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Integrated Advanced Oxidation Process (Ozonation) and Electrocoagulation Treatments for Dye Removal in Denim Effluents

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The present research aims to study the removal of indigo carmine dye used in industrial denim dyeing processes. For this purpose, integrated advanced oxidation process comprising ozone and electrocoagulation techniques were used. After ozone was applied 64% color removal, 78% turbidity removal and 3% COD reduction was observed. With the electrocoagulation treatment a 22%, 21% and 9% of color removal, turbidity removal and COD reduction were achieved, respectively. However; using the integrated process, 65% color removal, 76% turbidity removal and 37% COD reduction could be attained. The synergistics associated to coupling both processes yielded increased removal of color, COD and turbidity efficiencies as compared with the results obtained with the single treatments. The decrease in the intensity of the Uv-vis spectrum between the raw wastewater and the treated wastewater indicated that oxidation and organic's removal took place in the integrated process. This result is consistent with the cyclic voltammograms obtained.

Keywords: dye removal, denim effluents, electrocoagulation, ozone, process coupling.

1. INTRODUCTION

The wastewaters from textile industries are intensely colored, bearing quite frequently a complex and variable nature [1, 2]. It is estimated that more than 100,000 synthetic dyes are available in the world with over 7 × 10^5 tons of dyestuff produced annually [3]. Dye-containing effluents can obstruct light penetration in lakes, rivers or lagoons, thus inhibiting the biological processes based on photosynthesis. Moreover, these effluents can contain toxic chemicals, carcinogenic, mutagenic, or teratogenic to various microbiological or animal species [4, 5]. Conventional treatments of dye effluents include biological oxidation and adsorption [6]. Although less expensive than other approaches, the biological treatment is in effective for decoloration because the dyes are toxic [3],[6]. Adsorption onto activated carbon transfers most of the contaminant from the wastewater to the solid phase. This method therefore requires further disposal of the sludge [6]. An alternative approach to addressing the problem of color and toxicity in textile dyeing effluents, has involved the development of effluent treatment methods such as ozonation, advanced oxidation processes and electrochemical methods [5, 6].

Ozonation is particularly attractive for wastewater treatment because ozone, is soluble in water and can decompose quickly to form several free radicals including $OH^{\bullet}$ (hydroxyl), $HO_3^{\bullet}$, $HO_4^{\bullet}$ and O_2^{-} (superoxide). Such free radicals are readily available to react instantly with any organic compounds present in water, like the dyes [7, 8]

Further, the electrochemical techniques have been found particularly interesting for textile wastewater remediation due to advantages like: high efficiency, ease of operation and environmental compatibility since there is no need of adding chemicals [5, 9, 10]; this process involves the *in situ* generation of coagulants by electrolytic oxidation of an appropriate sacrificial anode upon application of a direct current [4, 11].

Given the advantages of ozonation and electrocoagulation for wastewater treatment, in the present research both processes are integrated in a batch reactor to increase the efficiency of wastewater color removal from dyeing denim compared with the treatments alone.

2. MATERIAL AND METHODS

The samples for this study were collected at the exit of denim's dyeing process, preserved and analyzed according to the standard methods for conventional characterization APHA/AWWA/WEF. The ozone, electrocoagulation and integrated processes were monitored through determining removal of color, turbidity, chemical oxygen demand (COD) and pH variation. Spectrophotometry at 465 and 860 nm, respectively, served to determine color and turbidity by means of an HACH 110 DR/4000U equipment. The chemical oxygen demand was analyzed according to closed reflux; colorimetric method. A Waterproof OAKTON pH/CON 300 Series, was used for pH measurement at different stages of the various treatments.

A comparison between the UV-VIS spectroscopy absorbance spectra of the oxidized products was realized using a Perkin Elmer Lambda 25 UV/VIS Spectrometer, USA.

Cyclic voltammetry of crude and treated wastewater were performed using a standard three-electrode cell. The waveforms were generated by an Epsilon™ Electrochemistry Basi Cell Stand C-3 Potentiostat; using a round carbon paste electrode (CPE) as working electrode, prepared from a 1:1 mix of 99.99% pure single-crystal graphite (Alfa Aesar) and nujol oil (Aldrich). The paste was transferred into a PVC tube and compacted to eliminate trapped air then a copper conductor was back-inserted before the paste set. The surface of the electrode was renewed through light polishing after each potential scan. The scan rate was 100 mVs^{-1} with an Ag/AgCl reference electrode and a glassy carbon counter electrode.

2.1 Ozonation process

Ozone was generated using a laboratory-scale ozone generator (LAB 21 ozone generator) capable of generating ozone continuously at a 5.2 g of O_3 h^{-1} rate, using air (20.95% O_2) as feed gas flowing at 10 Standard Cubic Feet per Hour (SCFH) rate and 6 psi of pressure. The generator used the corona discharge to produce ozone by passing dry air through a very strong electric field, which splits diatomic oxygen molecule (O_2) into two highly excited oxygen atoms (O^-) that due to their inherent instability combine readily with other oxygen molecules to form ozone [1].

The chemical oxidation experiments with ozone were performed in a laboratory-scale reactor comprising a 60 cm long acrylic column of 20 cm inner diameter (ID) fitted with a stone diffuser at the bottom to aid uniform distribution and good mixing of the ozone gas and the effluent. The reactor was run in a batch mode at 2.5 L effluent per batch: first, the ozone was supplied through the diffuser stone at the reactor's bottom, for 120 minutes. Samples were taken every 10 minutes; the sample pH was monitored during the treatment. The excess ozone flowed from the top of the reactor into the ozone trap containing a 0.1 M KI solution.

2.2 Electrocoagulation process

The electrocoagulation was carried out in the same laboratory scale reactor described previously for the ozone process; two rectangular commercial aluminum plates served as anode and cathode. The anodic and cathodic active surface area were 343 cm^2 immersed in wastewater with 0.1372 cm^{-1} of SA/V ratio. A DC power source supplied the system with 0.1 A, corresponding to a 0.2915 mA cm^{-2} current density that was kept for 1 minute every 10 minutes intervals during the experiment; the sample pH was monitored during the treatment. The electrocoagulation was performed without additional electrolyte. The electrodes were connected to a digital DC power supply (G^W ISTEK GPR-1820 HD, 0-18 V; 0-20 A, China). 25 mL of sample were taken every 10 minutes during the 2 h of electrocoagulation process. The samples were allowed to settle for 1 h, and then analyzed.

2.3 Ozone-electrocoagulation process

The ozone and electrocoagulation treatments were coupled into a combined ozone-electrocoagulation process and carried out simultaneously using the conditions described previously for each of the treatments alone. The samples also were taken every 10 minutes during 2 h and allowed to settle for 1 h before being analyzed.

3. RESULTS AND DISCUSSION

Table 1 shows the initial physicochemical parameters of wastewater from the dyeing denim process. The color value obtained is harmful to aquatic life obstructing light penetration in the water, inhibiting thus the photosynthesis-based biological processes [5]. On the other hand, substances such as indigo carmine dye forms chelates with metal ions, which results in high hardness. The high value of electric conductivity indicates an excessive mineralization that causes high solids levels and turbidity in wastewater; therefore filtration, flocculation or other processes should be used for remove them. The value of Biochemical Oxygen Demand (BOD_5) limits their discharge into water bodies due to harmful effects on living systems. The COD value shows high pollution due to organic and inorganic matter susceptible to be oxidized that favors the presence of color in this wastewater. The pH is similar to the natural waters value (7.2 to 7.8).

Table 1. Initial physicochemical parameters from treated wastewater

Parameter	*Value*	*Units*
BOD_5	1174	mg/L
COD	2308	mg/L
Color	630	Pt-Co
Turbidity	110	FAU
pH	7.23	
TS	3460	mg/L
Conductivity electric	1510	μS/cm
Chlorides	306	mg/L
Total Hardness	508	mg $CaCO_3$/L
Alkalinity (HCO_3^-)	224	mg /L

3.1 Color removal efficiency

The color, COD and turbidity removal efficiency (%) at the different processes were calculated using the equation 1:

$$E = \frac{C_0 - C_i}{C_0} X 100 \qquad (1)$$

Where E is the dye, COD or turbidity removal efficiency (%), C_0 is the initial value of the color of dye (Pt-Co), COD (mg/L) or turbidity (FAU) in the wastewater, and C_i is the color value of dye (Pt-Co), COD (mg/L) or turbidity (FAU) at time t after the different processes.

The treatment with the best efficiency for the removal of color at 120 min of reaction was the integrated process of ozone-electrocoagulation, which increased to 64.27% of color removal. A similar result, 63.63% of discoloration was obtained in the ozone process, as shown in figure 2. Further, the treatment with the lowest color removal efficiency corresponded to the electrocoagulation process, with 21.73%.

With the combined ozone-electrocoagulation process, the color removal increased gradually as the reaction time increased. Following the same tendency, values of color removal smaller than the prior process were obtained with the ozone process. Finally; color removal did not increase significantly from 10 to 120 minutes of reaction in the electrocoagulation process.

For the ozone process, the color reduction could be attributed to the ozone reaction with the unsaturated bonds of the indigo carmine, leading to the splitting of bonds and the dissociation of the rings, according to the Criegee mechanism [12]. In the electrocoagulation process, the Al^{3+} and OH^{-} ions generated at the electrode surfaces react in the wastewater to form aluminum hydroxide [13]; the amorphous and gelatinous aluminum hydroxide that displayed various shapes and sizes (flocs) [9] destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [14, 15]. Given the physicochemical characteristics of the treated wastewater; the hardness, chlorides, alkalinity, conductivity and TS could compete with the hydroxyl radicals by decreasing the efficiency of color removal in this treatment [13, 16]. The synergic effect associated to the integration of both processes (ozone and electrocoagulation) resulted in an increased color removal efficiency in the ozone-electrocoagulation process.

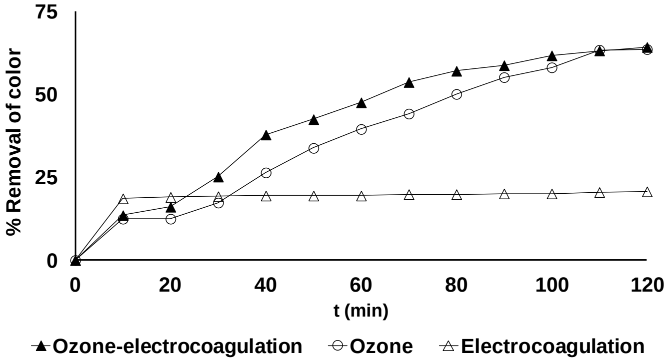

Figure 2. Color removal efficiency in the wastewater treated with different processes

3.2 COD removal efficiency

After 120 min of reaction; with 36.85% of COD reduction, the ozone-electrocoagulation process showed the higher efficiency on the values obtained by electrocoagulation and ozone processes; as shown in figure 3. Most COD removal in this process was obtained after the first 10 min of reaction (30.75%); from 10 to 120 min there was not a significant increase (6.1%). For the electrocoagulation and ozone processes, the efficiencies were the lowest achieved; 8.50% and 2.63% of COD removal at 120 min of reaction; respectively.

In the ozone process the chemical oxidation was accomplished by a hydroxyl radical reaction mechanism (indirect oxidation) under alkaline conditions [12, 17]. The oxidation activity of the hydroxyl radical might be limited by the presence of scavengers (hardness, chlorides, alkalinity, conductivity, TS) [12, 13, 16]; these ions terminate the chain reactions and inhibit ozone decay to hydroxyl radicals; which causes incomplete degradation of the organic loading of a sample [12].

The oxidation activity of hydroxyl radicals is limited by the presence of scavengers, which causes incomplete degradation of the organic loading of a sample. High alkalinity indicates the presence of carbonate and bicarbonate ions, which terminate the chain reactions and inhibit ozone decay to hydroxyl radicals, hence promoting ozonation through direct pathway-mechanism. Some researchers reported that during ozonation several substances were converted to other more hydrophilic and polar compounds. As a result, the removal of the produced substances by prolonged ozonation or by other techniques becomes even more difficult [12].

On the other hand, the electrocoagulation removes anions and organic compounds due to aluminum hydroxide formed that precipitates and adsorbs dissolved contaminants [9, 15]; due to contaminants in this matrix, the oxidation activity of hydroxyl radicals might be limited [12], thus decreasing the efficiency of COD removal [12, 13, 16]. Once again, the synergistic coupling of both processes increased the COD percent removal of the ozone-electrocoagulation process.

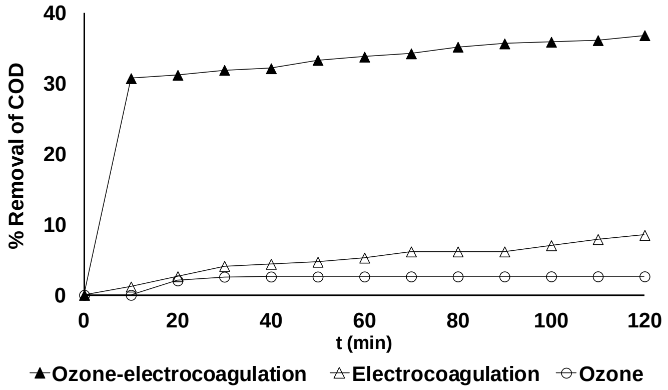

Figure 3. COD removal efficiency in the wastewater treated by means of three different processes

3.3 Turbidity removal efficiency

With slightly higher efficiencies, turbidity removal follows the same pattern as that of color removal in the different treatments after 120 reaction minutes. Again, the integrated process ozone-electrocoagulation and ozone treatment had obtained the highest efficiency values of 75.30% and 77.77%, respectively, as well as the electrocoagulation process showed that showed the lowest efficiency with 20.71% of turbidity reduction, as shown in figure 4.

The changes of the properties of the organics, such as a decrease in molecular size, could be the reason for the reduction in the turbidity from the wastewater after the ozone and ozone-electrocoagulation processes [18]. Electrocoagulation also removes turbidity [9] but the presence of scavengers in the wastewater caused low efficiency in its removal [12, 13, 16].

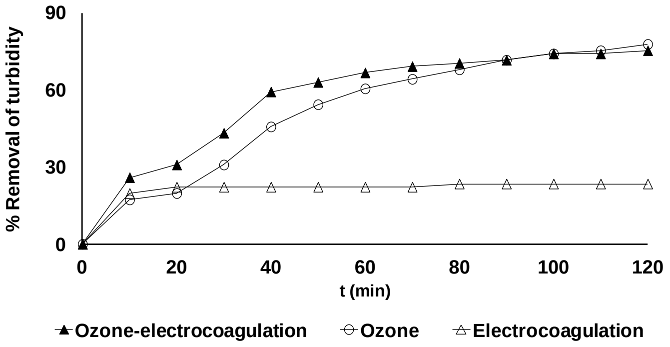

Figure 4. Turbidity removal efficiency in the wastewater treated by means of different processes

3.4 Evolution of pH in the different processes

There was no significant increase in pH values during the reactions for any of the three processes carried out; the pH values remained close to the initial value (7.23 pH) after 10 reaction minutes (8.34, 8.51 and 8.20 for ozone-electrocoagulation, ozone and electrocoagulation processes; respectively). Subsequently, the pH values were similar up until 120 minutes of reaction as shown in figure 5. The increase of wastewater pH during the processes is mainly attributed to the increase of hydroxide ions (HO^{-}) concentration [4].

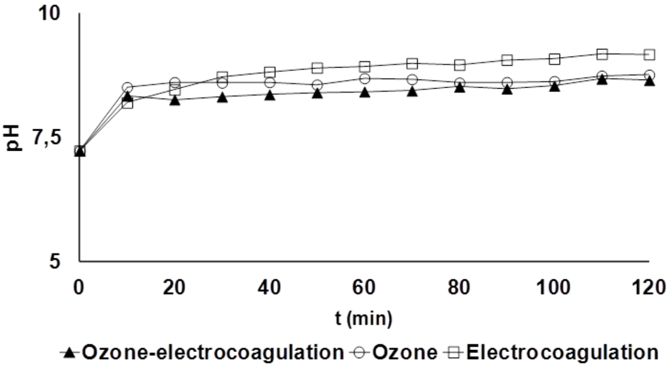

Figure 5. Evolution of pH in the wastewater treated by means of different processes

3.5 Kinetics of discoloration and turbidity removal of wastewater treated in ozone-electrocoagulation process

In this study, the kinetics of wastewater treated were evaluated by plotting $\frac{1}{[C_t]}-\frac{1}{[C_0]}$ values versus reaction time following equation 2

$$\frac{1}{[C_t]}-\frac{1}{[C_0]}=k_d t \qquad (2)$$

Where C_t and C_0 are the concentrations of color or turbidity at any reaction time (t) during the ozone-electrocoagulation process and the initial concentration of color or turbidity, respectively. k_d stands for the second-order reaction rate constant.

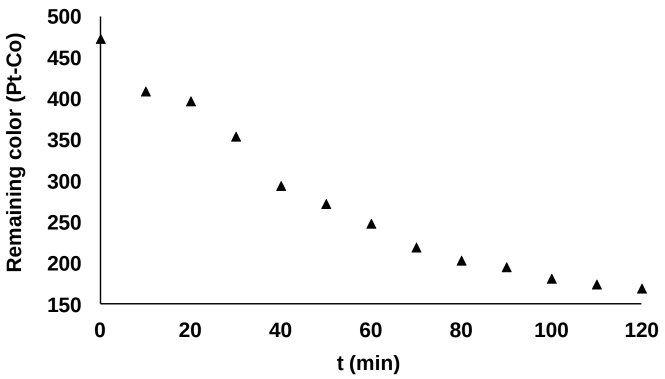

Figure 6. Remaining color as function of contact time of the wastewater treated in the ozone-electrocoagulation process.

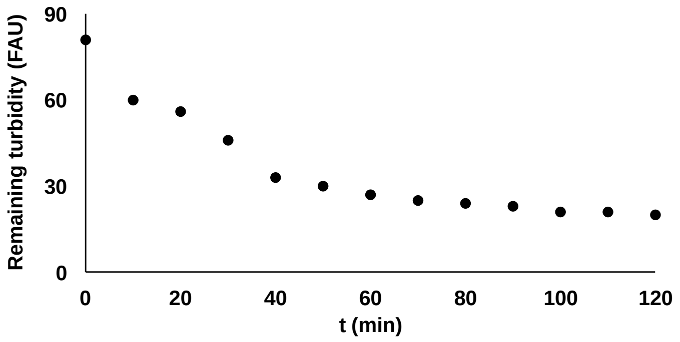

Figure 7. Remaining turbidity as function of contact time of the wastewater treated in the ozone-electrocoagulation process.

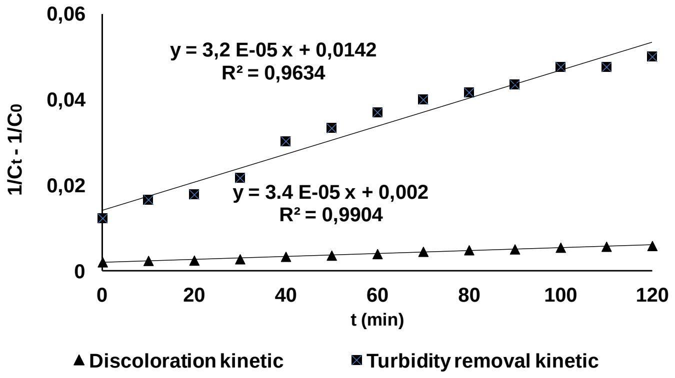

Figure 8. Kinetics of discoloration and turbidity of the wastewater treated in the ozone-electrocoagulation process

Figures 6 and 7 illustrate the disappearance of the concentration of color and turbidity versus time, respectively, which was fast in the first 70 min of reaction. Afterwards, the disappearance rate of color and turbidity was slower.

Using data obtained from equation 2; figure 8 shows that the second-order kinetics fitting curve followed well the experimental data for discoloration and turbidity removal, and the square of the correlative coefficient (r^2) of the experimental results was 0.9904 for the discoloration kinetic and 0.9634 for turbidity removal kinetics. The slope of the linear plot represents the second-order rate constants, which were 3.4 X 10^{-5} L mol^{-1} min^{-1} and 3.2 X 10^{-4} L mol^{-1} min^{-1} respectively.

The discoloration kinetic study as functions of ozonation time was investigated by Santana *et al*. in a synthetic water containing Reactive Orange 122; they state that using ozone constitutes an efficient technology for color removal [19]. Secula *et al*. report that electrocoagulation of synthetic wastewater containing indigo carmine dye obeys a second order reaction, which agrees with our results [4]. Durante *et al*. reported that when advanced oxidation processes (AOPs), such as ozonation or electrooxidation are applied in series with electrocoagulation (EC), a complete removal of the recalcitrant fractions of Cr in a synthetic wastewater, can be successfully achieved [16].

3.6 UV–Vis spectra of the wastewater in the ozone-electrocoagulation process

The spectrum for the raw wastewater (▲) presents a baseline with two absorbance peaks; the first at 290 nm and the second at 655 nm, which are associated with the contaminants in this matrix (2308 mg/L COD) and the color of the sample (630 Pt-Co).

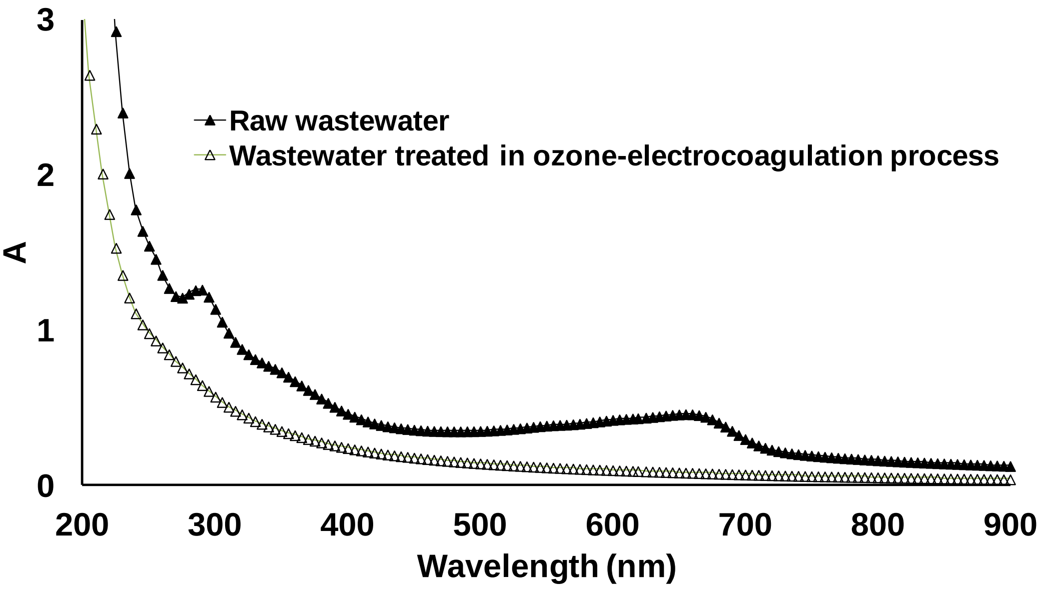

Figure 9. UV–Vis spectrum of the raw wastewater and treated wastewater in ozone-electrocoagulation process.

For 120 minutes of reaction, the wastewater treated in the ozone-electrocoagulation process (Δ) showed the highest efficiency in removing color (64.27%), turbidity (75.30%) and COD (36.85%) together with a decrease in the baseline and a decrease in the two absorbance peaks; as shown in figure 9. The oxidation of organic contaminants, the degradation of indigo carmine dye and the removal of inorganic contaminants were indicated by the decrease in the absorption band at 290 nm, 655 nm and baseline, respectively.

Song *et al*. presented the UV–vis spectra of the discoloration efficiencies of C.I. Reactive Blue 19 in synthetic water by applying a simultaneous electrocoagulation ozonation process; they found that this process is a promising alternative for treatment of wastewater with a high content of recalcitrant reactive dyes [20]. Cristóvão *et al.* investigated the degradation of a mixture of textile dyes, in synthetic water. The discoloration was appraised as a percentage of the absorbance reduction at the wavelength of maximum absorbance as total color removal based in spectrum. A significantly high discoloration was achieved indicating the applicability of this method for textile wastewater treatment [21]. These results agree with our results presented in Figure 9.

3.7 Cyclic voltammetry

Figure 10 shows the voltammograms of the raw and treated wastewater obtained by starting the potential scan in the positive direction, where the results show an oxidation process and a reduction process in the raw wastewater detectable at potentials lower than those corresponding to oxygen evolution due to pollutants present; also, a capacitive current is noted that can be related to degradation of the dye. When cyclic voltammetry was applied to the wastewater treated after the process of ozone-electrocoagulation, the peaks do not appear, indicating that pollutants in the raw wastewater have already been oxidized.

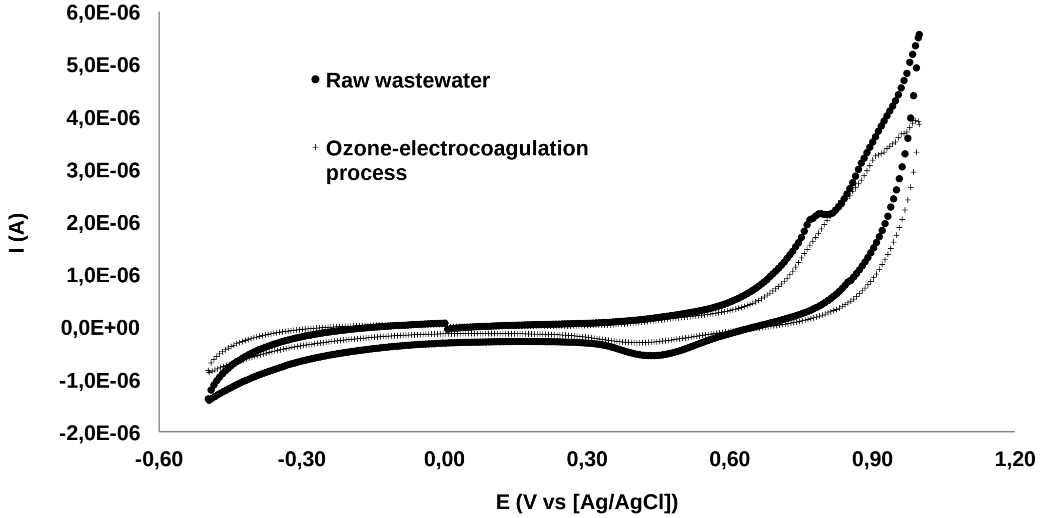

Figure 10. Cyclic voltammograms recorded at the CPE within the −0.6 to 1.2V potential window at 0.1Vs^{-1} scan rate.

Zhang *et al.* present the cyclic voltammogram of high discoloration efficiency of methyl red in synthetic water by synergistic effect of electrocoagulation and electrooxidation, they report that the Acid Red 2 can be oxidized, but not reduced, and the removal is related to its oxidation [22]. This agrees with the voltammogram that we present in Figure 10.

4. CONCLUSIONS

The effect of the integration of ozone and electrocoagulation treatments in the pulsed ozone-electrocoagulation process, resulted in increased removal efficiency of color, COD and turbidity compared with the efficiency obtained in treatments alone in the denim effluent researched; differences of 43.56%, 34.19% and 51.85% resulted respectively, compared to the less efficient process. The ozone process showed similar results to the integrated process for removing color and turbidity; though not so for COD removal. The lowest efficiencies of color removal and turbidity were obtained the through electrocoagulation process.

The reaction kinetics for the removal of color and turbidity in ozone-electrocoagulation pulses process were second-order indicating that the efficiencies obtained in the integrated process depend on the coupling of treatments (ozone and electrocoagulation).

The decrease in the intensity of the spectrum between the raw wastewater and the treated wastewater indicate the oxidation and removal of organic compounds in the integrated process. This result is consistent with the cyclic voltammogram obtained.

Given the physicochemical characteristics of the treated wastewater from the denim effluents, the hardness, chlorides, alkalinity, conductivity and TS could compete with the hydroxyl radicals by decreasing the efficiency of color, turbidity and COD removal in the treatments researched.

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