Optimization of sequential chemical coagulation - electro-oxidation process for the treatment of an industrial textile wastewater

Edison GilPavas[a,c,*], Izabela Dobrosz-Gómez[b], Miguel Ángel Gómez-García[c]

[a] GIPAB: Grupo de Investigación en Procesos Ambientales, Departamento de Ingeniería de Procesos, Universidad EAFIT, Cr 49 # 7 Sur 50, Medellín, Colombia
[b] Grupo de Investigación en Procesos Reactivos Intensificados con Separación y Materiales Avanzados – PRISMA, Departamento de Física y Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Colombia, Sede Manizales, Campus La Nubia, km 9 vía al Aeropuerto la Nubia, Apartado Aéreo 127, Manizales, Caldas, Colombia
[c] Grupo de Investigación en Procesos Reactivos Intensificados con Separación y Materiales Avanzados – PRISMA, Departamento de Ingeniería Química, Facultad de Ingeniería y Arquitectura, Universidad Nacional de Colombia, Sede Manizales, Campus La Nubia, km 9 vía al Aeropuerto la Nubia, Apartado Aéreo 127, Manizales, Caldas, Colombia

ARTICLE INFO

ABSTRACT

In this study, the sequential Chemical Coagulation-Electro-Oxidation (CC-EO) process was proposed as an alternative for the treatment of an industrial textile wastewater. Complete characterization of the effluent was made in the terms of its organic load (Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD$_5$)), biodegradability (BOD$_5$/COD ratio) and solids content (total solids and turbidity). For CC, the jar test was used to determine both the most favorable dosage of coagulant and pH of the process (i.e., 600 mg/L of Al$_2$(SO$_4$)$_3$ at pH of 9.3). CC let to remove *ca.* 93% of turbidity, 53% of COD and 24% of TOC. It also increased BOD$_5$/COD ratio of raw textile wastewater from 0.16 to 0.27. Next, CC effluent was treated by EO. Its performance was optimized using Box-Behnken experimental Design and Response Surface Methodology. The following EO optimal conditions were found: current density = 15 mA/cm^2, conductivity = 4.7 mS/cm and pH = 5.6. At these conditions, the sequential CC-EO process removed 100% of color, 93.5% of COD, and 75% of TOC after 45 min of electrolysis with an estimated operating cost of 6.91 USD/m^3. Moreover, the CC-EO process yield a highly oxidized (Average Oxidation State, AOS = 2.3) and biocompatible (BOD$_5$/COD > 0.4) effluent.

1. Introduction

Textile industry produces large amounts of effluents that are not amenable to chemical or biological treatment. High content of dyestuffs, surfactants and additives, generally organic compounds of complex structures, causes non-biodegradability of industrial textile wastewater (ITWW). Indeed, textile dyes themselves present low or any biodegradability.

So far, open literature concerning ITWW treatment has been scarce. Holkar et al. [1] presented a complete survey about different methods to treat textile wastewater along with cost per unit volume of treated water. Conventional methods applied for their handling include chemical coagulation (CC), adsorption, and filtration [2]. Indeed, CC process exhausts a large amount of flocculent reagent and can generate an extra sludge [3]. On the other hand, biological methods result useless if applied alone [4,5]. The recalcitrant nature of various dyes, together with their toxicity to microorganisms, makes aerobic treatment difficult

[6]. Nowadays, chemical oxidations by Advanced Oxidation Processes (AOPs) are of great interest. Although these methods are effective for color removal, they are also expensive and/or they can generate other pollutants [7–9]. Recently, special attention is paid to electrochemical technologies due to their large number of advantages: versatility, safety, selectivity, simplicity of automation, environmentally friendly and low investment costs [10]. However, in many cases, single treatment process results inadequate due to the nature of the ITWW.

Lately, the application of combined processes has been proposed to overcome the disadvantages of individual ones [11–13]. Electrochemical variations of AOPs, called Electrochemical Advanced Oxidation Processes (EAOPs), such as anodic oxidation (electro-oxidation, EO), electro-Fenton [13], and photo-electro-Fenton [15], have received a lot of attention due to its environmental compatibility and high efficiency. EO consists of pollutant oxidation by direct electron transfer to the anode (M), formed from water discharge on its surface at high current, as follows [10]:

$$M + H_2O \rightarrow M(HO^{\bullet}) + H^+ + e^- \tag{1}$$

According to the literature [9], the most effective anode material for EO is a non-active boron-doped diamond (BDD) thin-film electrode. This is due to its inert surface at low adsorption load, corrosion stability, and extremely high O_2-evolution overvoltage. BDD electrodes have been applied for the degradation of organic pollutants such as textile dyes [8], and herbicides [10]. The electrolysis of water to form HO· radicals, once the electric current passes through the BDD electrode, is presented in Eq. (2) [16]:

$$H_2O \rightarrow HO^{\bullet}_{Ads} + H^+ + e^- \tag{2}$$
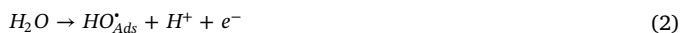
Different authors have recently addressed the combination of CC with an AOP. It was found to be highly efficient for the treatment of wastewaters coming from various industries, among them: sugar cane distillery [12], landfills [6], textile [11,17,18], winery [3] and others [19,20]. As far as we know, the coupled treatment of CC-EO for the treatment of ITWW has not been reported.

Here, the potential application of a sequential CC-EO process, at lab scale, for the treatment of textile effluents resulting from an industrial facility located in Medellín-Colombia, is presented. The ITWW was characterized for organic matter content (Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD_5)), solids amount (Total solids (TS), Turbidity, Conductivity (κ)) and biodegradability (BOD_5/COD). The influence of different operating conditions (for CC: pH and coagulant dose, and for EO: current density, conductivity and pH) on the efficiency of CC-EO process (removal of: color, COD, TOC and turbidity) was evaluated. The jar tests was used to determine operational variable values with the most significant influence on CC. EÓs performance was optimized using a Box-Behnken experimental Design (BBD) and Response Surface Methodology (RSM). The optimal operational conditions were validated experimentally.

2. Materials and methods

2.1. Samples handling and characterization

ITWW samples were collected from an equalization tank in a textile industrial plant located in Medellín (Colombia). They were dark blue color due to the mixture of several dyes (reactive, direct, dispersive, acid and cuba dyes) as well as other pollutants used during the textile processing. ITWW samples were kept refrigerated, to avoid compounds degradation during storage and transportation, following APHÁs standard procedures [21]. Samples resulting from the laboratory tests were analyzed by triplicate using a UV–vis double-beam spectrophotometer (Spectronic Genesys 2PC) in the range of 200–700 nm, with a 1 cm path length quartz cell. Standard methods were followed for the quantitative analysis of COD (the closed reflux method with colorimetric determination, method 5220D), TOC (method 5310D), BOD_5 (the respirometric method, 5210B), TS (method 2130B), Apparent Color (AC) (method 2120B) and turbidity (method 2540D) [21]. 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.

2.2. Reagents

All reagents were used as received from suppliers without any further purification. Their aqueous solutions were prepared using ultrapure water (Milli-Q system, Billerica, Massachusetts; conductivity < 1 μS/cm). Their pH values were adjusted with sulfuric acid (H_2SO_4; Merck, purity = 98%) or sodium hydroxide (NaOH; Carlo Erba, purity = 97%). Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, Merck, purity = 99%) was used for the chemical coagulation process. Anhydrous sodium chloride (NaCl; Merck; purity ≥ 99%) was used as support electrolyte to adjust solutions conductivity. MnO_2 (Sigma

Aldrich; reagent grade ≥ 90%) was also used as explained. For iodometric titration, KI (Merck, 99.5%) and $Na_2S_2O_3 \cdot 5H_2O$ (Panreac, 99.7%) were applied.

2.3. CC treatment

Aluminum salts are the most commonly used inorganic coagulants due to their good performance, high efficiency, low cost, easy handling, and availability. The CC efficiency and the quality of the treated effluents strongly depend on the amount of coagulant and treatment's pH. Insufficient coagulant dosage or its overdosing can result in poor performance of CC and its high cost. On the other hand, pH value affects the surface charge of coagulants and the stabilization of the suspension. Besides, the solubility of coagulant in aqueous solution is also influenced by pH level [4]. Following the D2035 ASTM standard method (v.g., the jar-test), the CC operational parameters were determined. Thus, aluminum sulfate dosage and pH of effluent were varied in the ranges of 300–1200 mg/L and 3–9, respectively. After completing each CC treatment, supernatan's color, turbidity, TOC and COD were measured. Their removal percentages were calculated as follows:

$$Color\ removal\ (\%) = \%RC = \frac{(Abs_i - Abs_t)}{Abs_i} \times 100 \tag{3}$$

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

$$Turbidity\ removal\ (\%) = RT\% = \frac{(T_i - T_t)}{T_i} \times 100 \tag{4}$$

where: T_i and T_t are the initial turbidity value (NTU) and the turbidity at time t, respectively.

$$COD\ or\ TOC\ degradation\ (\%) = \%DCOD\ or\ \%DTOC = \frac{Z_i - Z_t}{Z_i} \times 100$$
$$\tag{5}$$

where: Z_i and Z_t are the initial COD or TOC value (ppm) and the COD or TOC value at time t, respectively.

Finally, when CC was completed, the obtained supernatant was directly treated by EO.

2.4. EO treatment

A plexiglass, 0.12 L, batch continuously stirred jacketed reactor was used to perform EO experiments. It consisted of two vertically placed electrodes: (i) the anode, a boron-doped diamond (BDD) thin-film (0.5 mm thickness) on titanium substrate (supplied by NeoCoat, Switzerland), with a total area of 12.5 cm² (2.5cm × 5 cm), and (ii) the cathode, an iron (99.7%) electrode, with the following dimensions: 1.8 cm × 0.55 cm × 5 cm. Basing on our preliminary results (not shown here), the gap between electrodes was set at 1 cm. The voltage was regulated with a BK-Precision source (0–30 V, 0–5 A). The reaction mixture of 80 mL was stirred at 240 rpm during 15 min. The test temperature was maintained at 25 °C using a Polyscience 712 thermostat (Niles, Illinois) connected to the reactor jacket.

2.5. Experimental design and statistical analysis

Three factor's BBD, including 15 tests, was used to optimize EO performance (i.e., to maximize the organic matter degradation). The following independent variables (or operating factors) and their levels were chosen in accordance with our previous work [22]: (i) current density (j): in the range of 5–25 mA/cm²; (ii) solution conductivity (κ): ranging from 3.33 to 4.7 mS/cm; and (iii) pH, between 3 and 8.2. In all cases, the initial pollutant concentration corresponded to the industrial conditions of the ITWW. All experiments were made by triplicate and the average value of each response variable (%DCOD and operating cost) were used for statistical analysis.

Individual and synergistic effects of the operating factors on each response variables can be visualized in three-dimensional response surface plots. Details of the RSM can be consulted elsewhere [11,23,24]. Response variables were fitted to quadratic models of the operating factors, as in Eq. (6), using Statgraphics Centurion XVI Software.

$$Y_i = \beta_0 + \sum_1^3 \beta_i x_i + \sum_1^3 \beta_{ii} x_{ii}^2 + \sum_1^3 \sum_1^3 \beta_{ij} x_i x_j \qquad (6)$$

where: β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients for the intercept, linear, square, and interaction terms, respectively; and x_i and x_j are independent variables. Regression coefficients and their effects were analyzed using analysis of variance (ANOVA), Pareto diagrams, and p-values (with a confidence coefficient of 95%). It is important to remark that RSM was not used to understand the mechanism for wastewater degradation but to determine the optimal operational conditions using empirical models.

2.6. Operating cost

Operating cost (OC) is one of the most significant variables for the EO process. Indeed, it allows defining its economic feasibility. The OC evaluation of EO process must include, at least, the energy consumption (E_{EO}, kWh/m^3) and reactive consumption (RC, kg/m^3). In this study, OC (expressed in the terms of USD per m^3 of treated effluent) was calculated according to Eq. (7):

$$OC\left(\frac{USD}{m^3}\right) = a E_{EO} + b RC + CC \qquad (7)$$

where: a equals to 0.1867 USD/kWh; b varies as: 0.4 USD/kg for NaOH, 0.60 USD/kg for H$_2$SO$_4$ and 0.22 USD/kg for NaCl; and the cost for the CC process was estimated as 0.41 USD/m^3 (including cost of solids disposal) [11]. The E_{EO} was calculated as follows:

$$E_{EO} = \frac{VIt}{V_R} \qquad (8)$$

where: V is the cell voltage (V), I is the applied current (A), t is electrolysis time (hour) and V_R is the effluent volume (m^3).

3. Results and discussion

3.1. ITWW sample characterization

A summary of raw textile wastewater characteristics together with the governmental limits (according to the Colombian environmental legislation for ITWW) is presented in Table 1. Notice that pH, COD, and BOD$_5$ values do not fulfill Colombián environmental regulations.

Table 2
%RC, %DCOD, and %RT for different coagulant dosage and pH́s value.

pH	Al$_2$(SO$_4$)$_3$·18H$_2$O dose (mg/L)	RC (%)	DCOD (%)	RT (%)	pH$_{final}$
9.3	300	16.75	23	17.68	6.4
9.3	400	40.70	32	32.93	6.2
9.3	600	97.27	53	93.29	5.6
9.3	900	97.89	58	93.90	4.48
9.3	1200	98.14	56	94.51	4.29
7	300	14.64	27	11.59	6.19
7	400	75.68	43	71.34	6.0
7	600	97.02	56	92.07	4.66
7	900	97.15	56	93.29	4.27
7	1200	97.40	58	93.90	4.15
5	300	17.12	22	9.15	3.9
5	400	24.32	26	14.63	3.78
5	600	28.79	24	17.68	3.7
5	900	39.83	28	29.27	3.63
5	1200	50.12	39	38.42	3.58
3	300	22.46	21	14.02	2.84
3	400	28.29	22	14.63	2.84
3	600	29.90	27	8.54	2.83
3	900	31.64	31	8.54	2.83
3	1200	39.95	34	13.41	2.82

Indeed, the wastewater displays an intense blue color, due to the presence of indigo dye, implying high content of organic compounds. In addition, due to the presence of salts, the sample grants high conductivity. High COD value, more than twice of that of permissible limit, infers the presence of large amounts of non-biodegradable organic matter. In fact, the BOD$_5$/COD ratio, equaled to 0.16 (< 0.4), indicates that the effluent is not biodegradable [25]. Although, the legally permissible limit for organic compounds is usually expressed in the terms of COD, in this study the TOC evolution was also monitored. This parameter gives a direct measurement of carbon content without interference from oxidizable inorganic substances also present in the studied sample.

3.2. The efficiency of CC for ITWW treatment

The jar test was used to determine the effect of both coagulant dosage and treatment́s pH on %RC, %DCOD and %RT. The obtained results are presented in Table 2. Notice that the use of high coagulant dosage and high pH value led to significant removal of color and COD. Under increasing dosage of coagulant from 300 to 600 mg/L, the total COD removal increases from *ca.* 21–56%, while the corresponding color elimination changes from *ca.* 14.6–97.3%, respectively. However, the addition of larger dosages of coagulant caused decrease in effluent pH, due to the hydrolysis of Al^{3+} ions, provoked by the release of H$^+$ ions into the solution [7]. Contrariwise, it is well known that effective

Table 1
Main characteristics of raw ITWW, together with the corresponding legislation limits, and values obtained after CC and CC-EO processes. In addition, global treatment efficiency, at optimized operational conditions, along with the respective process operating costs is summarized.

Parameter	Raw ITWW sample	Emission limit[a]	After CC process	After CC-EO process		Global treatment efficiency (%)	
				30 min	45 min	30 min	45 min
pH	9.3	6–9	5.7	4.0	4.7	–	–
Abs (660 nm)	1.2	–	0.033	0	0	100	100
Conductivity (μS/cm)	4010	–	3300	4087	4100	–	–
Turbidity (NTU)	161	–	11	0	0	100	100
COD (mg O$_2$/L)	720	400	338	109.87	46.96	84.74	93.48
TOC (mg C/L)	164	–	124.4	51.12	41.53	68.83	74.68
BOD$_5$ (mg O$_2$/L)	115	200	90.5	60.56	59.88	47.34	47.93
BOD$_5$/COD ratio	0.16	0.5	0.27	0.55	0.83	–	–
Generated sludge (kg/m^3)	–	–	0.456	0	0	–	–
Global operating costs (USD/m^3)	–	–	0.41	4.79	6.91	–	–

[a] Emission limit values for industrial wastewater discharges into the municipal sewer system according to Res. 0631, 17/03/2015, issued by the Ministry of Environment and Sustainable Development, Colombia.

formation of flocculants is favored in a range of pH between 7 and 9, using $Al_2(SO_4)_3 \cdot 18H_2O$ as coagulant agent [25,26]. Therefore, determining an optimum coagulant dosage became very important. Finally, it was possible to reach *ca.* 53% of COD, 97% of color and 93% of turbidity removals (see Table 2), using 600 mg/L of $Al_2(SO_4)_3 \cdot 18H_2O$ and pH of 9.3 (the most efficient conditions for CC treatment). These results are comparable with those reported by Aquino et al. [17] for an industrial textile effluent characterized with initial COD and TOC of 963 mg O_2/L and 358.5 mg C/L, respectively. They suggested a coagulant dose ($Al_2(SO_4)_3 \cdot 18H_2O$) of 1000 mg/L and a pH in the range of 5–10 as the most suitable conditions for effective CC treatment.

The supernatant obtained after CC process, realized at the most proper conditions, was also characterized (Table 1). Although CC pretreatment eliminates wastewater turbidity, it was inefficient in removing surfactants and other soluble organic pollutants existing in the sample. Notice that CC was able to reduce efficiently organic load (e.g., COD decreases from 720 to 400 mg O_2/L). However, the BOD_5/COD ratio increased only from 0.16 to 0.27, indicating that this effluent still cannot be considered as biodegradable. This implies that an additional wastewater treatment is required before its final discharge into the surface waterbodies. Thus, EO was chosen to complete the ITWW handling and to reach the permissible legislation discharge limits.

3.3. Electro-oxidation (EO) process

EO process was applied to reduce COD concentration and to increase the biodegradability of the effluent resulting from CC process. The BBD and RSM analysis were used to determine the individual effects of EO operational parameters and their interactions on EO efficiency. The experimental design together with the obtained results is presented in Table 3. Notice that the additional COD removal percentages achieved by EO varied between *ca.* 17 and 55%. The following most efficient experimental conditions were found: $j = 25$ mA/cm^2, pH = 5.6, and $\kappa = 4.7$ mS/cm. However, the OC was considerably high at such settings. To optimize the EO operating conditions (*v.g.*, both to maximize %DCOD and to minimize OC), the data were adjusted to a second order polynomial (Eqs. (9) and (10)). These empirical models represent the %DCOD and OC as a function of three independent process variables (j, pH, and κ), respectively. Model predictions match accurately to the experimental results, with determination coefficients of $R^2 = 98.54\%$ and $R^2_{adj} = 95.92\%$ for %DCOD and of $R^2 = 99.70\%$ and $R^2_{adj} = 99.15\%$ for OC (Table 4).

The ANOVA was used to determine statistical significance of main factors and their interactions. It consists of classifying and cross-classifying statistical results, decomposing the contribution of each variable

Table 3
The experimental and predicted results of %DCOD and OC, according to the BBD. Electrolysis time 15 min.

Run	j (mA/cm^2)	pH	κ (mS/cm)	DCOD (%)		OC (USD/m^3)	
				y_{exp}	y_{pred}	y_{exp}	y_{pred}
1	5	8.2	4.015	17	17	0.772	0.7942
2	15	3	4.7	36	38	2.245	2.3620
3	25	8.2	4.015	51	53	4.892	4.8860
4	15	5.6	4.015	36	35	2.229	2.3280
5	5	3	4.015	19	19	0.552	0.5574
6	15	8.2	4.7	38	40	2.155	2.2554
7	25	5.6	3.33	49	51	5.206	5.3293
8	5	5.6	4.7	17	16	0.724	0.6010
9	15	5.6	4.015	33	35	2.333	2.3280
10	25	3	4.015	49	49	5.064	5.0410
11	15	5.6	4.015	38	35	2.422	2.3280
12	15	8.2	3.33	42	41	2.961	2.8435
13	15	3	3.33	43	42	2.755	2.6550
14	25	5.6	4.7	55	54	4.730	4.6358
15	5	5.6	3.33	22	23	0.694	0.7887

Table 4
The ANOVA for %DCOD and OC, as a function of j (A), pH (B), and κ (C), according to the BBD.

DCOD (%)	Sum of squares	Degree of freedom	Mean square	F value	P value
A:j	0.2155	1	0.2155	320.04	0.0000
B:pH	0.0002	1	0.0002	0.24	0.6445
C:κ	0.0010	1	0.0010	1.41	0.2891
AA	0.0023	1	0.0023	3.36	0.1263
AB	0.0008	1	0.0008	1.21	0.3221
AC	0.0029	1	0.0029	4.33	0.0919
BB	0.0013	1	0.0013	1.88	0.2290
BC	0.0003	1	0.0003	0.51	0.5078
CC	0.0028	1	0.0028	4.22	0.0950
Error total	0.0034	5	0.0007		
Total (corr.)	0.2308	14			
$R^2 = 98.54\%$	$R^2_{adj} = 95.92\%$				
OC (USD/m^3)					
A:j	36.7691	1	36.7691	1590.63	0.0000
B:pH	0.0034	1	0.0034	0.14	0.7192
C:κ	0.3883	1	0.3883	16.80	0.0094
AA	0.5928	1	0.5928	25.65	0.0039
AB	0.0384	1	0.0384	1.66	0.2541
AC	0.0640	1	0.0640	2.77	0.1572
BB	0.0306	1	0.0306	1.32	0.3022
BC	0.0218	1	0.0218	0.94	0.3764
CC	0.0447	1	0.0447	1.93	0.2231
Error total	0.1156	5	0.0231		
Total (corr.)	38.0275	14			
$R^2 = 99.70\%$	$R^2_{adj} = 99.15\%$				

(or factors) and their double-interactions in the variance of each response variable. The *p*-values were used to identify experimental parameters that present statistical influence on particular response. If *p*-value is lower than 0.05, it is considered that the specific variable shows statistical significance within the 95% confidence level [22].

The ANOVA results are presented in Table 4. Notice that the *p*-value of *j* was lower than 0.05 for both response variables (%DCOD and OC). In the case of OC, κ and *j-j* interactions also presented this characteristic. Therefore, they can be considered as statistically relevant in the performance of EO process. The factor with the major effect on %DCOD was *j*. Indeed, the oxidation of pollutants and production of oxidizing species depend on the potential difference in the electrochemical cell. The use of high *j* values maintains the anode activity and promotes the simultaneous oxidation of pollutants and water. Conversely, at low *j* values, O_2 evolution is avoided causing the loss of anode activity due to the adsorption on its surface of intermediates formed from direct anodic oxidation, making this procedure not useful for wastewater remediation in practice [10]. Such effect on the response variable will be discussed subsequently.

$$\%DCOD = 1.5456 + (0.0049*j) - (0.058*pH) - (0.579*\kappa) - (0.0003*(j)^2)$$
$$+ (0.0006*j*pH) + (0.0039*j*\kappa) + (0.0027*(pH)^2)$$
$$+ (0.0052*pH*\kappa) + (0.0591*(\kappa)^2) \quad (9)$$

$$OC\left(\frac{USD}{m^3}\right) = 3.1017 + (0.1894*j) + (0.0799*pH) - (1.6948*\kappa)$$
$$+ (0.004*(j)^2) - (0.0038*j*pH) - (0.0185*j*\kappa)$$
$$+ (0.0135*(pH)^2) - (0.0414*pH*\kappa) + (0.2344*(\kappa)^2) \quad (10)$$

Response surface plots were used to observe the simultaneous effects of two factors over each response variable. They were constructed, from Eqs. (9) and (10), for a fixed pH value of 5.7 (Figs. 1(a) and (b)). As it can be seen, the application of the highest *j* let to achieve the highest %DCOD, *ca.* 53%, if both of independent parameters (*j* and κ) were kept at their maximum values. Consequently, OC also increased. The enhancement in COD degradation as well as in decolorization efficiency, obtained under increasing *j*, can be associated to the
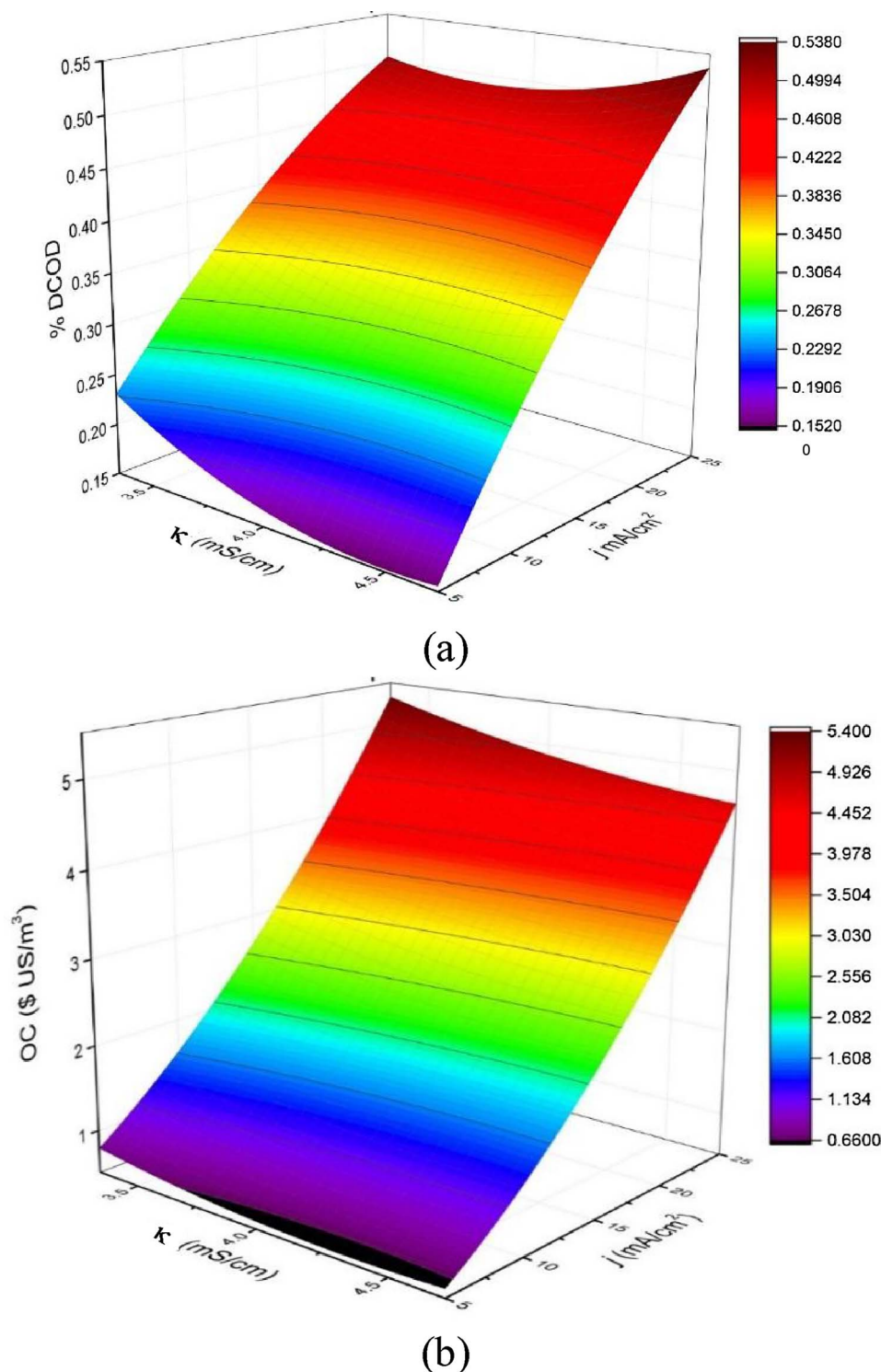
(a)

(b)

acceleration of reaction (1) on the anodic surface, which regulates the amount of produced oxidant (HO·). Thus, larger quantities of (HO·) can be generated (Eq. (2)) and the conjugated chromophore system of organic matter (OM) can be destroyed [13]. In particular, it is known that (HO·) radicals can be completely mineralized, due to their high oxidation potential (E_0 = 2.80 V), contrary to active chlorine, leading to contaminant transformation into CO_2 and H_2O [10]. Regarding to the effect of κ (*e.g.,* NaCl), although the derived chloro oxidant species are not capable of mineralizing textile wastewater, owing to their low oxidation potentials (E_0 = 1.36 V for chlorine, 1.63 V for hypochlorous acid and 0.90 V for hypochlorite), they can result in the formation of

different intermediates [9]. These compounds can be produced through a number of reaction pathways, including oxidation, addition and substitution [15]. Low efficiencies of EO process realized at high κ (Figs. 1a and 1b) can be related to the production of persistent oxy-chloro species that delay or even inhibit complete mineralization [27]. On the other hand, low chloride concentrations can also contribute to organic matter mineralization due to the formation of chlorine radicals (Cl· and $Cl_2{}^{·-}$) [21]. Finally, the pH value of 5.6 was slightly bene-ficial to COD removal. Thus, as it can be seen in Table 4 (e.g. runs 2, 6 y 9), at studied conditions, effluents' pH does not present influence on the rate of removal of the organic load. This probably because under acidic

conditions, the formation of chlorates (ClO_3^-) and perchlorates (ClO_4^-), mediated by $HO\cdot$ radicals and the consequent depletion of these radicals at the electrode surface, is reduced [14]. Panizza and Cerisola [28] also obtained similar results, for the electrochemical degradation of an azo dye, using BDD and PbO_2 anodes. Fig. 1b shows high increase in OC with an increasing current density, as expected by the increase in applied cell voltage. Indeed, applied j is a key factor in electrochemical treatments and it deserves special attention in view of its economic as well as performance implications. Thus, the optimal conditions that let to achieve simultaneously high %DCOD and low OC (USD/m^3) were obtained from RSM models and calculated by Minitab 15 software. The following conditions were selected to study the evolution of the reaction with time: $j = 15\,mA/cm^2$, pH = 5.6 and $\kappa = 4.7$ mS/cm.

3.4. The evolution of color, %DCOD and%DTOC during the sequential CC-EO process

Validation of results obtained by BBD-RSM methodology was performed experimentally at optimized conditions. The variations of color removal, %DCOD and %DTOC, as a function of time, during the sequential CC-EO process are summarized in Fig. 2. COD removal efficiency felt within the 95% prediction intervals, confirming the model's prediction capability. During CC stage, color removal reaches *ca.* 97%. Further EO treatment, after 30 min of electrolysis, let to reach *ca.* 100% of discoloration. On the other hand, the combined CC-EO let to decrease COD and TOC in *ca.* 94% and 75%, respectively (after 45 min of electrolysis). Fig. 2 also presents the OC estimated for the CC-EO process. OC highly increases with electrolysis time, with an associated operating cost of *ca.* 7 USD/m^3 after time 45 min of electrolysis. Notice that OC can be reduced to 4.8 USD/m^3 (with expected removal of *ca.* 100, 85, and 69% of color, COD, and TOC, respectively, and BOD_5/COD ratio = 0.55), if 30 min of electrolysis time is used during the EO process. Under these conditions, the Colombian permissible limits for the industrial wastewater discharges are fulfilled.

3.5. An improvement of wastewater biodegradability and sequential treatment efficiency

Useful additional information, regarding on the reaction progress during wastewater treatment, can be obtained analyzing the Average Oxidation State (AOS) of the treated sample (Fig. 3). AOS was calculated as follows [29]:
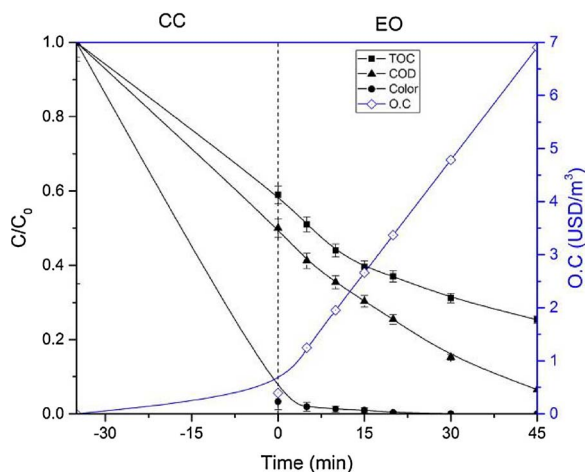
Fig. 2. The evolution of color, COD and TOC removal and the OC of wastewater treated using CC-EO process. Experimental conditions: CC ($Al_2(SO_4)_3\cdot18H_2O$) = 600 mg/L and pH (9.3). EO process pH = 5.6, $\kappa = 4.7$ mS/cm, $j = 15\,mA/cm^2$, BDD anode and Fe cathode.

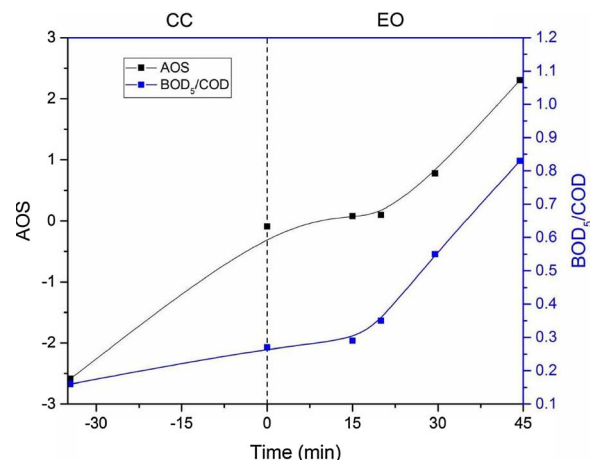**Fig. 3.** Chemical and biological characteristics of wastewater during CC-EO process. Experimental conditions: CC ($Al_2(SO_4)_3\cdot18H_2O$) = 600 mg/L and pH (9.3). EO process pH = 5.6, $\kappa = 4.7$ mS/cm, $j = 15\,mA/cm^2$, BDD anode and Fe cathode.

$$AOS = 4 - 1.5\frac{COD}{TOC} \tag{11}$$

where: TOC and COD are expressed in mg of C/L and mg of O_2/L, respectively. The AOS can take a value between -4 (for the most reduced state of carbon, CH_4) and $+4$ (for the most oxidized state of carbon, CO_2). The CC treatment produces only a small amount of oxidized organic intermediates (AOS value is equal to *ca.* -0.0756). The AOS rises gradually up to *ca.* 2.3, after 45 min of EO (Fig. 3). This implies that organic intermediates go through different oxidation-mineralization reactions. Even if high AOS values are frequently associated to biocompatible solutions, this is not always the case for traces of highly toxic compounds. The BOD_5/COD ratio is customarily used for the assessment of physicochemical processes as a pretreatment before the biological ones [30]. Fig. 3 shows its evolution during EO. The BOD_5/COD of raw wastewater was 0.16 (Table 2), indicating that the biodegradability of this wastewater was very low. This value increased up to *ca.* 0.27 after the CC process and then progressively up to *ca.* 0.83 after 45 min of electrolysis. This last value implies that the final effluent is highly biocompatible (BOD_5/COD ratio > 0.4).

4. Conclusions

According to the findings of this research, sequential Chemical Coagulation (CC, using $Al_2(SO_4)_3\cdot18H_2O$ as coagulant) – Electro-Oxidation (EO, using BDD anode) process appears as an efficient alternative for the treatment of textile wastewater characterized with low biodegradability and high amount of recalcitrant compounds. The ecological parameters such as color, COD and TOC decreased significantly. The obtained BOD_5/COD ratio implies further biological processes to work more effectively.

CC stage removed *ca.* 97% of color, 53% of COD and 24% of TOC. Nevertheless, its biodegradability improvement was quite low (BOD_5/COD ratio increased from *ca.* 0.16–0.27), excluding biological methods as alternative for the following stage of its treatment. At these levels, the CC presents an operating cost of 0.39 USD/m^3.

The CC effluent was subsequently treated by EO. Its operational conditions were optimized by BBD and RSM ($j = 15\,mA/cm^2$, $\kappa = 4.7$ mS/cm, and pH = 5.6). At such conditions, after 45 min of electrolysis, removals of 100% of color, > 90% of COD and > 70% of TOC were reached. Moreover, wastewater biodegradability increased up to BOD_5/COD = 0.83, with an operating cost of 6.91 USD/m^3. Finally, during the EO process, the AOS raised from -0.0756 to 2.3.

If 30 min of electrolysis is applied, at optimized conditions, high efficiencies can be also reached (*v.g.*, reductions of 100% of color, 85% of COD, 69% of TOC and BOD_5/COD of 0.55) with lower operating

costs (*ca.* 4.8 USD/m^3), accomplishing Colombian permissible limits for the textile industrial wastewater discharges.

Acknowledgements

References

[1] C.R. Holkar, A.J. Jadhav, D.V. Pinjari, N.M. Mahamuni, A.B. Pandit, A critical review on textile wastewater treatments: possible approaches, J. Environ. Manag. 182 (2016) 351–366.

[2] F. El-Gohary, A. Tawfik, Decolourisation and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process, Desalination 249 (2009) 1159–1164.

[3] N. Amaral-Silva, R.C. Martins, C. Paiva, S. Castro-Silva, R.M. Quinta-Ferreira, A new winery wastewater treatment approach during vintage periods integrating ferric coagulation Fenton reaction and activated sludge, J. Environ. Chem. Eng. 4 (2016) 2207–2215.

[4] S. Bhatia, Z. Othman, A.L. Ahmad, Coagulation-floculation process for POME treatment using Moringa oleifera seeds extract: optimization studies, Chem. Eng. J. 133 (2007) 205–212.

[5] P.A. Soares, R. Souza, J. Soler, T.F. Silva, S. Guelli, R.A.R. Boaventura, V.J.P. Vilar, Remediation of a synthetic textile wastewater from polyester-cotton dyeing combining biological and photochemical oxidation processes, Sep. Purif. Technol. 172 (2017) 450–462.

[6] C. Amor, J.A.P. Torres-Socías, M.I. Maldonado, I. Oller, S. Malato, M.S. Lucas, Mature landfill leachate treatment by coagulation-flocculation combined with Fenton and solar photo-Fenton processes, J. Hazard. Mater. 286 (2015) 261–268.

[7] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manag. 93 (2012) 154–168.

[8] E. GilPavas, I. Dobrosz-Gómez, M.A. Gómez-García, Decolorization and mineralization of Diarylide Yellow 12 (PY12) by photo-Fenton process: the Response Surface Methodology as the optimization tool, Water Sci. Technol. 65 (10) (2012) 1795–1800.

[9] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters, Appl. Catal. B: Environ. 202 (2017) 217–261.

[10] 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.

[11] 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 wastewater treatment, J. Environ. Manag. 191 (2017) 189–197.

[12] C.S. Rodrigues, A. Neto, R. Duda, R. Oliveira, R. Boaventura, L.M. Madeira, Combination of chemical coagulation photo-Fenton oxidation and biodegradation for the treatment of vinasse from sugar cane ethanol distillery, J. Clean. Prod. 142 (2017) 3634–3644.

[13] J. Zou, X. Peng, M. Li, Y. Xiong, B. Wang, F. Dong, B. Wang, Electrochemical oxidation of COD from real textile wastewaters: kinetic study and energy consumption, Chemosphere 171 (2017) 332–338.

[14] K. Cruz, O. Torres, A. García, E. Brillas, A. Hernández, J.M. Peralta, Optimization of electro-Fenton/BDD process for decolorization of a model azo dye wastewater by means of response surface methodology, Desalination 286 (2012) 63–68.

[15] J. Ruiz, C. Arias, E. Brillas, A. Hernández-Ramírez, J.M. Peralta-Hernández, Mineralization of Acid Yellow 36 azo dye by electro-Fenton and solar photoelectro-Fenton processes with a boron-doped diamond anode, Chemosphere 82 (2011) 495–501.

[16] Y. Yavuz, S. Koparal, U. Ogutveren, Treatment of petroleum refinery wastewater by electrochemical methods, Desalination 258 (2010) 201–205.

[17] J. Aquino, G. Pereira, R. Rocha, N. Bocchi, S. Biaggio Combined Coagulation and, Electrochemical process to treat and detoxify a real textile effluent, Water, Air, Soil Pollut. 227 (8) (2016) 266.

[18] D. Manenti, A. Módenes, P. Soares, F. Espinoza, R. Boaventura, R. Bergamasco, V.J. Vilar, Assessment of a multistage system based on electrocoagulation solar photo-Fenton and biological oxidation processes for real textile wastewater treatment, Chem. Eng. J. 252 (2014) 120–130.

[19] L. Guerreiro, C.S.D. Rodrigues, R.M. Duda, R.A. Oliveira, R.A. Boaventura, L.M. Madeira, Treatment of sugarcane vinasse by combination of coagulation/flocculation and Fenton's oxidation, J. Environ. Manag. 181 (2016) 237–248.

[20] E. Hernández-Francisco, J. Peral, L.M. Blanco-Jerez, Removal of phenolic compounds from oil refinery wastewater by electrocoagulation and Fenton/photo-Fenton processes, J. Water Process Eng. 19 (2017) 96–100.

[21] Standard Methods for the Examination of Water and Wastewater, 22th edn., APHA, American Public Health Association, Washington DC, USA, 2012.

[22] E. GilPavas, I. Dobrosz-Gómez, M.A. Gómez-García, Electrochemical degradation of acid yellow 23 by anodic oxidation–optimization of operating parameters, J. Environ. Eng. 142 (2016) 5 (ASCE).

[23] M.S. Secula, C.S. Stan, C. Cojocaru, B. Cagnon, I. Cretescu, Multi-objective optimization of indigo carmine removal by an electrocoagulation/GAC coupling process in a batch reactor, Sep. Sci. Technol. 49 (6) (2014) 924–938.

[24] 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.

[25] M. Lapertot, S. Ebrahimi, S. Dazio, A. Rubinelli, C. Pulgarin, Photo-Fenton and biological integrated process for degradation of a mixture of pesticides, J. Photochem. Photobiol. A: Chem. 186 (2007) 34–40.

[26] V. Golob, A. Vinder, M. Simonic, Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents, Dyes Pigm. 67 (2005) 93–97.

[27] M. Sales, C.K. Costa de Araújo, J. Vieira de Melo, J.M. Peralta-Hernandez, D. Ribeiro da Silva, C.A. Martínez-Huitle, Decontamination of real textile industrial effluent by strong oxidant species electrogenerated on diamond electrode: viability and disadvantages of this electrochemical technology, Appl. Catal. B: Environ. 130–131 (2013) 112–120.

[28] M. Panizza, G. Cerisola, Electrochemical degradation of methyl red using BDD and PbO$_2$ anodes, Ind. Eng. Chem. Res. 47 (2008) 6816–6820.

[29] F. Vogel, J. Harf, A. Hug, P.R.V. Rohr, The mean oxidation number of carbon (MOC) a useful concept for describing oxidation processes, Water Res. 34 (2000) 2689–2702.

[30] Y.C. Hsu, H.C. Yang, J.H. Chen, The enhancement of the biodegradability of phenolic solution using preozonation based on high ozone utilization, Chemosphere 56 (2) (2004) 149–158.