



Research article

Integrated electrocoagulation-electrooxidation process for the treatment of soluble coffee effluent: Optimization of COD degradation and operation time analysis



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ABSTRACT

Soluble coffee production generates wastewater containing complex mixtures of organic macromolecules. In this work, a sequential Electrocoagulation-Electrooxidation (EC-EO) process, using aluminum and graphite electrodes, was proposed as an alternative way for the treatment of soluble coffee effluent. Process operational parameters were optimized, achieving total decolorization, as well as 74% and 63.5% of COD and TOC removal, respectively. The integrated EC-EO process yielded a highly oxidized (AOS = 1.629) and biocompatible ($BOD_5/COD \approx 0.6$) effluent. The Molecular Weight Distribution (MWD) analysis showed that during the EC-EO process, EC effectively decomposed contaminants with molecular weight in the range of 10–30 kDa. In contrast, EO was quite efficient in mineralization of contaminants with molecular weight higher than 30 kDa. A kinetic analysis allowed determination of the time required to meet Colombian permissible discharge limits. Finally, a comprehensive operational cost analysis was performed. The integrated EC-EO process was demonstrated as an efficient alternative for the treatment of industrial effluents resulting from soluble coffee production.

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1. Introduction

During soluble coffee production, ca. 40–45 L of wastewater per kilogram of coffee are generated (Oller et al., 2011). This effluent contains dark brown pigments and high Chemical Oxygen Demand (COD) causing significant ecological and aesthetic damage to receiving water bodies (Panchangam and Janakiraman, 2015; Tomizawa et al., 2016). Decolorization and degradation of this wastewater is mandatory. Thus, the last environmental Colombian

regulation (Ministerio de Ambiente y Desarrollo Sostenible, 2015) requires the development of alternative wastewater treatment techniques in order to meet the standards for its disposal (Table 1).

The effluent coming from soluble coffee production contains different compounds (e.g., caffeine, lipids, chlorogenic acids, melanoidins) and macromolecules (e.g., lignins, tannins, humic acid, polysaccharides and proteins) (Farah, 2012; Mussatto et al., 2011; Rodrigues and Bragagnolo, 2013). Their complexity renders useless conventional physico/chemical treatments (e.g., coagulation-flocculation followed by sand filtration). In general, these conventional processes are most effective for removal of suspended solids and high-molecular-weight organic compounds, whereas soluble organic compounds and color remain almost unaffected. The use of some biological treatments (e.g., UASB) have been reported in the literature (Dinsdale et al., 1997a, 1997b; Fernandez and Forster,

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1993). However, the concentration of pollutant to be mineralized should be relatively low due to the presence of inhibitory compounds. More recently, Advanced Oxidation Processes (AOPs) have emerged as alternatives for industrial wastewater treatment. Among them, UV/H₂O₂, UV/O₃ and UV/H₂O₂/O₃ under acidic conditions after chemical flocculation pre-treatment (Zayas Pérez et al., 2007), the photo-Fenton processes (Tokumura et al., 2008; Yamal-Turbay et al., 2012) and electrochemical advanced oxidation processes (EAOPs) using boron-doped diamond (BDD) electrodes have been reported for the decolorization of dark brown colored coffee effluent. The main drawback of the AOPs is their relatively high operating and/or capital costs (Kliaugaite et al., 2013; Wang and Xu, 2012). Thus, their coupling with other treatment methods can enhance their efficiency and reduce the operational costs (Daghrir and Droguí, 2013; Vilhunen and Sillanpää, 2010).

In the present study, the electrocoagulation (EC) and the electro-oxidation (EO) processes were integrated for the treatment of soluble coffee effluent. They were combined sequentially, in the same electrochemical cell, leading to development of a compact system with the following benefits: environmental compatibility, versatility, energy efficiency, amenability to automation, cost effectiveness and safety (Hakizimana et al., 2017; Sirés et al., 2014). Aluminum and graphite were chosen as electrode materials, considering their low cost, availability, and efficiency.

In the EC process, the anode gets dissolved by electrical current, generating *in situ* an active coagulant (in this case, aluminum ion) (Kabdaşlı et al., 2012; Moussa et al., 2017), as follows:



At the cathode, hydroxide ion and H₂ are produced according to the complementary reaction:



Next, the Al⁺³ and OH⁻ ions react to form various Al species, including monomeric (e.g., Al(OH)₂⁺, Al₂(OH)₂⁺⁴, Al₃(OH)₄⁺⁵) and polymeric complexes (e.g., AlO₄Al₁₂(OH)₂₄(H₂O)₁₂⁺⁷) (Hu et al., 2016; Kobya and Gengec, 2012). At appropriate pH, they destabilize and aggregate suspended particles to convert them into settleable flocs (Mollah et al., 2010; Sirés and Brillas, 2012). Al-based coagulation can also promote subsequent separation of natural organic matter (NOM) from water (Edzwald and Tobiason, 1999). Soluble monomeric and polymeric species can also produce amorphous metal hydroxide precipitates by complex precipitation mechanisms. Finally, metal hydroxides and flocs are easily separated from aqueous media by sedimentation or flotation (Barrera-Díaz et al., 2011). EC methods have been used successfully to remove color (Kliaugaite et al., 2013; Robić and Miranda, 2010) and pollutants from food industry wastewater (Gadd et al., 2010; Gengec et al., 2012; Thirugnanasambandham et al., 2016). However, as far as we know, their application for the treatment of soluble coffee effluents is very scarce in the literature.

Similarly, EO has become a promising technology for wastewater treatment (Särkkä et al., 2015; Zhu et al., 2010). In this

process, organic matter can be oxidized in two ways: (i) by direct oxidation, proceeding on anode surfaces to produce mainly water and CO₂; and (ii) by indirect oxidation, occurring in the presence of electrochemically produced strong oxidants (chlorine, hypochlorite, peroxodisulfate and ozone), which react with organic compounds, perhaps leading to its complete mineralization to CO₂, H₂O and/or other inorganic components (Moreira et al., 2017; Radjenovic and Sedlak, 2015). If wastewater contains NaCl, the most probable electrochemical oxidant generated in the process is chlorine (hypochlorite, in neutral or alkaline media). If the industrial wastewater contains colloidal material, along with dissolved organics, COD degradation by EC can become extremely slow and incomplete. However, EO can remove remaining soluble pollutants (Linares-Hernández et al., 2010). Notice that EO requires higher energetic consumption than EC.

Here, the integrated of EC-EO process was proposed as an alternative for the treatment of soluble coffee wastewater. The effects of the main operational parameters (EC and EO current densities and pH) on COD removal were studied. The EC-EO integrated process was optimized. Finally, the operation time of each stage, their energy consumption and operational costs were globally analyzed.

2. Materials and methods

2.1. Wastewater samples

Effluent (dark brown colored) samples were taken directly from the wastewater stream of a soluble coffee industrial plant, located in the Colombian coffee region. Before analysis and treatment in the laboratory, samples were kept refrigerated in order to minimize degradation during storage and transportation, following standard procedures (APHA, 2005). Table 1 presents their subsequent main characteristics. The COD of this liquid was more than three times higher than the permissible limit in Colombia, implying the presence of large amount of organic matter. Moreover, its initial BOD₅/COD ratio suggested that the analyzed effluent was not amenable to biodegradation.

2.2. Experimental set-up and procedure

A borosilicate glass-made batch jacketed cell with a 150-ml working volume was used for wastewater treatment. It contained two vertical plate electrodes, connected in a monopolar arrangement to a DC power source (BK-Precision 0–30 V, 0–5 A) to operate in galvanostatic mode. The voltage and current of the cell were measured with a multimeter (FLUKE 76 True RMS). The electrode materials were aluminum (Al-1100, content of pure aluminum > 99%) and graphite (EC-12 grade), each one having an effective surface area of 20 cm² (with dimensions: 5 cm width, 4 cm height). The solution was stirred mechanically. On the top of the cell, a PT-100 sensor (± 0.01 K) was placed to measure solution temperature. All experiments were performed at room temperature (293 K). The temperature of treated effluent was maintained constant, within ±0.05 K, using a thermostated water bath (F-12,

Table 1

Characterization of effluent from soluble coffee production and permissible discharge limits, as defined by Colombian legislation.

Parameter	pH	COD (g/L)	TOC (g/L)	BOD ₅ (g/L)	BOD ₅ / COD	Color (Pt-Co units)
Sample	4.6	3.465	1.301	1.267	0.35	3168
Permissible limits ^a	6 –9	1.0	No reported	0.6	0.6	No reported

^a Ministerio de Ambiente y Desarrollo Sostenible (2015).

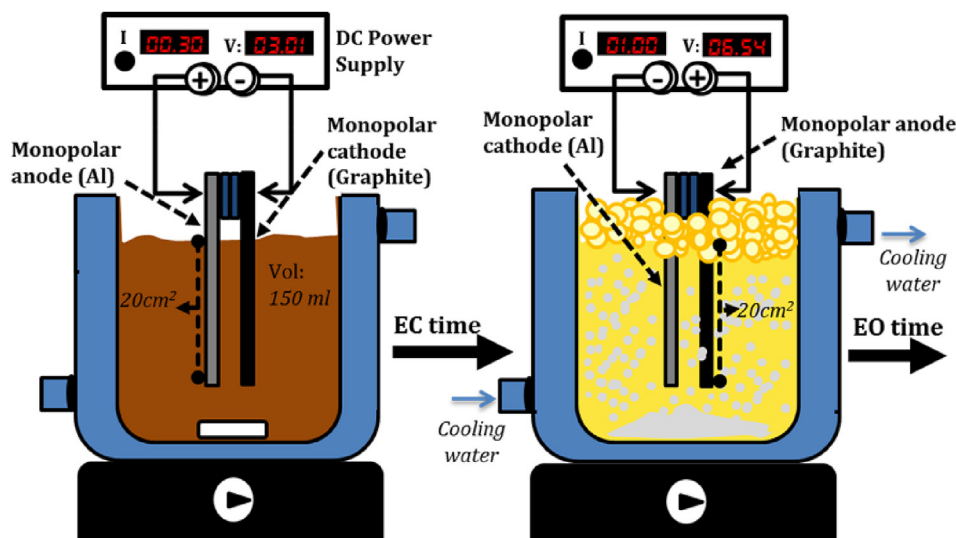


Fig. 1. Schematic of EC-EO integrated batch process with aluminum and graphite as electrodes.

Julabo - Germany), supplying water to the cell jacket with a rate of 10 L/min. Fig. 1 shows the schematic of the electrochemical cell.

Before each run, the aluminum electrode was rubbed with sand paper and dipped in a concentrated solution of HCl (35 v/v %) for ca. 5 min to remove impurities from the surface. Then, it was rinsed with distilled water. The graphite electrode was dipped into deionized water for 5 min. Both electrodes were dried in an oven (Thermo Scientific™ Heratherm™) at 105 °C.

Wastewaters used in the experiments contained 6.3 g/L of NaCl (from NaCl 99 wt. %, Carlo Erba, Italy) as a support electrolyte. For each experiment, sample pH was adjusted by addition of NaOH (97 wt. %, Carlo Erba, Italy) or H₂SO₄ (95 wt. %, Merck, Germany) and controlled using a pH-meter (Fisher Scientific™ accumet™ AB15 Basic).

Preliminary experiments (not shown here) demonstrated that for the studied conditions, stirring speed and the gap between the electrodes did not have a measurable effect on pollutant degradation. For all experiments, these parameters were maintained at 170 rpm and 1 cm, respectively.

The electrochemical integrated process was started when the DC power supply was switched on. Thus, for the EC process (1 h), the aluminum electrode was used as the anode and graphite served as the cathode (Fig. 1). The current density was adjusted to the desired EC value. Next, in order to perform EO process (during 1 additional hour), the electrode polarities were switched. Thus, graphite became the anode and the current density was set again to the desired EO value (Fig. 1).

Sludge generation and electrode consumption were measured as a function of EC time. To determine the amount of sludge, the effluent was filtered and solid residue was dried until constant weight. To measure electrode consumption, the aluminum electrode was washed with demineralized water, dried, and weighed before and after each EC test.

At the end of each run, a 2 ml sample was taken and centrifuged at 2000 rpm for 10 min, before analysis.

2.3. Analytical methods

The samples were evaluated for COD using the closed reflux method with colorimetric measurements (method 5220D) (APHA, 2005). Mineralization was evaluated by measurement of total organic carbon (TOC) using a Shimadzu analyzer (model TOC-Lcph/

n). Color was measured according to *Standard Methods* (method 2120C) (APHA, 2005) using a UV–Vis spectrophotometer (NANO-COLOR® UV/VIS). The Molecular Weight Distribution (MWD) analysis of some samples was performed by membrane ultrafiltration (Lai et al., 2007; Leiviskä et al., 2009; Zhu et al., 2011), which was achieved with a stirred cell (Amicon, Model 8400), employing regenerated cellulose ultrafiltration membranes with nominal molecular weight limits (NMWL) of 30, 10, 5 and 1 kDa (EMD Millipore). The operational pressure of ultrafiltration, provided by steady supply of highly pure N₂ (99.99%), was 0.2 MPa. Before using, the membranes were washed for 30 min with 0.1 M NaOH and flushed with deionized water, according to manufacturer instructions. TOC was analyzed for each molecular weight fraction.

2.4. Experimental design and statistical analysis

The influence of parameters such as: pH (x_1), EC current density (x_2), EO current density (x_3) on the EC-EO efficiency was investigated by means of three-level Box–Behnken experimental Design (BBD). This represents a class of rotatable second-order design, based on three-level incomplete factorial design (Ferreira et al., 2007). This approach is often used to improve efficiency and economics of experiment design relative to the corresponding three-level full factorial designs if the factor number is higher than 2 (Dean et al., 2017; Montgomery, 2012). The BBD for three factors (x_1 , x_2 and x_3) involved fifteen runs, including three replicates and a center point. The experiments were randomized by Statgraphics X64 software. The variable levels are presented in Table 2. The range of each variable was selected based on preliminary experimental results (not shown here). COD degradation percentage (% D_{COD}) was used as the response variable of the designed experiments (Y_1) and calculated as follows:

Table 2
Variables (factors) and their levels for experimental design.

Factor	Factor levels		
Initial pH, pH ₀	2.5	5.25	8
EC current density, J_{EC} , (A/m ²)	50	100	150
EO current density, J_{EO} , (A/m ²)	200	350	500

$$\%D_{COD} = \frac{(COD_0 - COD_t)}{COD_0} \times 100 \quad (3)$$

where: COD_0 and COD_t represent the COD concentration of wastewater sample before (time zero) and after treatment (total time of analysis), respectively (in g/L).

In order to find the optimal operational conditions, statistical analysis and modeling of the responses were performed with analysis of variance (ANOVA), Pareto charts and surface response modeling (RSM). RSM allows evaluation of possible relationships between experimental factors and measured response variables, according to one or more selected criteria (Mu'azu et al., 2013; Zarei et al., 2010).

2.5. Economical and energy evaluation

Once the optimal conditions for the highest COD degradation were determined, the operational cost and energy consumption of the integrated process were assessed to optimize the EC operation time. Total operation cost ($TopC$) was calculated, in the terms of US dollars per cubic meter of treated effluent (USD/m^3), as follows:

$$TopC = a \times SA + b \times AMC + c \times (J_{EC} + J_{EO}) \quad (4)$$

where: a , b , and c are the current market prices of electrode materials, sludge disposal and electricity, respectively. Aluminum electrode cost was estimated as 1.13 USD/kg; sludge disposal costs, including transportation and excluding drying costs, were evaluated at 0.014 USD/kg; and electricity price for industrial use was estimated as 0.17 USD/kWh. These data correspond to the Colombian market and they were updated to the year 2016, employing the cost index reported by the Colombian official agency of statistics (Departamento Administrativo Nacional de Estadística DANE, 2016). Moreover, the sludge amount ($SA = \text{kg of sludge}/m^3$ of treated effluent), the anode material consumption ($AMC = \text{kg of aluminum}/m^3$ of treated effluent), and the electrical energy consumption per m^3 of wastewater (E in kWh), for EC or EO processes, were evaluated as follows:

$$E_{EC} = \frac{V_{EC} \times I_{EC} \times t_{EC}}{60 \times V_R} \quad (5)$$

$$E_{EO} = \frac{V_{EO} \times I_{EO} \times t_{EO}}{60 \times V_R} \quad (6)$$

where: V is the average voltage (in V), I is the current (in A), t is the operation time (in h) and V_R is the reactor volume (in L). The economic calculations were based on the experimental results and fitted functions of sludge generation and anode consumption, as discussed below.

3. Results and discussion

3.1. Effect of operating parameters on COD reduction and optimization of EC-EO performance

Details of the experimental design, the obtained experimental data and the regression analysis (to fit $\%D_{COD}$ data to a second-order multi-variable polynomial model) are given in the Supplementary material (Pages S2 and S3).

Analysis of variance (ANOVA) was used to identify significant main and interaction effects among factors influencing $\%D_{COD}$. This involved classifying and cross-classifying statistical results. The Fisher F test, defined as the ratio of respective mean-square effect

and mean-square error, was used to evaluate the presence of significant differences from control responses and to calculate standard errors. The bigger the magnitude of the F statistic, more significant the corresponding coefficient. P values were used to identify experimental parameters that had a statistically significant influence on a particular response. If a P value was lower than 0.05, it is statistically significant with the 95% confidence level (Montgomery, 2012). According to ANOVA results (presented in the Supplementary Material, Table SM2), only two variables (EC and EO current densities) yielded P values ≤ 0.05 , implying that they generated statistically significant effects on $\%D_{COD}$. In contrast, the effect of initial pH on $\%D_{COD}$ was not significant in the analyzed experimental range (2.5–8). This was probably due to the minor changes in effluent alkalinity proportioned by the pH_0 variations, as compared to OH^- production described by eq. (2). The quality of the adjusted model was analyzed based on the coefficient of determination (R^2). The R^2 value was found to be 0.9779, being in good agreement with the adjusted one ($R^2_{Adj} = 0.9382$).

The Pareto analysis was used to identify factors presenting the greatest cumulative effect on $\%D_{COD}$, and to screen out the least significant ones. The result of this analysis can be presented as a series of bars, arranged in descending order of heights from left to right, where height reflects the frequency or impact of each factor. Therefore, the factors represented by the tall bars were more significant. Here, a Pareto analysis was also carried out to determine the percentage effect of each factor (PE_i) according to eq. (7)

$$PE_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \quad (i \neq 0) \quad (7)$$

where b_i represents the value of each i factor. Thus, statistically important factors correspond to all those values that surpass the inner vertical line (Fig. 2). This corresponds to the t value in the student's t distribution, with 95% confidence and 14 degrees of freedom. Next, this value was compared with the values of each effect and interaction of analyzed factor. The comparison defines the statistical significance of each factor in the analyzed process. Therefore, EO current density, J_{EO} , (A) and EC current density, J_{EC} , (B) were identified as the main parameters influencing the $\%D_{COD}$. Both variables were directly proportional to $\%D_{COD}$; however, the J_{EO} can be considered as the most dominant factor. Note that initial pH accounted for only 1.1%, in the studied range.

In order to determine the integrated effect of both J_{EO} and J_{EC} on the response variable, a three-dimensional Box-Behnken response surface plot, at constant pH value, was used (Fig. 3). Notice that the

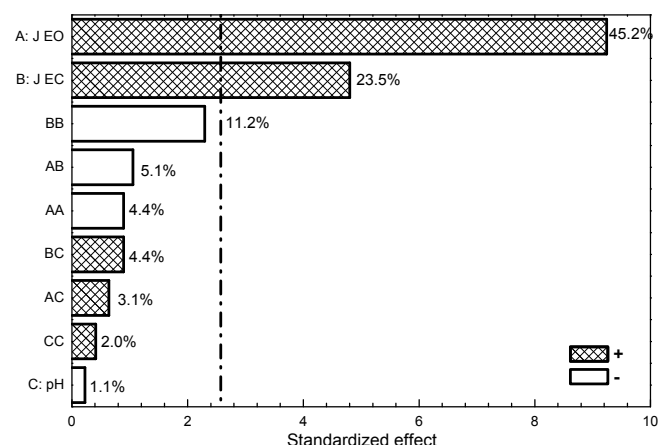


Fig. 2. Pareto diagram for $\%D_{COD}$.

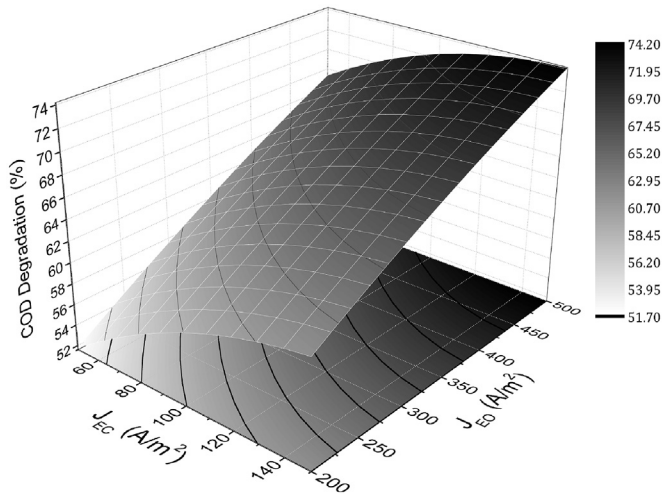


Fig. 3. Three-dimensional surface response plot for the interactive effect of J_{EO} and J_{EC} on $\%D_{COD}$ (pH = 4.6).

Table 3
Optimal conditions and experimental verification.

Factor	Optimal values	Predicted $\%D_{COD}$	Experimental				
			$\%D_{COD}$	Color removal (%)	TOC removal (%)	Final BOD ₅ (g/L)	Final pH
J_{EC} , (A/m ²)	149.23	74.14	73.90	100	63.5	0.57	8.02
J_{EO} , (A/m ²)	500						
pH ₀	7.98						

$\%D_{COD}$ increased with an increase in J_{EC} . At high J_{EC} values, the bubble production rate and the size of the flocs increased (Liu et al., 2010), promoting sludge flotation and sedimentation. Thus, the higher J_{EO} is, the higher COD degradation can be expected due to the improvement in oxidant production (García-García et al., 2015).

Table 3 summarizes the determined optimal operational conditions and $\%D_{COD}$ predicted by the model. It also contains the result of its experimental verification, in an independent run, together with color and TOC removal percentages. Notice that it is possible to achieve total decolorization and high mineralization of the studied wastewater. Moreover, the final effluent also met the last environmental Colombian regulation with regard to BOD₅ content and pH.

3.2. Kinetic studies

For the optimized EC-EO conditions, a kinetic analysis was developed. COD and TOC were monitored as a function of time (Fig. 4). Different kinetic power law expressions were tested for both COD and TOC data. Next, the parameters with the highest R^2_{Adj} were selected (Supplementary Material, Table SM3). Thus, the following rate expressions for COD degradation and TOC removal, during EC and EO processes, were obtained:

$$r_{COD}^{EC} = 6.4348 \times 10^{-4} \times (C_{COD}^{EC})^{5.2} \quad (8)$$

$$r_{COD}^{EO} = 0.00901 \times (C_{COD}^{EO})^{2.0} \quad (9)$$

$$r_{TOC}^{EC} = 0.0376 \times (C_{TOC}^{EC})^{5.9} \quad (10)$$

$$r_{TOC}^{EO} = 0.00865 \times (C_{TOC}^{EO})^{2.0} \quad (11)$$

The variations of COD and TOC vs. time were non-linear (Fig. 4). For the EC process, the reaction order was of 5.2 and 5.9 for COD and TOC, respectively. This was due to the rapid drop in COD and TOC concentrations during the first 20 min of treatment and slow degradation rate after that time. This behavior can be related to the complex physicochemical mechanisms involved in the EC process (i.e., aggregation of suspended particles followed by precipitation and adsorption of dissolved contaminants). On the other hand, the dynamic behavior of the EO process implies a less complex chemical mechanism (direct and indirect oxidations), denoted by gradual COD and TOC removal, fitted to the second order kinetic expression. Fig. 4 also includes the COD Colombian legislation limits for wastewater disposal. The hybrid EC-EO process was able to treat water to conform to the permissible limits. TOC mineralization reached 72% after 2.5 h of treatment.

Valuable additional information, regarding the reaction progress during the EC-EO wastewater treatment, can be obtained analyzing the Average Oxidation State (AOS) of the treated sample. AOS can be calculated as follows (Zapata et al., 2010):

$$AOS = 4 - 1.5 \times \frac{C_{COD}}{C_{TOC}} \quad (12)$$

The AOS takes a value between -4 (for the most reduced state of carbon, CH₄) and $+4$ (for the most oxidized state of carbon, CO₂). One can see (Fig. 4) that EC produces only a small amount of oxidized organic intermediates (after 60 min of treatment, AOS = 0.149). In fact, during EC, COD or TOC changes are mainly due to colloidal destabilization and enmeshment of dissolved substances by hydroxide precipitation. During EO, the AOS rises gradually up to 1.629 implying that organic intermediates go through different oxidation-mineralization reactions. Thus, it can be inferred that the EC-EO effluent contains highly oxidized compounds. This characteristic usually improves the wastewater biodegradability (Torres et al., 2003). In fact, the effluent BOD₅/COD ratio was of ca. 0.6, corroborating its biocompatible characteristics.

3.3. Destination of organic pollutants

MWD analysis of EC-EO treated samples was performed to gain insight into the possible fate of organic pollutants after each treatment stage. MWD was evaluated in the terms of TOC concentration in each molecular weight fraction (Fig. 5).

The raw wastewater sample was also analyzed (Fig. 5). It comprised primarily high molecular weight compounds (ca. 60% of its TOC shows a MWD higher or equal than 5 kDa) due to the presence of large number of macromolecules (e.g., proteins, polysaccharides, melanoidins and lipids) in coffee grains. After EC, the TOC concentration decreased. This process effectively eliminated contaminants with MW in the range of 10–30 kDa. However, an increase in TOC was observed for MW above 30 kDa, probably due to the formation of soluble polymeric species of aluminum with organic molecules. After EO, only ca. 24% of EO effluent comprised compounds with MW equal or higher than 5 kDa. The EO process was effective for elimination of contaminants originally present in coffee effluent as well as those produced during EC (MW > 30 kDa). However, in the case of compounds with MW ≤ 1 kDa, the TOC concentration remained essentially unchanged from completion of EC to completion of EO. These findings are in agreement with previously published results (GilPavas et al., 2014; Panizza and

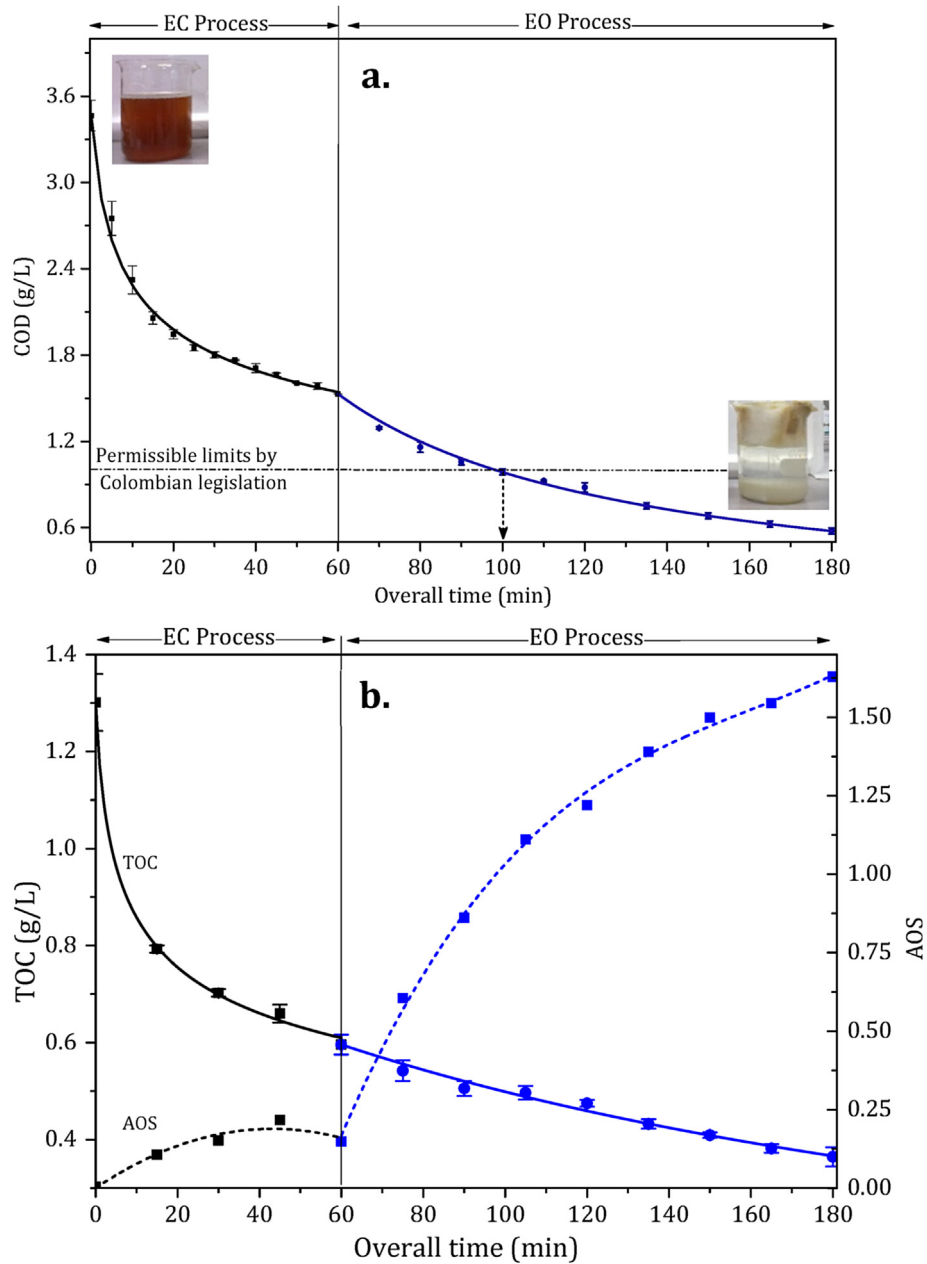


Fig. 4. Evolution of: (a) COD and (b) TOC and AOS during the EC-EO process ($J_{EO} = 149 \text{ A/m}^2$, $J_{EC} = 500 \text{ A/m}^2$, $\text{pH}_0 = 4.6$).

Cerisola, 2005) reporting low efficiency of EO for oxidation of e.g., aldehydes, ketones, and carboxylic acids.

3.4. EC and EO operation time

The EO operation time, t_{EO} , and the overall treatment time ($t = \text{EC operation time} + \text{EO operation time}$) were determined as a function of EC operation time, t_{EC} . A target COD value (in the processed effluent) was defined at 73.9%, based on the optimized EC-EO conditions (see Table 1 and Fig. 4a). Thus, using the rate law expressions (eqs. (8) and (9)), t_{EO} was calculated as follows (details in Supplementary Material, page S6):

$$t_{EO} = \frac{1}{0.00901} \left(\frac{1}{C_{COD}^f} - \left(\frac{1}{C_{COD}^0 4.2} + 0.0027 \times t_{EC} \right)^{-\frac{1}{4.2}} \right) \quad (13)$$

The relationship of t as a function of t_{EC} passed through a minimum (Supplementary Material, Fig. S2). This can be expected since, during the first minutes COD degradation is faster using EC than that using EO. For instance, the process requires ca. 94 min employing only EO ($t_{EC} = 0$), whereas it needs ca. 88 min using EC-EO hybrid process (at the optimum t_{EC}). By contrast, long t_{EC} only increases the overall treatment time (Supplementary Material, Fig. S2). Thus, to achieve the target $\%D_{COD}$, the EC process should be followed by EO in all analyzed cases.

3.5. Total Operation Cost of the integrated EC-EO process

Total Operation Cost (TOpC) of the integrated EC-EO process corresponds to the sum of EC (ECOpC) and EO (EOOpC) Operation Costs. For their calculation, the consumption of energy (E_{EC} and E_{EO}) and anode material (AMC) as well as the amount of produced sludge (SA) were considered (eqs. (4)–(6)). For all analyzed cases,

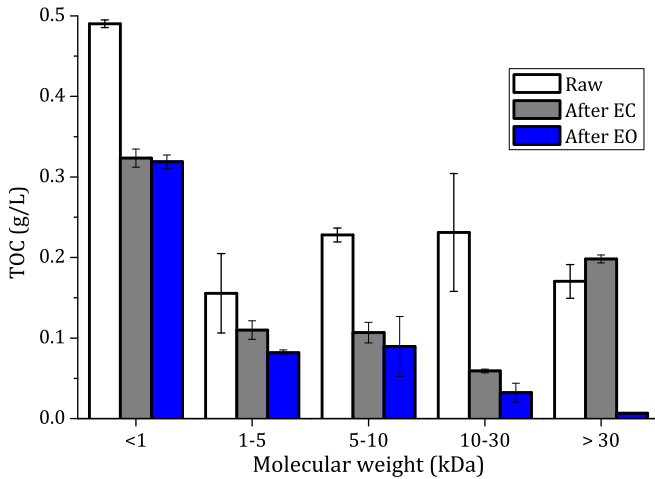


Fig. 5. MWD analysis of raw and EC-EO treated samples, in the terms of TOC.

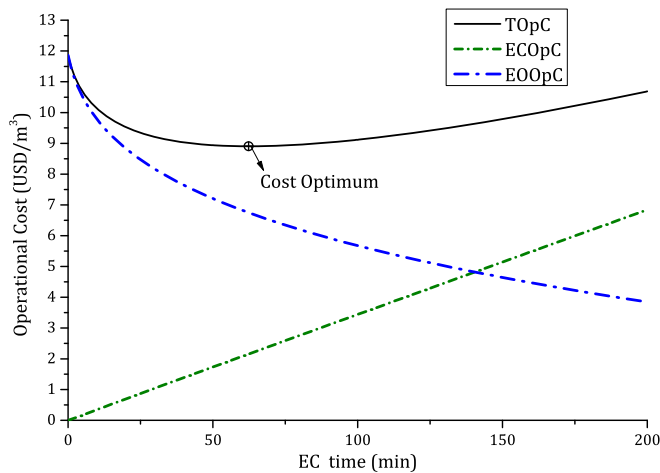


Fig. 6. Operational Cost variation as a function of t_{EC} .

E_{EC} was lower than the E_{EO} (Supplementary Material, Fig. S3). Thus, to minimize overall energy consumption, the use of EC as a first treatment stage is recommended. However, its long operation time implies an increase in overall treatment time as well as overall energy consumption.

Anode consumption (AMC) was observed to increase linearly with t_{EC} (Supplementary Material, Fig. S4). The experimental data were fitted as follows:

$$AMC \left(\text{kg} / \text{m}^3 \right) = 0.0138 \times t_{EC} \quad (14)$$

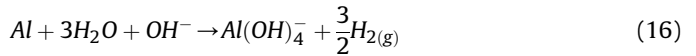
According to Faraday's Law, AMC is directly proportional to the current applied to an electrolytic cell (dashed line in Fig. S4, Supplementary Material) (Harif et al., 2012). The experimental data exceeded values that were predicted theoretically. This suggests contributions from reactions different than those attributable to electrochemical contributions, such as aluminum dissolution under acidic (during first minutes of EC, eq. (15)) or basic conditions (during last minutes of EC, eq. (16)):



Table 4

Comparison of the performance of EO and EC-EO processes in the terms of treatment time, energy consumption and TopC.

Case	EC time (min)	TopC (USD/m ³)	Energy (kWh/m ³)	Treatment time (min)
EO	–	11.86	68.34	94.1
EC-EO	62.33	8.90	45.28	115.8



Such behavior has also been previously reported in the literature (Cañizares et al., 2007; Fekete et al., 2016; Jiménez et al., 2012; Lacasa et al., 2012; Mouedhen et al., 2008).

The amount of produced sludge (SA) was higher with and increasing t_{EC} (Supplementary Material, Fig. S5). During the *ca.* first 5 min of the treatment, SA was very low, difficult to determine quantitatively, and it was assumed to be zero. Thus, eq. (17) was fitted to the experimental data obtained for experimental time higher than 5.2 min:

$$SA \left(\frac{\text{kg}}{\text{m}^3} \right) = 0.2493 \times (t_{EC} - 5.2)^{0.67} \quad (17)$$

Finally, based on all experimental results and correlations, ECOpC, EEOpC, and TopC were also calculated as a function of t_{EC} (Fig. 6). Notice that an important factor increasing the ECOpC is anode consumption (*ca.*, 40–50%). In fact, in the studied range, sludge management did not exceed 5% of total ECOpC. On the other hand, the EEOpC depended mainly on energy costs. Thus, one can see that TopC passes through a minimum. Savings of 25% of TopC are expected if the EC-EO process operates at the optimized conditions. Table 4 presents a comparison of the performance of EO and EC-EO processes in the terms of treatment time, energy consumption and TopC. The EC-EO integrated process, operating at minimum TopC, involves lower energy consumption, offering savings of *ca.* 34%, comparing to EO alone. This shows that coupled EC-EO process can be an efficient alternative for the treatment of industrial effluents coming from soluble coffee production.

It is important to remark that, availability of chloride ions in wastewater promotes formation of active chlorine and its use may stimulate the formation potential of undesired by-products such as Adsorbable Organic Halogen, Trihalomethanes (THMs) and haloacetic acids (HAAs) (Chaplin, 2014). If the EC-EO integrated process generates halogenated products, they could be removed by sorption to activated carbon (Katsoni et al., 2014), or additional electrochemical oxidation and/or reduction processes (Radjenovic and Sedlak, 2015).

4. Conclusions

An EC-EO integrated process was applied as an alternative for the treatment of wastewater resulting from soluble coffee production. At optimum operational conditions ($pH_0 = 7.98$, $J_{EC} = 149.2 \text{ A/m}^2$ and $J_{EO} = 500 \text{ A/m}^2$), the integrated process achieved total discoloration, COD reduction of 89% and TOC mineralization of 72%. Additionally, the process yielded a highly oxidized ($AOS = 1.629$) and biocompatible ($BOD_5/COD \approx 0.6$) effluent. The MWD analysis demonstrated that EC effectively decomposed contaminants with the MW in the range of 10–30 kDa. In contrast, EO was quite efficient in mineralization of contaminants with MW > 30 kDa. A comprehensive operational cost showed savings of 25% when the EC-EO hybrid process operates in the following time mode: EC (62 min) and EO (53 min), compared to overall treatment by EO. It

also offered 34% of savings in total energy consumption. The coupled EC-EO process was demonstrated as an efficient alternative for the treatment of industrial effluents coming from soluble coffee production.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2017.05.095>.

Abbreviations

AMC	Anode Material Consumption (kg/m ³)
BOD ₅	Five-day biochemical oxygen demand (g/L)
COD	Chemical oxygen demand (g/L)
C	Concentration (g/L)
DC	Direct current
E	Electrical Energy Consumption (kWh)
EC	Electrocoagulation
ECOpC	EC Operation Costs (USD/m ³)
EO	Electrooxidation
EOOpC	EO Operation Costs (USD/m ³)
J	Current density (A/m ²)
MWD	Molecular Weight Distribution
NMWL	Nominal Molecular Weight Limits (kDa)
PE	Pareto analysis percentage effect
r	Reaction rate (g/L.min)
SA	Sludge Amount (kg/m ³)
TOC	Total Organic Carbon
TOpC	Total operation cost (USD/m ³)

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