = 3% (ASTM D-2866). Before each experiment, the AC was washed with pure water (Milli-Q System, Billerica, Massachusetts; conductivity <1 $\mu S.cm^{-1}$), baked at 175 °C for 1 week to remove volatile impurities, and then kept in the oven at 105 °C. Before its use, AC was moved into a desiccator to let it cool down to room temperature. Adsorption was conducted, at 25 °C, in a glass column (inner diameter = 28 mm, effective length = 120 mm, AC loading = 45 g), flow rate = 20 mL/min, retention time = 3.7 min. After the adsorption process, the effluent was filtered through a 0.45 μm membrane filter; then, free and total chlorine concentrations and acute toxicity were measured.

2.5. Experimental design and statistical analysis

(EC + EO) process performance was optimized (i.e., to maximize the organic matter degradation) using a Box-Behnken experimental Design (BBD) and a constrained nonlinear optimization algorithm. The independent variables (or operating factors) and their levels were selected based on preliminary experimental results (not shown here) and our previous work [27] as follows: (i) EC current density (j_{EC}) = 5–15 mA/cm^2; (ii) EO current density (j_{EO}) = from 10 to 30 mA/cm^2; and (iii) pH_{EO} = between 3 and 10. In all cases, the initial pollutant concentration corresponded to the industrial TWW. BBD involved 15 tests (including three centered experiments). They were designed using Statgraphics® Centurion XVI statistical software. Experiments were run randomly. All experiments were made by triplicate and the average value of each response variable was used for the statistical analyses.

The response variables for the experimental design were the percentage of COD degradation (%DCOD), calculated with Eq. (10),

$$\%DCOD = \frac{COD_i - COD_t}{COD_i} x100 \tag{10}$$

where, COD_i is the initial COD and COD_t is the COD at time t; and operation cost (OC), calculated with Eq. (11).

$$OC\left(\frac{USD}{m^3}\right) = \frac{1}{V_r}\left[\left(1.08\frac{MIt}{nF} + 2 \times 10^{-4}VIt + 0.2S + 0.027D\right)\right] + C_{AC} \tag{11}$$

where V_r (m^3) is the reaction volume for both EC and EO stages; the first term in the right-hand side represents the cost of the consumed anode

(USD/kg), per Faraday's law with a safety factor of 20% (i.e. Faraday's law is multiplied by 1.2), where M is the anode molecular weight (kg/kmol), I is the electric current (A), t is the electrolysis time (h), n is the number of electrons transferred, and F is Faraday's constant (26,801.4 Ah/kmol); the second term corresponds to the energy spent in the process with V as the applied voltage (V), S is the amount of H_2SO_4 used (kg), D is the sludge generated (kg) and C_{AC} is the cost of the adsorption process. OC was calculated using data from Colombian official agency of statistics for 2019 (i.e., anode's material cost = 0.9 USD/kg, energy cost = 0.2 USD/kWh, H_2SO_4 = 0.28 USD/kg, C_{AC} cost = 0.08 USD/m^3 and solids disposal = 27 USD/ton of sludge).

The percentage of color removal, %DC, was estimated using Eq. (12).

$$\%DC = \frac{Abs_i - Abs_t}{Abs_i} \times 100 \qquad (12)$$

where, Abs_i and Abs_t are the initial absorbance at 660 nm, and absorbance at 660 nm, at time t, respectively.

BBD results were adjusted to a second-order model as in Eq. (13) using Statgraphics Centurion XVI Software:

$$Y_i = \beta_0 + \sum_{i=1}^{3}(\beta_i X_i) + \sum_{i=1}^{3}(\beta_{ii} X_{ii}^2) + \sum_{i=1}^{3} \cdot \sum_{j=1}^{3}\left(\beta_{ij} X_i X_j\right) \qquad (13)$$

Where β_0, β_i, β_{ii}, β_{ij} are the regression coefficients for the intercept, linear, square, and interaction terms, respectively; and X_i and X_j are independent variables. The quality and validity of the model and its capacity to estimate experimental results were assessed with the adjusted determination coefficient, R^2_{adj}; and the Akaike information criterion, AIC. Details of this methodology has been reported elsewhere [2]. With the regression models and an optimization searching algorithm, using Excel VB, the optimal operation conditions (v.g., minimize OC while reaching a fixed % DCOD) were defined.

2.6. Sample isolation and fractionation

The Molecular Weight Distribution (MWD) analysis of raw and treated wastewater samples was performed by membrane ultrafiltration, with nominal molecular weight limits of 30, 10, 5, and 3 kDa [28]. The ultrafiltration process was conducted in a 50 mL ultrafiltration system (Amicon® Stirred Cell, EMD Millipore- Merck, Germany), with operational pressure of ultrafiltration was kept constant at 0.2 MPa by a steady supply of highly

pure N_2 (99.999% vol.), employing regenerated cellulose ultrafiltration membranes (44.5 mm, Millipore Corporation, Germany) with MW cut-offs of 3 kDa, 5 kDa, 10 kDa, and 30 kDa. Before each test, membranes were washed for 30 min with 0.1 M NaOH and flushed with deionized water and then preserved in 10% ethanol/water solution at 4 °C (from membrane manufacturer instructions). Samples were passed through ultrafiltration membranes with different MW cut-offs. The initial and final 5 mL of filtrate from each ultrafiltration process was discarded. Afterwards, TOC concentration of each filtrate fraction was determined.

2.7. Toxicity assessment

Acute toxicity tests with *Artemia salina* (Carolina Biological Supply Company) were performed by triplicate with raw and after-treatment samples [29]. The toxicity assays were done evaluating the immobilization of *Artemia salina*. The artemia was bred in an aqueous culture medium whose salinity resembled the conditions for the survival and development of these micro-crustaceans. Test plates containing twenty *Artemia salina* crustaceans, in the presence of 9.5 mL of the sample solution and 0.5 mL of saline medium, were incubated for 24 h at 25 ± 1 °C and with lateral illumination by a light tube (3500 Lux) during the test period. No nourishment was provided to these crustaceans between hatching and test steps. Acute toxicity was assessed by noting the effects of the test compounds on the mobility of *Artemia salina*. The crustaceans were considered immobile if after 24 h incubation they remained at the bottom of the test container or remained still within 15 s of observation. Acute toxicity is expressed as a percentage of immobilization compared to a nontoxic control, where an artemia immobilization of 10% is accepted after 24 h of exposure. The mortality of *Artemia salina* was calculated with the following equation:

$$Mortality = \frac{N_0 - N_t}{N_0} \times 100 \qquad (14)$$

where N_0 and N_t were initial and at time t *Artemia salina* living members.

3. Results and discussion

3.1. Industrial wastewater samples

The effluent sample shows an intense blue color mainly due to the presence of indigo dye, which represents a high percentage of the total organic load. Table 1 presents its main characteristics. The COD of this effluent was

Table 1
Characterization of industrial effluent, after treatment (EC, EC + EO and EC + EO + AC) samples and permissible discharge limits, as defined by Colombian legislation.

Parameter	TWW Sample	Permissible Limit[a]	After EC	After EC + EO	After EC + EO + AC	Global treatment Efficiency (%)	
						EC + EO	EC + EO + AC
pH	9.28	6–9	8.6	3.6	6.1	–	–
Conductivity (mS/cm)	2.76	–	2.55	2.71	2.32	–	–
Absorbance (660 nm)	1.44	–	0.1	0.00	0.00	100	100
Color (Pt—Co units)	1310	–	92	53	49	96	96
ISO 7887:2012–04 (B·C)	$\lambda_{436} = 64$		$\lambda_{436} = 11.7$	$\lambda_{436} = 2.9$	$\lambda_{436} = 2.5$	$\lambda_{436} = 95.5$	$\lambda_{436} = 96$
$\lambda = 436$–525-620 nm (m^{-1} B)	$\lambda_{525} = 60$		$\lambda_{525} = 5.4$	$\lambda_{525} = 1.2$	$\lambda_{525} = 1.0$	$\lambda_{525} = 98$	$\lambda_{525} = 98$
	$\lambda_{620} = 83$		$\lambda_{620} = 2.9$	$\lambda_{620} = 0.9$	$\lambda_{620} = 0.8$	$\lambda_{620} = 99$	$\lambda_{620} = 99.2$
Chloride - Cl$^-$ (mg/L)	1156	1200	1080	1064	1015	8.0	12.2
Free/total chlorine (mg/L)	0.0	–	15/22	23/52.5	0.0/0.0	–	–
Turbidity (NTU)	142	–	25	7	3	95	98
Total Solids (g/L)	4.59	–	2.1	0.0	0.0	100	100
COD (mg O$_2$/L)	720	400	391	86	72	88	90
TOC (mg C/L)	164	–	96	34	30	79	82
BOD$_5$ (mg O$_2$/L)	101	200	89.93	49.88	47	51	54
BOD$_5$/COD ratio	0.14	0.40	0.23	0.58	0.65	–	–
Mortality (%)	100	–	60	100	0.0	–	–
Generated sludge (kg/m^3)	–	–	0.936	0.936	0.936	–	–
Operation cost (USD/m^3)	–	–	0.625	3.75	3.83	–	–

[a] Res 0631, 17/03/2015, issued by the Ministry of Environment and Sustainable Development, Colombia.

Table 2
The experimental and model predicted results of %DC, %DCOD and OC,
according to the BBD. The initial EC operating conditions were (Table 1): initial solution pH_{EC} = 9.28 and conductivity = 2.756 mS/cm.

Run	j_{EC} mA/cm^2	j_{EO} mA/cm^2	pH_{EO}	Sludge kg/m^3	%DC		%DCOD		OC (USD/m^3)	
					Y_{exp}	Y_{pred}	Y_{exp}	Y_{pred}	Y_{exp}	Y_{pred}
1	15	20	3.0	1.93	96.83	95.26	84.72	87.85	10.1	9.99
2	10	20	6.5	1.51	98.54	98.70	76.11	78.38	9.2	9.25
3	10	20	6.5	1.43	98.78	98.70	79.03	78.38	9.2	9.25
4	5	20	10	0.95	96.95	98.52	73.89	70.77	8.0	8.11
5	10	10	3.0	1.49	97.44	97.75	79.17	80.64	4.4	4.48
6	10	30	3.0	1.50	89.04	91.63	100.0	99.95	17.3	17.51
7	10	20	6.5	1.44	98.78	98.70	80.00	78.38	9.3	9.25
8	5.0	30	6.5	1.05	98.66	97.40	85.42	90.02	16.4	16.42
9	10	30	10	1.50	97.20	96.89	97.78	96.31	17.2	17.09
10	15	20	10	1.92	94.76	96.09	81.00	85.54	9.4	9.64
11	5	10	6.5	1.14	95.13	96.15	59.72	62.79	3.5	3.65
12	15	10	6.5	1.92	97.08	98.34	78.47	73.87	5.1	5.17
13	15	30	6.5	1.91	93.06	92.04	98.61	95.54	18.3	18.15
14	5	20	3.0	1.03	97.32	95.99	90.56	86.02	8.5	8.27
15	10	10	10	1.44	98.42	95.83	66.67	66.72	4.6	4.38

almost two times higher than the permissible limit in Colombia, implying the presence of a large amount of organic matter. The initial BOD_5/COD ratio of 0.14 (< 0.4) indicates that the effluent is not biodegradable [30]. Moreover, it is toxic to *Artemia salina*. Notice also that the TWW has a high-conductivity value, due to the presence of different salts used during the tanning process.

3.2. Effect of operating parameters on COD reduction and optimization of EC + EO performance

Details of the experimental tests and the obtained data (expressed as % DC, %DCOD, and OC) are presented in Table 2. %DC varied between ca. 89 and 99%, %DCOD ranged from ca. 59 and 99%, while the OC varied from 3.5 to 17.3 USD/m^3. The pH variation during EC tests was also monitored. It changed in the range $8.8 < pH_{EC,final} < 9.8$. In contrast to chemical coagulation, EC treatment can increase the solution pH as a consequence of cathodic OH^- formation as indicated in Eq. (2) [31]. Before the EO step, solution pH was adjusted as defined by the experimental design run (Table 2).

%DC, %DCOD, and OC data were adjusted to second-order multivariable polynomial models (Table 3). Analysis of variance (ANOVA) was used to identify significant main and interaction effects among factors influencing the response variables. It can be seen, by examining p-values, that just the factors j_{EC} and j_{EO}, and the quadratic term j_{EO}^2 are statistically significant for OC. In the case of %DC, the factor j_{EO}, the interactions j_{EC}-j_{EO} and j_{EO}-pH_{EO} and the quadratic term j_{EO}^2 are significant. For %DCOD, only j_{EO} yielded p-value <.05. None of the other factors, quadratic terms and interactions, are statistically significant in the analyzed experimental range. This was probably due to the minor changes in the treated effluent alkalinity proportioned by the pH_{EO} variations.

The quality of adjusted model was evidenced from the coefficient of determination (R^2). In all cases, the R^2 value was found to be higher than 0.92, being in good agreement with the adjusted one, $R^2_{Adj} > 0.83$. The models for %DC, %DCOD and OC are shown in Eqs. (15)–(17)

$$\%DC = 83.28 + 1.4661 \times j_{EC} + 0.6493 \times j_{EO} + 0.8851 \times pH - 0.0356 \\ \times j_{EC}^2 - 0.0378 \times j_{EC} \times j_{EO} - 0.0243 \times j_{EC} \times pH - 0.0183 \times j_{EO}^2 \\ + 0.0513 \times j_{EO} \times pH - 0.1099 \times pH^2 \quad (15)$$

$$\%DCOD = 94.90 + 0.6588 \times j_{EC} - 0.0845 \times j_{EO} - 9.62 \times pH - 0.0234 \\ \times j_{EC}^2 - 0.0278 \times j_{EC} \times j_{EO} + 0.185 \times j_{EC} * pH + 0.0277 \\ \times j_{EO}^2 + 0.0734 \times j_{EO} \times pH + 0.3883 \times pH^2 \quad (16)$$

$$OC \left(\frac{USD}{m^3} \right) = 0.7190 + 0.2661 \times j_{EC} - 0.0446 \times j_{EO} + 0.1579 \\ \times pH - 0.0054 \times j_{EC}^2 + 0.0011 \times j_{EC} \times j_{EO} - 0.0028 \\ \times j_{EC} \times pH + 0.0173 \times j_{EO}^2 - 0.0023 \times j_{EO} \\ \times pH - 0.0092 \times pH^2 \quad (17)$$

In order to determine the integrated effect of each factor on the response variables, three-dimensional Box-Behnken surface plots, constructed from the polynomial models described by Eqs. (13) to (15) at constant j_{EC} = 5 mA/cm^2, were prepared (Fig. 1). The color removal rate increases with an increase in current density (Fig. 1(a)). This behavior suggests dye elimination through direct anodic oxidation (adsorption dye molecules to electrode surface) and indirect oxidation by means of its reaction with electrogenerated •OH radicals and powerful active chlorine species (Cl_2/ $HClO$/ClO^-), electrogenerated from the direct oxidation of chloride ions at the anode (Eqs. (3)–(5)) [14,15] (notice that the current textile wastewater exhibited a chloride content of around 1156 mg/L). In the studied pH range, almost no variation on the %DC was observed.

The higher %DCOD corresponds to low pH values. Additionally, the higher j_{EO} is, the higher %DCOD was observed. This is probably due to the •OH radicals and chloro active species (Cl_2, HOCl and ClO^-) formation during the EO process. At acid pH values, oxidants such as Cl_2, HOCl and $^•$OH radicals are generated [22]. They can mediate COD and color removals by direct oxidation of organic compounds on the surface of BDD anode. In fact, it has been reported that the adsorption rate of •OH radicals on the surface of BDD decreases when pH increases and that this generated •OH can be transformed into oxidants with lower oxidation potential compounds, such as H_2O_2 and $HO_2^•$ [13]. Furthermore, at high pH values, chlorine active species OCl^- predominate over Cl_2 and HOCl; and COD removal must be mediated by H_2O_2 and HO_2• and OCl^-.

Fig. 1(c) shows effect of pH and current density (j_{EO}) on the OC. As expected for electrolytic systems, it was found that the OC increases with an increase in j_{EO}, with almost no significant influence of pH. However, it is important to notice that low pH values are better for the EC + EO combined process and that the cost of the H_2SO_4 required to adjust pH is low compared to the energy cost. According to Brillas and Martínez-Huitle [14], electrochemical oxidation with NaCl as support electrolyte is faster in acid than in alkaline medium (the predominant active chlorine species for the pH range 3–8 is HClO, and that for pH >8.0 is ClO^-). In this study, the efficiency of the process (%DCOD) was significantly higher at low pH values. Similar results were reported by Chatzisymeon et al. [32]. However, other researchers reported different pH effect: some treatment process favored at high pH values [5], while some other showed no pH dependence [33]. All these studies suggest that the effect of pH and

Table 3

ANOVA results of the response surface quadratic model, according to %DC, %DCOD and OC data.

Response variable % DC	Sum of squares	Degree of freedom	Mean square	F value	p value
A: j_{EC}	5.009	1	5.009	0.92	0.3825
B: j_{EO}	12.777	1	12.777	5.34	0.0287
C: pH_{EO}	5.611	1	5.611	1.03	0.3758
AA	2.917	1	2.917	0.53	0.4979
AB	14.251	1	14.251	6.61	0.0167
AC	0.723	1	0.723	0.13	0.7311
BB	12.348	1	12.348	5.26	0.0493
BC	12.888	1	12.888	2.36	0.0318
CC	6.692	1	6.692	1.22	0.3190
Error total	27.3377	5	5.468		
Total (corr.)	97.9779	14			
$R^2 = 95.96\%$ $R^2_{adj} = 87.10\%$					
Response variable % DCOD	**Sum of squares**	**Degree of freedom**	**Mean square**	**F value**	**p value**
A: j_{EC}	137.863	1	137.863	5.13	0.0730
B: j_{EO}	1195.12	1	1195.12	44.44	0.0011
C: pH_{EO}	154.089	1	154.089	5.73	0.0621
AA	1.3017	1	1.3017	0.05	0.8346
AB	7.7284	1	7.7284	0.29	0.6149
AC	41.9256	1	41.9256	1.56	0.2671
BB	28.3051	1	28.3051	1.05	0.3520
BC	26.4196	1	26.4196	0.98	0.3671
CC	83.5271	1	83.5271	3.11	0.1383
Error total	134.451	5	137.863		
Total (corr.)	1807.34	14			
$R^2 = 92.56\%$ $R^2_{adj} = 82.63\%$					
Response variable OC (USD/m³)	**Sum of squares**	**Degree of freedom**	**Mean square**	**F value**	**p value**
A: j_{EC}	5.271	1	5.271	96.36	0.0002
B: j_{EO}	331.36	1	331.36	6057.89	0.0000
C: pH_{EO}	0.1278	1	0.1278	2.34	0.1870
AA	0.0662	1	0.0662	1.21	0.3215
AB	0.0115	1	0.0115	0.21	0.6661
AC	0.0095	1	0.0095	0.17	0.6948
BB	11.067	1	11.067	202.32	0.0000
BC	0.0262	1	0.0262	0.48	0.5194
CC	0.0471	1	0.0471	0.86	0.3959
Error total	0.2735	5	0.0547		
Total (corr.)	348.601	14			
$R^2 = 99.92\%$ $R^2_{adj} = 99.78\%$					

the role of active chlorine in EO are circumstantial and depend on other factors involved, such as: the type of pollutants, the electrode used, and the current density applied.

To determine the operation conditions allowing to achieve simultaneously the minimum OC and the maximum %DCOD (constrained to a minimum value of 77%, which guarantees to accomplish Colombian legislation limits), the constrained nonlinear optimization problem depicted in Eq. (18), coupled with Eqs. (15)–(17), was solved using MS Excel's solver.

$$\min OC(j_{EC}, j_{EO}, pH_{EO})$$

s.t.

$$DCOD \geq 77\%$$

$$5 \leq j_{EC} \leq 15$$

$$10 \leq j_{EO} \leq 30$$

$$3 \leq pH_{EO} \leq 10 \tag{18}$$

As the objective function for the operating cost OC (j_{EC}, j_{EO}, pH_{EO}) is flat near its minimum value and OC is a discrete variable, multiple optimum values can be detected. This optimization problem, solved using different initial guesses for j_{EC}, j_{EO} and pH_{EO}, converged in the vast majority of the cases to $pH_{EO} = 3$ and $j_{EC} = 5$ mA/cm². When varying j_{EO} from 10 to 30 mA/cm², at $pH_{EO} = 3$ and $j_{EC} = 5$ mA/cm², OC changes from 3.56 to

16.46 USD /m³, respectively. These outcomes agree with data reported by de Oliveira et al. [34] and Kaur et al., [35]. Therefore, $pH_{EO} = 3$, $j_{EC} = 5$ mA/cm² and $j_{EO} = 10$ mA/cm² were chosen. They allow us to reach 80% of DCOD at OC equals to 3.56 USD/m³. These results were experimentally verified, in an independent run, following TOC, COD and color removal (Fig. 2). The dye degradation process was faster for color removal than for COD and TOC, which implied that chromophoric groups were easily degraded by the electrochemical process. This indicated effective decoloration ability of electrochemical oxidation, which agrees with other studies [2,34]. After 20 min of electrolysis, the dark blue dye wastewater became colorless (Fig. 2(a)). COD and TOC reduction were also very effective. After the treatment, COD decreased from 720 mg/L to 86 mg/L (meeting the last environmental Colombian regulation). The TOC removal rate was slightly lower than that of COD, from 164 mg/L to 34 mg/L, which implied that part of organic compounds was degraded to other organic by-products and another large part of the organic compounds was mineralized to CO_2. Fig. 2(a) shows that the coupled EC + EO process stabilized at a DCOD around ca. 85% agreeing with the predicted value of 80%, within a reasonable level of experimental error. EC + EO process contributes to DCOD and DTOC more than EC (i.e., after EC + EO, DCOD and DTOC are 88% and 79%, respectively). This is because EC works by suspended solids destabilization and, therefore, it is highly efficient for dyes removal [36]. On the other hand, EO's mechanism is explained by the chemical oxidation of the pollutants with •OH radicals formed at the electrodes where this type of reaction is more efficient with soluble compounds (e.g., detergents present at low concentrations). In addition to %DCOD, other TWW's physical-chemical parameters changed after EC + EO. Table 1 shows the physical-chemical properties of TWW before and after EC and EC + EO processes. After EC + EO, TOC is reduced by 79% and BOD_5 is reduced by 51%, implying that EC is efficient to remove a high content of organic load. Turbidity removal was 95%, meaning that almost all suspended solids were removed from water by EC and that the remaining pollutants are soluble organic compounds that would require a more energy-intensive electrooxidation stage to be completely removed. Also, in Table 1, BOD_5/COD increased from 0.14 (raw water) to 0.58 (after EC + EO processes), suggesting that the sequential process effectively increases wastewater biodegradability. The chloride ions removal was of 8% (after EC + EO processes). This result can be explained by the oxidation of Cl^- to Cl_2 and/or to hypochlorite ClO^- at the anode according to the reactions (3)–(5).

TWW UV–vis spectrum showed three main characteristic absorption bands: at 230; 290 nm assigned to benzenic rings; and at 660 nm assigned to indigo dye (Fig. 2 (b), initial curve). It has been reported that absorption band with λ above 200 nm, generally indicates the presence of aromatic compounds (Workman, 2001). UV absorption band with λ signals in the range of 200–250 nm is generally attributed to ketones, acids, aldehydes, phthalates, esters, alkanes etc…., and that at between $250 < \lambda < 275$ nm represents alcohols, ketones, aldehydes etc. [37,38]. Notice that, after 40 min of electrolysis, peaks at λ value ~290 and ~660 nm have completely disappeared. This implies that some of the organic compounds were degraded/oxidized by the oxidant species (•OH, H_2O_2, $HO_2^•$ and HOCl) generated during the EO process, and only very small intensity band between $250 < \lambda < 275$ nm remained.

3.3. Treated effluent disposability

MWD, acute toxicity, and chromatography analysis of EC + EO treated samples (at the optimum operation condition) were performed to gain insight into the possible fate of organic pollutants. Raw TWW samples were also analyzed for comparison. MWD was evaluated in terms of COD, TOC, color (quantified as dye concentration, Pt—Co units, and by spectrophotometry) and toxicity (Fig. 3). TWW comprises primarily low MW compounds (< 3 kDa, ca. 42%; that can be attributed to the presence of formaldehyde, acetic acid, formic acid, oxalic acid, etc….) and high MW compounds (> 30 kDa, ca. 33%; which probably correspond to auxiliary chemicals used during the dyeing process, like surfactants, starch, waxes,
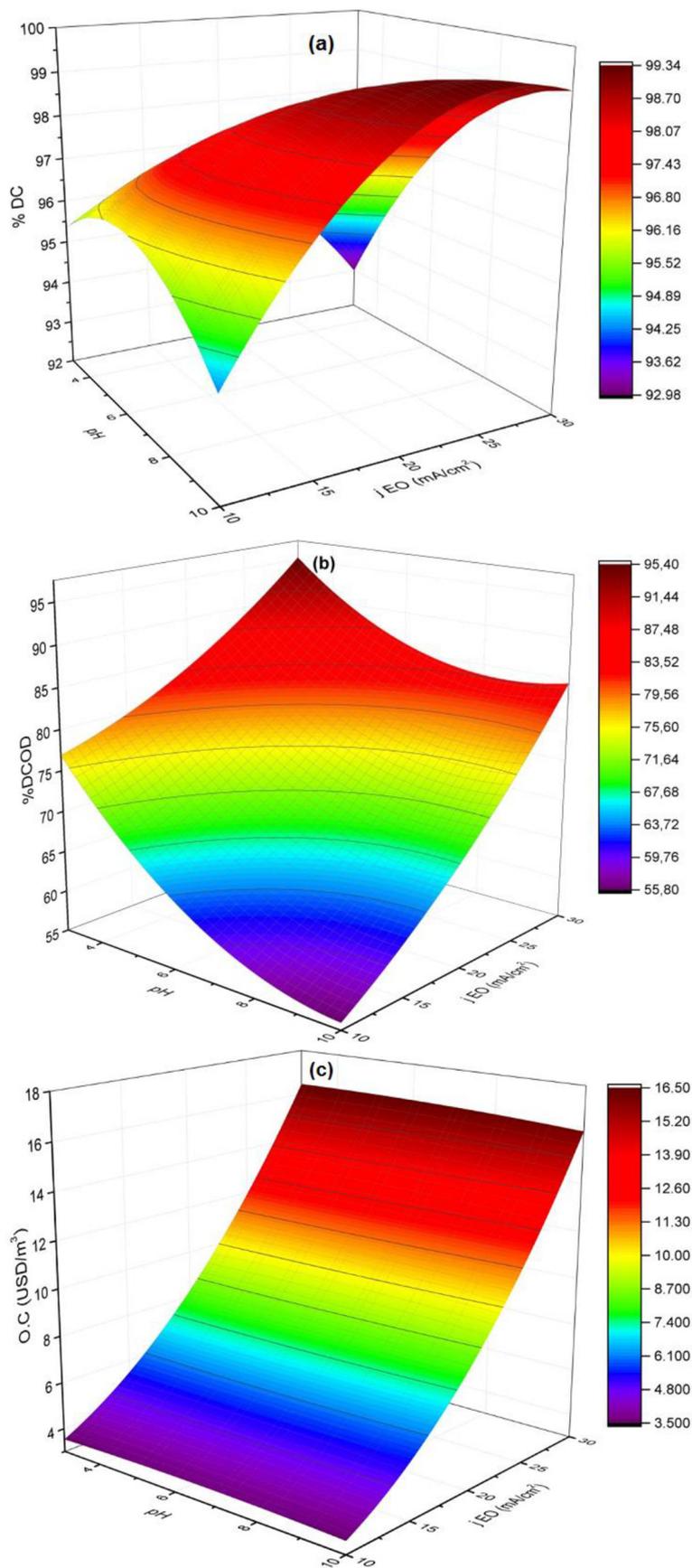
Fig. 1. Three-dimensional response surface plots for the interactive effect of j_{EO} and pH_{EO} on: (a) %DC, (b) %DCOD and (c) OC for EC + EO process (electrolysis time = 10 min for EC and 30 min for EO, temperature = 25 °C).
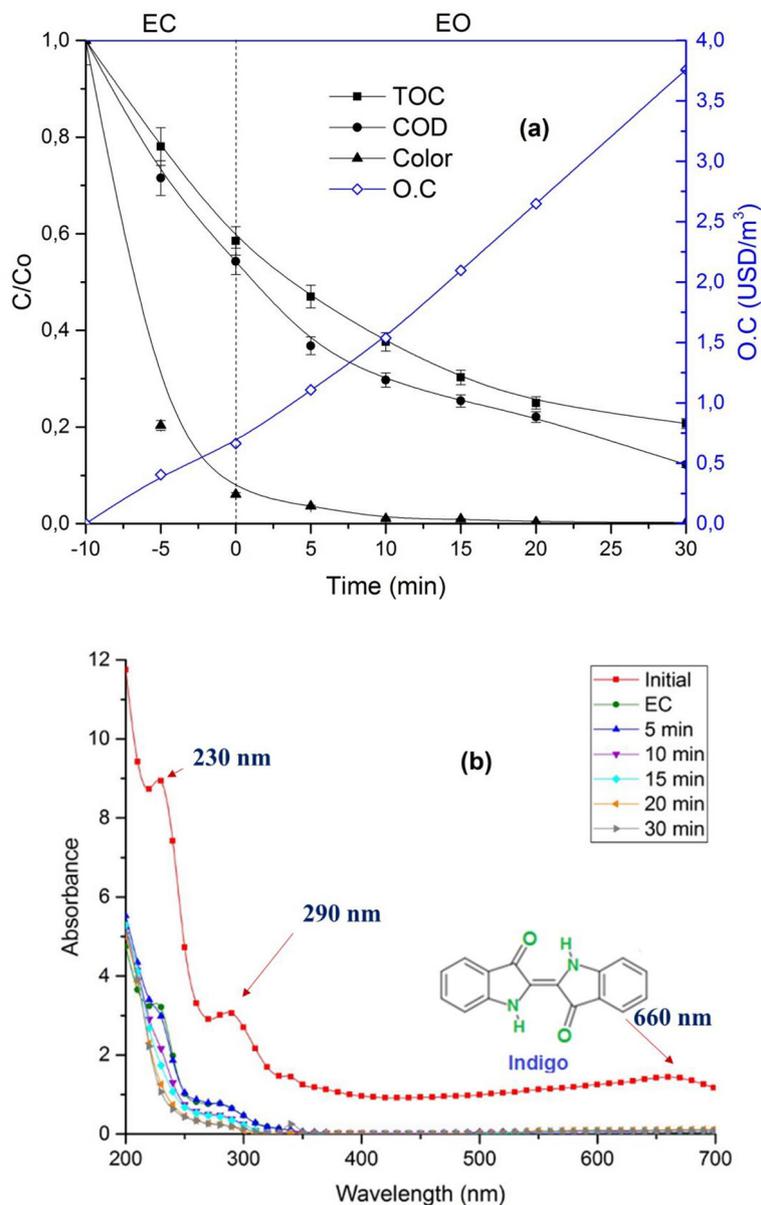
Fig. 2. (a) The evolution of the color, COD and TOC removals, and the OC of TWW during EC + EO process. Experimental conditions: EC process: Fe anode and BDD cathode, $j_{EC} = 5\,mA/cm^2$, pH = 9.28, 60 RPM and 10 min of electrolysis time; EO process: BDD anode and Fe cathode; pH = 3, $j_{EO} = 10\,mA/cm^2$, 240 RPM, and 30 min of electrolysis time. (b) UV-VIS absorption spectra of raw (initial) and treated samples.

oils, organic stabilizers, resins, carboxymethyl cellulose, etc.…) (Fig. 3a). EC + EO process effectively eliminated contaminants in the complete range of analyzed MW, reaching ca. 74% of TOC removal that corresponds to compounds with MW < 3 kDa (ca. 71%). These results suggest a substantial increase in the TWW mineralization, which can be associated with the formation of low molecular-weight carboxylic acids (final products of an oxidative reaction) or the conversion to CO_2, H_2O and mineral acids [14].

Color variation during the EC + EO process agrees with the MWD evolution. Indeed, color degradation increased with an increase in COD and TOC degradation. However, the treated effluent remains toxic to *Artemia salina* (Fig. 3a and b). To understand these results, the evolution of four representative carboxylic acids were followed by ion-exclusion HPLC (Fig. 4). Maleic acid is produced from the oxidative breaking of the benzenic ring of aromatic byproducts, which are subsequently oxidized to malonic, oxalic and formic acids [39,40]. Oxalic and formic acids are ultimate carboxylic acids since they are directly converted into CO_2. At the end of the EC + EO process, 78 mg/L of formic acid and 18 mg/L of malonic acid were detected

(Fig. 4). They represent 26 mg/L of TOC, i.e., equivalent to ca. 77% of the remaining TOC (Fig. 3). That suggests that the TWW is mostly degraded to short-linear carboxylic acids, whose persistence explains the enlargement of its mineralization. In fact, some residual formic and malonic acids were distinguished after EC + EO treatment. Carboxylic acids were not detected after EC.

Although the treated effluent considerably reduced its COD concentration after 40 min of EC + EO process, meeting the Colombian environmental legislation limit (< 400 mg/L), its toxicity needs to be monitored. Fig. 5 shows the toxicity evolution of the TWW, before and after each treatment. The raw TWW is highly toxic (100%) for *Artemia salina*, due to the presence of high dye content and of some of the raw materials used during the textile process. After the EC process, the mortality of *Artemia salina* decreased to ca. 60% (Table 1). However, although EC + EO treatment reaches ca. 96% of color degradation as well as reducing the total organic load (Table 1), the EC + EO final effluent was highly toxic (the mortality of *Artemia salina* increased to 100%). Such toxicity increase after EO step can be due to the formation of organochlorinated compounds as well as
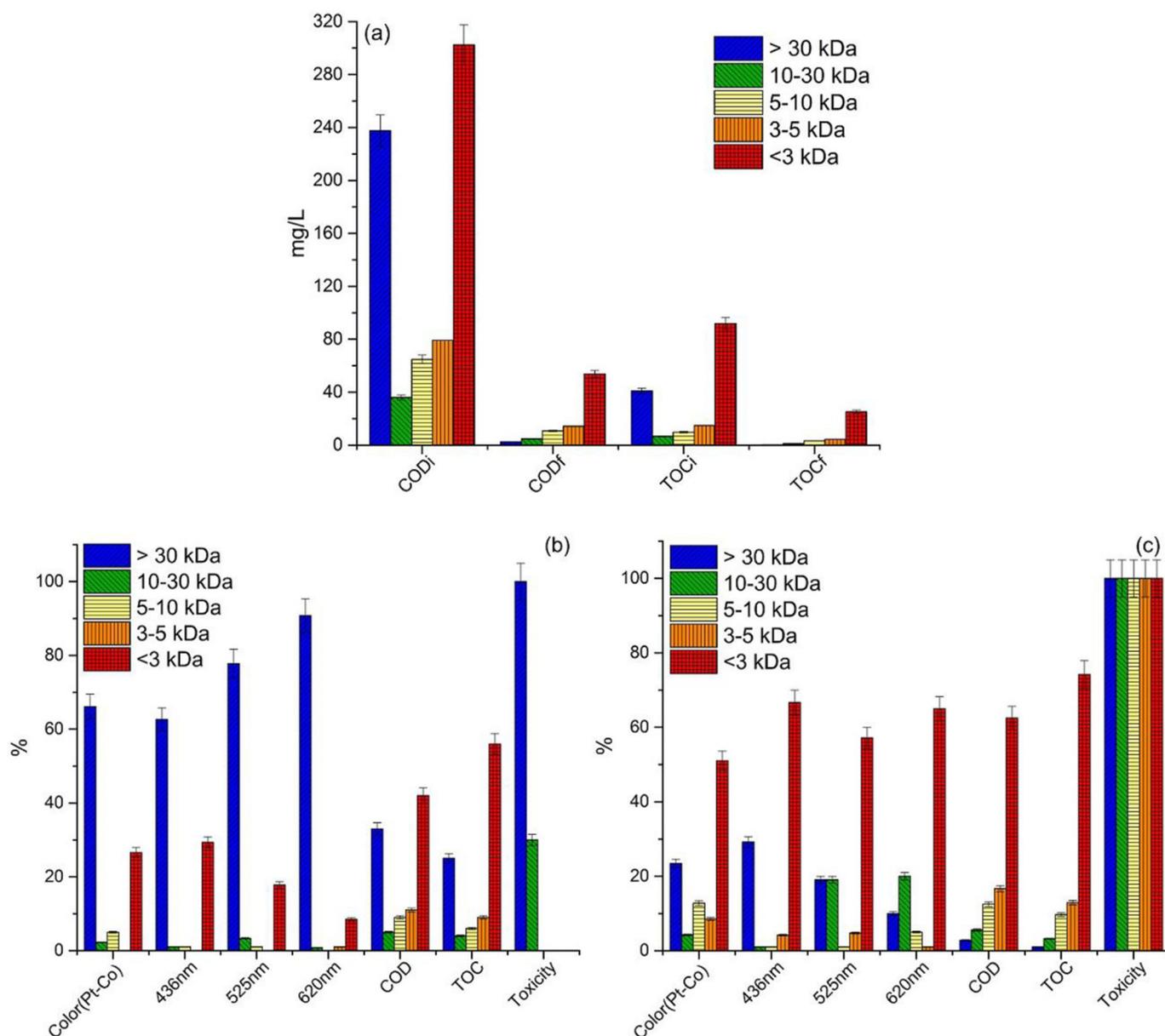
Fig. 3. MWD analysis of raw and EC + EO treated samples textile wastewater, in terms of: (a). initial, $_i$, and final, $_f$, COD and TOC in mg/L; (b). Color, COD, TOC and Toxicity in % (raw sample); (c). Color, COD, TOC and Toxicity in % (EC + EO treated sample). Experimental conditions for: EC process: Fe anode and BDD cathode, j_{EC} = 5 mA/cm^2, pH = 9.28, 60 RPM and 10 min of electrolysis time; EO process: BDD anode and Fe cathode, j_{EO} = 10 mA/cm^2, pH = 3, 240 RPM, and 30 min of electrolysis time.

secondary residual oxidants that remained in the reaction mixture after 30 min of EC. Similar results were reported by Chatzisymeon et al. **[32]**. They investigated the electrochemical treatment of textile effluents over titanium–tantalum–platinum–iridium anode and found that although the untreated effluent's toxicity was weak, it sharply increases after the electrochemical oxidation.

Notice that the additional adsorption step with AC (v.g., EC + EO + AC processes) was very efficient for toxicity removal (0% of *Artemia salina* mortality after 24 h). It can be attributed to AC reaction with free chlorine to produce oxygen-containing organic compounds on the carbon surface or CO_2 as the final product, according to Eqs. (6)–(9). After the EC + EO + AC treatment, the biodegradability, COD, and TOC of the effluent were equal to 0.65, 72 mg/L, and 30 mg/L, respectively (Table 1). This implies that the treated effluent can be discharged directly or channeled to a wastewater treatment plant. Therefore, AC treatment was necessary to remove chlorinated organic compounds before its disposal.

4. Conclusions

A combined Electrocoagulation, Electro-oxidation, and Activated Carbon Adsorption (EC + EO + AC) process was assessed as an alternative for the treatment and industrial textile wastewater (TWW). The effluent presented high organic load (COD = 720 mg/L, TOC = 164 mg/L, total amount of solids = 4.59 g/L, and turbidity = 142 NTU), strong toxicity (*Artemia salina* mortality = 100%) and a low biodegradability ($BOD_5/$ COD = 0.14). At optimum EC + EO operational conditions operation (for EC: j_{EC} = 5 mA/cm^2, pH = 9.3, 60 RPM, using Fe anode, Boron Doped Diamond (BDD) cathode, and 10 min of electrolysis; for EO: j_{EO} = 10 mA/cm^2, pH = 3, 240 RPM, BDD as anode and Fe as cathode), the sequential process achieved total discoloration, COD reduction of 88% and TOC mineralization of 79%. Additionally, the EC + EO process yielded a biocompatible effluent (BOD_5/COD = 0.58). The operation cost was estimated at 3.83 USD/m^3. However, toxicological tests, based on the *Artemia*
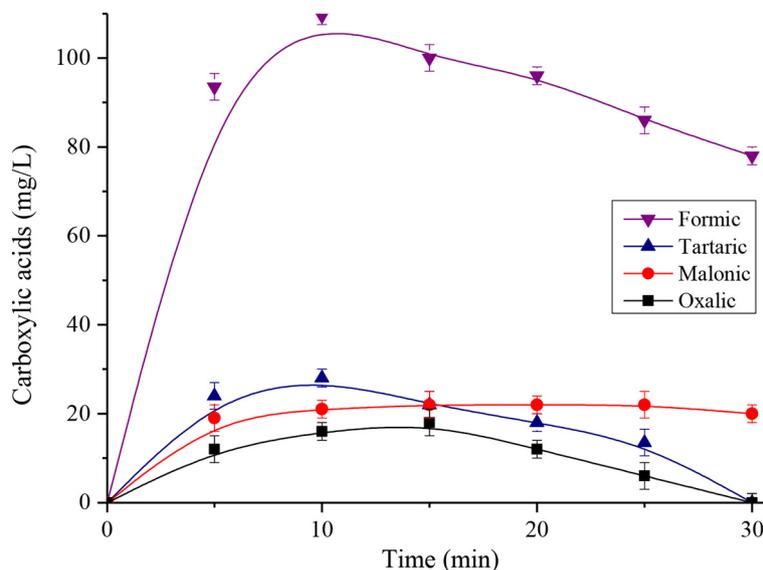
Fig. 4. Evolution of carboxylic acids generated during the degradation of TWW by EC + EO treatment under the same conditions of Fig. 2.
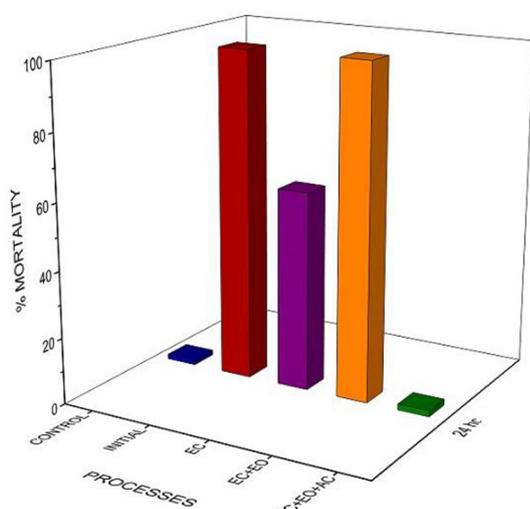

Fig. 5. Effect of each treatment process (EC, EC + EO and EC + EO + AC) on *Artemia salina* mortality percentage (after 24 h). Electrochemical conditions as in Fig. 2. Adsorption treatment conditions: flow rate = 20 mL/min, T = 25 °C, retention time = 3.7 min and AC load = 45 g.

salina assays, showed that effluent's toxicity remains very high. Thus, and additional treatment step using activated carbon (EC + EO + AC) increased the effluent's biodegradability (BOD_5/COD = 0.65) and decreased its toxicity (*Artemia salina* mortality = 0%). These results suggest that the coupled EC + EO + AC process can be considered as an efficient alternative for the treatment of effluents coming from the textile industry.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

Acknowledgements

References

[1] K. Paździor, L. Bilińska, S. Ledakowicz, A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment, Chem. Eng. J. 376 (2019) 120597, https://doi.org/10.1016/j.cej.2018.12.057.

[2] F. Ghanbari, M. Moradi, A comparative study of electrocoagulation, electrochemical Fenton, electro-Fenton and peroxi-coagulation for decolorization of real textile wastewater: electrical energy consumption and biodegradability improvement, J. Environ. Chem. Eng. 3 (2015) 499–506, https://doi.org/10.1016/j.jece.2014.12.018.

[3] H. Zazou, H. Afanga, S. Akhouairi, H. Ouchtak, A. Ait Addi, R. Ait Akbour, A. Assabbane, J. Douch, A. Elmchaouri, J. Duplay, A. Jada, M. Hamdani, Treatment of textile industry wastewater by electrocoagulation coupled with electrochemical advanced oxidation process, J. Water Process Eng. 28 (2019) 214–221, https://doi.org/10.1016/j.jwpe.2019.02.006.

[4] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. 114 (2004) 199–210, https://doi.org/10.1016/j.jhazmat.2004.08.009.

[5] S. Garcia-Segura, M.M. Eiband, J. Vieira de Melo, C.A. Martínez-Huitle, Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other technologies, J. Electroanal. Chem. 801 (2017) 267–299, https://doi.org/10.1016/j.jelechem.2017.07.047.

[6] A.L. Müller, E. Eyng, C. Lionço, S. de Oliveira, A.A. de Almeida, M.R. Fagundes-Klen, E. Sehn, Spectral deconvolution associated to the Gaussian fit as a tool for the optimization of photovoltaic electrocoagulation applied in the treatment of textile dyes, Sc. Total Environ. 713 (2020) 136301 https://doi.org/10.1016/j.scitotenv.2019.136301.

[7] K. Hendaoui, F. Ayari, I.B. Rayana, R.B. Amar, F. Darragi, M. Trabelsi-Ayadi, Real indigo dyeing effluent decontamination using continuous electrocoagulation cell: study and optimization using response surface methodology, Process. Saf. Environ. Prot. 116 (2018) 578–589, https://doi.org/10.1016/j.psep.2018.03.007.

[8] B. Khemila, B. Merzouk, A. Chouder, R. Zidelkhir, J-P. Leclerc, F. Lapicque, Removal of a textile dye using photovoltaic electroco-agulation, Sustainable Chem. and Pharmacy 7 (2018) 27–35. doi:https://doi.org/10.1016/j.scp.2017.11.004.

[9] O.Tünay, M. Şimşeker, I. Kabdaşlı, T., Ölmez-Hancı, Abatements of reduced sulphur compounds, colour, and organic matter from indigo dyeing effluents by electrocoagulation, Environ. Technol., 35 (2014) 1577–1588, doi:https://doi.org/10.1080/09593330.2013.873824

[10] M. Vepsalainen, H. Kivisaari, M. Pulliainen, A. Oikari, M. Sillanpaa, Removal of toxic pollutants from pulp mill effluents by electrocoagulation, Sep. Purif. Technol. 81 (2011) 141–150, https://doi.org/10.1016/j.seppur.2011.07.017.

[11] A.M. Faouzi B., Nasr, G. Abdellatif, Electrochemical degradation of anthraquinone dye Alizarin Red S by anodic oxidation on boron-doped diamond, Dyes and Pigments, 73 (2007) 86–89. doi:https://doi.org/10.1016/j.dyepig.2005.10.013.

[12] M. Panizza, G. Cerisola, Application of diamond electrodes to electrochemical processes, Electrochim. Acta 51 (2005) 191–199, https://doi.org/10.1016/j.electacta.2005.04.023.

[13] P. Aravind, V. Subramanyan, S. Ferro, R. Gopalakrishnan, Eco-friendly and facile integrated biological-cum-photo assisted electrooxidation process for degradation of textile wastewater, Water Res. 93 (2016) 230–241, https://doi.org/10.1016/j.watres.2016.02.041.

[14] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods, An updated review. Appl. Catal. B: Environ. 166–167 (2015) 603–643, https://doi.org/10.1016/j.apcatb.2014.11.016.

[15] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sires, O. Scialdone, Single and coupled electro-chemical processes and reactors for the abatement of organic water pollutants: A critical review, Chem. Rev. 115 (2015) 13362–13407, https://doi.org/10.1021/acs.chemrev.5b00361.

[16] A. Thiam, M. Minghua Zhou, E. Brillas, I. Sires, Two-step mineralization of Tartrazine solutions: study of parameters and by-products during the coupling of electrocoagulation with electrochemical advanced oxidation processes app. Catal. B. En-viron. 150–151 (2014) 116–125. doi:https://doi.org/10.1016/j.apcatb.2013.12.011.

[17] N. Flores, E. Brillas, F. Centellas, R.M. Rodrıguez, P.L. Cabot, J.A. Garrido, I. Sires, Treat-ment of olive oil mill wastewater by single electrocoagulation with different electrodes and sequential electrocoagulation/electrochemical Fenton-based processes, J. Hazard. Mater. 345 (2017) 58–66, https://doi.org/10.1016/j.jhazmat.2017.12.059.

[18] C.A. Martínez-Huitle, M Panizza, electrochemical oxidation of organic pollutants for wastewater treatment, Current Opinion in Electrochemistry 11 (2018) 62–71, https://doi.org/10.1016/j.coelec.2018.07.010.

[19] J. Lemus, M. Martin-Martinez, J. Palomar, L. Gomez-Sainero, M.A. Gilarranz, J.J. Rodriguez, Removal of chlorinated organic volatile compounds by gas phase adsorption with activated carbon, Chem. Eng. J. 211–212 (2012) 246–254, https://doi.org/10.1016/j.cej.2012.09.021.

[20] Y. Zhou, J. Lu, Y. Zhou, Y., Liu, recent advances for dyes removal using novel adsor-bents: A review, Environ. Pollut. 252 (2019) 352–365, https://doi.org/10.1016/j.envpol.2019.05.072.

[21] B. Pavoni, D. Drusian, A. Giacometti, M. Zanette, Assessment of organic chlorinated compound removal from aqueous matrices by adsorption on activated carbon, Water Res. 40 (2006) 3571–3579, https://doi.org/10.1016/j.watres.2006.05.027.

[22] M. Deborde, U. von Gunten, Reactions of chlorine with inorganic and organic com-pounds during water treatment—kinetics and mechanisms: A critical review, Water Res. 42 (2008) 13–51, https://doi.org/10.1016/j.watres.2007.07.025.

[23] X.D. Zhang, J.D. Hao, W.S. Li, H.J. Jin, J. Yang, Q.M. Huang, D.S. Lu, H.K. Synergistic effect in treatment of C.I. Acid Red 2 by electrocoagulation and electrooxidation. Xu. J. Hazard. Mater. 170 (2009) 883–887. doi:https://doi.org/10.1016/j.jhazmat.2009.05.050.

[24] G.B. Raju, M.T. Karuppiah, S.S. Latha, S. Parvathy, S. Prabhakar, Treatment of wastewa-ter from synthetic textile industry by electrocoagulation–electrooxidation, Chem. Eng. J. 144 (1) (2008) 51–58, https://doi.org/10.1016/j.cej.2008.01.008.

[25] APHA, Standard methods for the examination of water and wastewater. 22a ed. American Public Health Association. Washington, 2012.

[26] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, J. Hazard.Mater. 100 (2003) 163–178, https://doi.org/10.1016/S0304-3894(03)00102-X.

[27] E. GilPavas, I. Dobrosz-Gómez, M.A. Gómez-García, Coagulation-flocculation sequential with Fenton or photo-Fenton processes as an alternative for the industrial textile waste-water treatment, J. Environ. Manag. 191 (2017) 189–197, https://doi.org/10.1016/j.jenvman.2017.01.015.

[28] K. Ravndal, E. Opsahl, A. Bagi, R., Kommedal, wastewater characterization by combin-ing size fractionation, chemical composition and biodegradability, Water Res. 131 (2018) 151–160, https://doi.org/10.1016/j.watres.2017.12.034.

[29] B.M. Da Costa Filho, V.M. Da Silva, J. De Oliveira Silva, AE. da Hora Machado, A.G. Trovo, Coupling coagulation, flocculation and decantation with photo-Fenton process for treatment of industrial wastewater containing fipronil: Biodegradability and toxicity assessment. J. Environ. Manag. 174 (2016) 71–78. doi:https://doi.org/10.1016/j.jenvman.2016.03.019.

[30] E. GilPavas, I. Dobrosz-Gómez, M.A. Gómez-García, Optimization and toxicity assess-ment of a combined electrocoagulation, H_2O_2/Fe^{2+}/UV and activated carbon adsorp-tion for textile wastewater treatment, Sc. Total Environ. 651 (2019) 551–560, https://doi.org/10.1016/j.scitotenv.2018.09.125.

[31] G. Mouedhen, M., Feki, M.D.P. Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process. J. Hazard. Mater. 150 (2008) 124–135. doi:https://doi.org/10.1016/j.jhazmat.2007.04.090.

[32] E. Chatzisymeon, N.P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mantzavinos, Elec-trochemical treatment of textile dyes and dye house effluents, J. Hazard. Mater. 137 (2006) 998–1007, https://doi.org/10.1016/j.jhazmat.2006.03.032.

[33] R.E. Palma-Goyes, F.L. Guzmán-Duque, G. Peñuela, I. González, J.L. Nava, R.A. Torres-Palma, Electrochemical degradation of crystal violet with BDD electrodes: effect of elec-trochemical parameters and identification of organic by-products, Chemosphere 81 (1) (2010) 26–32, https://doi.org/10.1016/j.chemosphere.2010.07.020.

[34] G.R. De Oliveira, N., S., Fernandes, J. V. De Melo, D.R. Da Silva, C. Urgeghe, C.A. Mar-tínez-Huitle, Electrocatalytic properties of Ti-supported Pt for decolorizing and remov-ing dye from synthetic textile wastewaters. Chem. Eng. J., 168 (2011) 208–214. doi:https://doi.org/10.1016/j.cej.2010.12.070.

[35] P. Kaur, J.P. Kushwaha, V.K. Sangal, Evaluation and disposability study of actual textile wastewater treatment by electro-oxidation method using Ti/RuO_2 anode, Process. Saf. Environ. Prot. 111 (2017) 13–22, https://doi.org/10.1016/j.psep.2017.06.004.

[36] U.U. Tezcan, E. Aytac, E., Electrocoagulation in a packed bed reactor-complete treat-ment of color and cod from real textile wastewater. J. Environ. Manag. 123 (2013) 113–119. doi:https://doi.org/10.1016/j.jenvman.2013.03.016.

[37] H.M. Pinheiro, E., Touraud, O., Thomas, Aromatic amines from azo dye reduction: sta-tus review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. Dyes and Pigments 61 (2004) 121–139. doi:https://doi.org/10.1016/j.dyepig.2003.10.009.

[38] J. Workman Jr., The Handbook of Organic Compounds, First edition Academic Press, USA, 2001.

[39] M.A. Oturan, M. Pimentel, I. Oturan, Sirés, Reaction sequence for the mineralization of the short-chain carboxylic acids usually formed upon cleavage of aromatics during elec-trochemical Fenton treatment, Electrochim. Acta 54 (2008) 173–182, https://doi.org/10.1016/j.electacta.2008.08.012.

[40] M. Skoumal, C. Arias, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, E. Brillas, E., Mineralization of the biocide chloroxylenol by electrochemical advanced oxidation processes. Chemosphere, 71, (2008) 1718–1729. doi:https://doi.org/10.1016/j.chemosphere.2007.12.029.