

Polishing of treated textile effluent using combined electrochemical oxidation and ozonation technique

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ABSTRACT

Textile effluents are known to be complex matrices, requiring a combination of treatment techniques to achieve conditions that allow effluent to be discarded into environment. The electrocoagulation technique manages to remove most of the pollutants present in textile effluents, but generally does not achieve complete removal. This work studied the efficiency of combined electrochemical oxidation and ozonation techniques in the post-treatment of a real textile effluent after electrocoagulation and decantation processes. The experiments were carried out in batch mode using Ti/RuO₂ electrodes (2 plates) and an ozone generator ($0.875 \text{ g·h}^{-1}\text{L}^{-1}$). Three current densities were studied, 33.3, 66.6, and 133.3 A·m⁻². The turbidity, color, dissolved organic carbon, and pH were analyzed to evaluate the treatment process. The results showed higher efficiency for removing color and dissolved organic carbon with increasing current density. Applying the ozonation process alone had the lowest color and dissolved organic carbon removal efficiencies. The best experiment was with the current density of 66.6 A·m⁻² integrated with O₃ promoted removal percentages of 91.77%, 33.02%, and 91.09% for turbidity, dissolved organic carbon, and color, respectively.

Keywords: Textile effluent; Electrochemical oxidation; Ozonation

1. Introduction

Textile industries are known for their high-water consumption and consequent generation of high volumes of effluents [1]. These effluents are complex and may include dyes, bases, surfactants, hydrogen peroxide, fiber residues, and heavy metals [2–4], leading to high chemical oxygen demand (COD) values, and high salinities and toxicities. Furthermore, textile dyes are often toxic, mutagenic, and carcinogenic and may cause human diseases such as skin irritations, headaches, nausea, respiratory ailments, and congenital malformations [5,6]. Various processes have been used to treat textile effluents, such as adsorption [7,8], biological processes [9–11], electrocoagulation [12–14], electro-oxidation [15–17], advanced oxidation processes [18–20], ozonation [21,22], and combinations of the above [23–27].

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Electrolytic processes are attracting attention in the treatment of textile effluents. These processes involve applying an electric current through one or more pairs of electrodes (an anode and a cathode) submerged in a solution (electrolyte) to trigger specific electrochemical reactions. The electrocoagulation (EC) process is an evolution of the conventional chemical coagulation mechanism, which has been developed to meet the need for alternative wastewater treatment technologies with viable pollutant removal applications [28,29]. EC uses sacrificial electrodes (such as aluminum and iron base), with the anode undergoing oxidation and releasing coagulant to the medium and the cathode reducing water molecules. The solute (Mⁿ⁺ ion) may react with water or hydroxyl molecules to form species of amorphous mononuclear and polynuclear hydroxides [30].

EC occurs in three successive stages [31]: (a) formation of coagulants by electrolytic oxidation of the "sacrificial electrode"; (b) destabilization of contaminants, suspension of particles, and breakdown of emulsions; (c) aggregation of the destabilized phases to form flocs. The treatment of textile effluents using EC removes suspended solids and part of the dissolved organic molecules. However, there are cases where a soluble fraction of the organic compounds remains in the solution, evidencing the need for a subsequent process to remove the pollutants altogether [32].

Electro-oxidation (EO) or electrochemical oxidation is another electrolytic process used for water and effluent treatment. The oxidation of organic pollutants at the anode occurs through two distinct mechanisms: direct anodic oxidation and indirect oxidation [33,34]. In direct anodic oxidation, charge transfer occurs directly between the electrode surface and the pollutant molecule. The mechanism is only promoted through exchanging electrons capable of oxidizing organic pollutants at defined potentials above the oxygen evolution potential. For this step to occur, adsorption of the pollutant on the electrode surface is required. Indirect oxidation occurs by generating species with high oxidation potential on the electrode surface. Several species can be generated during electrooxidation, particularly reactive oxygen and chlorine species.

An essential advantage of EO is the potential to oxidize organic pollutants to CO_2 and H_2O completely, thus avoiding the problem of contaminants being transferred from one phase to another [35]. EO's ability to produce hydroxyl radicals (HO[•]) at the electrode surface can be considered an advanced oxidative process [36,37]. Comninellis [38] describes the combustion/conversion of compounds on oxide anodes. Anodes are divided into reactive and non-reactive anodes. Active anodes can only convert organic matter, while non-reactive anodes achieve complete degradation of organic matter. The electrodes doped-SnO₂/ boron-doped diamond (BDD), and PbO₂ are considered non-reactive anodes, whereas Pt, IrO₂, and RuO₂ electrodes are considered reactive anodes [36,39,40].

Ozone has been used to treat effluents containing refractory organic compounds due to its oxidizing power and efficiency in removing organic matter, including dyes [3,41]. Additionally, using ozone does not generate sludge at the end of the treatment [42]. There are two routes for removing organic matter by ozone: (a) a direct reaction between the ozone molecule and the organic matter; (b) an indirect reaction through the generation of the hydroxyl radical [43,44].

The characteristics (chemical, physical, and biological) of the effluent define the types and amounts of treatment processes that will be used in an effluent treatment plant. As textile effluents have a variety of chemical compounds, the application of only one process is not enough to make the effluent suitable for disposal.

The combination of EO and ozonation in wastewater treatment has become attractive. Amado-Piña et al. [45] applied the combination of EO and ozonation in an aqueous phenol solution and achieved removals of 98.0% and 98.5% for COD and total organic carbon, respectively, as well as total elimination of toxic effects in lettuce (*Lactuca sativa*) seeds. A complete removal of COD from an effluent containing melanoidins was achieved using the association of ozonation and EO in 62 min of treatment [46]. García-Morales et al. [47] also used the association of EO and ozonation in the treatment of industrial effluent, obtaining 99.9% of COD removed in 60 min of experiment. Montero-Guadarrama et al. [48] obtained a removal of 95.5% of UV-Vis absorption in 12 min of treatment in a solution containing phenol red.

There are studies that applied the combination of electrolytic and ozonation processes in the treatment of textile effluent, but they are EC processes [49–52]. Thus, the combination of EO and ozonation has not been widely applied to a real textile effluent, especially when the effluent comes from an electrocoagulation–decantation process. Therefore, this work's objective was to study the application of the association of EO and ozonation in the post-treatment of a real textile effluent from the electrocoagulation–decantation processes. Color, dissolved organic carbon and turbidity were the parameters used for the evaluation of the processes.

2. Materials and methods

2.1. Textile effluent

The effluent was collected from a hammock manufacturer located in Jaguaruana-CE, Brazil, and was treated in two stages: EC and decantation (DEC). The operating conditions are shown in Fig. 1. The EC step employed four sets of electrodes connected in a bipolar arrangement in series; each set contained ten plates of 304 stainless steel electrodes. On the day the effluent was sampled, the raw effluent contained the dyes (Reactive Blue 19, Reactive Orange 107, and Reactive Red 198), a compound based on fatty acid derivatives, combined organic polymers, organic salts, organic ester, and dispersants. The characterization of the effluent sample after the DEC (step 4) is shown in Table 1.



Fig. 1. Design of the effluent treatment plant.

2.2. Electrolytic cell and experiments

The experiments were carried out in an electrolytic cell consisting of a cylindrical acrylic reactor with a 4 L capacity, which was operated in batches under the agitation of a magnetic bar at 800 rpm (Fig. 2). The current intensity was supplied by a MINIPA MDL-3305 source in galvanostatic mode, and the ozone was supplied by an ozone generator $(0.875 \text{ g}\cdot\text{h}^{-1}\cdot\text{L}^{-1} - 70 \text{ Wh}; \text{GO5000AA-INX ozone line})$. The two electrodes used were composed of a titanium metallic alloy with ruthenium oxide (Ti/RuO₂) (Magneto® Special Anodes, Netherlands), with dimensions 300 mm × 50 mm × 1 mm and an inter-electrode distance of 2 mm. The total experiment time was 60 min, with samples collected at 10, 20, 30, 45, and 60 min. The current densities used were 33.3, 66.6, and 133.3 A·m⁻². The presence of ozone was evaluated for each current density; one experiment only applied ozone. The experiments were repeated twice. The choices of current

Table 1

Characterization of the effluent sample

Parameters		Mean ± Standard deviation			
Turbidity (NTU)		36.00 ± 6.80			
Temperature (°C)		33.40 ± 2.20			
Electrical conducti	vity (mS/cm)	$5,100 \pm 274$			
pН		8.54 ± 0.40			
DOC^{a} (mg·L ⁻¹)		48.84 ± 1.98			
	436 nm	18.55 ± 2.33			
$DFZ^{b}(m^{-1})$	525 nm	11.60 ± 1.75			
	620 nm	8.05 ± 1.11			

^aDOC – dissolved organic carbon; ^b DFZ – Visual color number (German abbreviation of DurchsichtFarbZahl).



Fig. 2. Design of the electrolytic cell for the experiments. 1-Reactor, 2-Electrodes, 3-Power supplier, 4-Ozone generator, 5-Multiparametric probe, 6-Magnetic stirrer, 7-Sample port, 8-Magnetic bar.

and ozone flowrate values were determined by the limitation of the equipment used.

2.3. Instrumental analysis

The pH was monitored in situ using a multiparametric probe (HI-7629829, HANNA, USA) and meter (HI-98290, HANNA, USA). The turbidity of the solution was measured with a turbidimeter (HI-98703, HANNA, USA). Dissolved organic carbon (DOC) was measured using an organic carbon analyzer (SHIMADZU, TOC-L, Japan) equipped with an autosampler (OCT-L); the sample had been previously filtered (0.45 µm). The color was determined by measuring the absorbance at 436 nm (DFZ₄₃₆), 525 nm (DFZ₅₂₅), and 620 nm (DFZ₆₂₀) using a spectrophotometer (SHIMADZU, 800, Japan), according to the DIN EN ISO 7887:2012 standard. The DFZ-value method was chosen to evaluate color removal because the effluent does not show sufficiently sharp and distinguished absorption maxima. The DFZvalue was obtained by Eq. (1). The treatment efficiency for DOC, color, and turbidity was obtained by Eq. (2).

$$\mathrm{DFZ}\left(m^{-1}\right) = \frac{A}{b} \tag{1}$$

where A is absorbance and b is the light path in m.

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100$$
(2)

where %R is the removal percentage, C_o is the initial value of each parameter, and C_t is the parameter's value at a given experiment time. The electrical energy consumption per volume of treated effluent (kWh·m⁻³) and electrical energy consumption per DFZ removal (kWh·m) were obtained in Eqs. (3) and (4):

$$EEC(kWh m^{-3}) = \frac{TIt + P_{oz}}{1000V}$$
(3)

$$EEC(kWh m) = \frac{Tlt + P_{oz}}{1000(DFZ_i - DFZ_f)}$$
(4)

where *T* is the applied tension (V), *I* is the electrical current (A), *t* is the time of the experiment (h), *V* is the volume of solution (m³), P_{oz} is the power (Watts) of the ozone generator, and DFZ_i and DFZ_f are the initial and final DFZ values (m⁻¹), respectively.

3. Results and discussions

3.1. Behavior of color, DOC, turbidity, and pH parameters

Fig. 3A–D show the DOC and color removals. For DOC (Fig. 3A), experiments using only EO achieved removals of 10.48%, 20.14%, and 34.11% for 33.3, 66.6, and 133.3 A·m⁻², respectively. The EO + O₃ improved DOC removal, except for the condition 133.3 A·m⁻²/O₃, obtaining removals of 18.83%, 33.02%, and 23.95% for 33.3, 66.6, and 133.3 A·m⁻²/O₃, respectively. The increase in current density promotes a better generation of oxidizing species on the anode surface.

However, higher values of electric current may promote a decrease in pollutant removal efficiency due to side reactions and gas evolution, which may explain a decrease of the efficiency using 133.3 A·m⁻²/O₃ [53,54]. Another possible reason for the decrease in DOC removal efficiency is the excess of oxidizing agents (generated by the electrolytic process) and ozone reacting with each other. The results show a trend toward the stabilization of DOC removal (Fig. 3A). Pollutant removal by the Ti/RuO₂ electrode occurs via the generation of the MO_{x+1} species [Eqs. (5) and (6)], known as chemisorbed "active oxygen" that can only convert the pollutant (RO) instead of promoting combustion [Eq. (7)] [38], which may explain the DOC removal results.

$$MO_{x} + H_{2}O \rightarrow MO_{x}(HO^{\bullet}) + H^{+} + e^{-}$$
(5)

$$MO_{x}(HO^{\bullet}) \rightarrow MO_{x+1} + H^{+} + e^{-}$$
(6)

$$R + MO_{x+1} \rightarrow RO + MO_x \tag{7}$$

The ozone-only DOC reached 10.24%. The degradation of pollutants by O_3 may have occurred by direct ozone-organic matter reaction under acidic conditions [Eq. (8)], attacking conjugated double bonds, or via oxidizing species generated by the decomposition of ozone in solution under basic conditions [Eqs. (9)–(15)], generating hydroxyl radical and other radical species [43,55].

$$R + O_3 \rightarrow R_{oxid} \tag{8}$$

$$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^{\bullet}$$
⁽⁹⁾

$$\mathrm{HO}_{2}^{\bullet} \leftrightarrow \mathrm{O}_{2}^{\bullet-} + \mathrm{H}^{+} \tag{10}$$

$$O_3 + O_2^{\bullet-} \to O_3^{\bullet-} + O_2 \tag{11}$$

$$\mathrm{HO}_{3}^{\bullet} \leftrightarrow \mathrm{O}_{3}^{\bullet-} + \mathrm{H}^{+} \tag{12}$$

$$HO_{3}^{\bullet} \rightarrow HO^{\bullet} + O_{2} \tag{13}$$

$$\mathrm{HO}^{\bullet} + \mathrm{O}_{3} \to \mathrm{HO}_{4}^{\bullet} \tag{14}$$

$$\mathrm{HO}_{4}^{\bullet} \to \mathrm{O}_{2} + \mathrm{HO}_{2}^{\bullet} \tag{15}$$

The color removal results show that at the beginning of the treatment, the current density 33.3 A·m⁻² had a lower removal rate than 66.6 and 133.3 A·m⁻² (Fig. 3B–D). However, at the end of the treatment, the color removal values using only EO were similar (Fig. 3B–D). The association of techniques (EO + O₃) provided the best color removal, with the first twenty minutes having the highest removal rates. However, increasing current density slightly influenced color removal (Fig. 3B–D). Excess oxidizing agents may have led to a lower color removal efficiency using 66.6 and 133.3 A·m⁻² in the first 10 min of the experiment. Fig. 4 shows each experiment's average removal values (between DFZ_{436'} DFZ_{525'} and DFZ₆₂₀). It is evident that using only EO resulted in 73.92%, 78.55%, and 76.87% removal for 33.3,



Fig. 3. Color and dissolved organic carbon removal for the experiments.

66.6, and 133.3 A·m⁻², respectively, while the EO + O_2 experiments obtained 92.66%, 91.09%, and 96.16% for 33.3, 66.6, and 133.3 A·m⁻²/O₂, respectively. Pinto et al. [17] obtained 100% color removal (at 436, 525, and 620 nm) of textile effluent using Si/BDD anode with 60 and 100 mA·cm⁻² in 10 h of experiment. Interesting results were also obtained by Saleh et al. [15], achieving 96.6% color removal using graphite electrodes with 150 A·m⁻² at pH 5 and for 120 min. The application of ozone alone had the lowest color removal, 67.64%. The short contact time between the ozone and organic matter caused by the quick rise of ozone bubbles to the top of the reactor may have caused the low color and DOC removal efficiencies. Using ozone as a pre-treatment of textile effluent on a pilot scale, Somensi et al. [56] achieved color removals of 67.5% at pH 9.1 (via oxidizing species generated). Cardoso et al. [57] obtained better color removal from textile effluent by ozone at pH 3 (direct reaction between the ozone molecule and the organic matter).

The compound oxidation may have also achieved color and DOC removal via reaction with hypochlorous acid and/or hypochlorite anion. Chloride in solution undergoes oxidation at the anode, which can lead to the formation of chlorine gas (Cl₂), hypochlorous acid (HClO), and the hypochlorite anion (ClO⁻), [Eqs. (16)–(18)] [58–60]. With a pKa 7.49, HClO is considered a weak acid. Fig. 5A and



Fig. 4. Average color removal for the experiments.



Fig. 5. UV-Vis spectra profiles.

B show the UV-Vis absorbance spectrum of the initial and treated effluent. It is possible to observe the formation of the absorption band at 290 nm, which can be characteristic of chlorine species.

$$2\mathrm{Cl}^{-}_{(\mathrm{aq})} \to \mathrm{Cl}_{2(g)} + 2\mathrm{e}^{-} \tag{16}$$

$$Cl_{2(g)} + H_2O \leftrightarrow HClO_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)}$$
(17)

$$HClO_{(aq)} \leftrightarrow H^{+}_{(aq)} + ClO^{-}_{(aq)}$$
(18)

When the pH values are lower than pKa, the main species is hypochlorous acid, and for pH values higher than pKa, it will be the hypochlorous anion. The reduction potentials (E°) for hypochlorous acid and hypochlorite anion are 1.49 and 0.89 V, respectively, indicating that hypochlorous acid is a stronger oxidant than hypochlorous anion. Fig. 6 shows the pH values of the solution during the experiments. These values were consistently above the pKa value of hypochlorous acid, indicating that the hypochlorite anion was the majority species, which may have led to a low DOC removal. Also, the treatment of the effluent by ozone took place by generating the hydroxyl radical and other radical species.

The results of turbidity removal showed that, among the experimental conditions studied, the association of ozonation with electro-oxidation provided the highest removal percentage (Fig. 7). High turbidity removal was also observed with increasing current density. Mass transfer possibly controls the process at high current densities and favors secondary reactions such as oxygen evolution, as shown in Eq. (19) [61–63]. A higher current density generates more H₂ [Eq. (20)]. The increase in bubble generation (H₂ and O₂) allowed more flotation of suspended solids. The best turbidity removal results were observed under current density conditions of 66.6 and 133.3 A·m⁻²/O₃ reaching 91.77% (final turbidity of 2.98 NTU) and 89.41% (final turbidity of 2.88 NTU) of removal, respectively.

$$\mathrm{MO}_{x+1} \to \mathrm{MO}_{x} + \frac{1}{2}\mathrm{O}_{2(g)}(\text{at anode})$$
(19)



Fig. 6. Behavior of pH values throughout the experiments.

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^- (at cathode)$$
(20)

3.2. Kinetic study

It is necessary to determine the speeds and mechanisms of chemical reactions, as it is a fundamental issue both from a scientific and a practical point of view. In practice, the sizing of reactors for the treatment of effluents will depend on the kinetic constant and the initial concentration of the substance to be removed, as well as the volume (or flow rate) of the effluent.

The kinetic models zero-order, first-order, and second-order were applied for the color (DFZ₄₃₆) and DOC removals [Eqs. (21)–(23)], where *C* and *C*_o are the concentrations at time *t* and the initial concentration (mg·L⁻¹), respectively. The kinetic constants ($k_{0'}$ k_1 , and k_2) and coefficient of determination (R^2) are shown in Table 2. The adjustments of the models were carried out according to the R^2 values.

$$C_t = C_0 - k_0 t (\text{zero-order})$$
(21)

$$\ln C_t = \ln C_0 - k_1 t (\text{first-order})$$
(22)

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \left(\text{second-order} \right)$$
(23)

For the DFZ_{436} removal, the outcomes of the experiments using EO alone evidence a change in the reaction's order

with the current density increase. A zero and a first-order mechanism were obtained for the lowest (33.3 A·m⁻²) and the highest current density value (133.3 A·m⁻²). In contrast, for the intermediate value (66.6 A·m⁻²), the R^2 values for the zero and first-order were very close; thus, it can be considered an intermediate mechanism between these models. The addition of the ozonation process to EO verified that the DFZ₄₃₆ removal processes followed a second-order process, showing a possible mutual mechanism of indirect oxidation through the oxidizing species (chlorine and hydroxyl radical) and ozone on the media. The experiment where only



Fig. 7. Percentage of turbidity removal for the experimental conditions.

Table 2

Kinetics rate constants and determination coefficient for color and DOC removal

Treatment	Parameters	Zero-order First-order		st-order	Second-order		
		$k_0^{\ a}$	R^2	k_{1} (min ⁻¹)	R^2	$k_2^{\ b}$	R^2
33.3 A⋅m ⁻²	DFZ_{436} (m ⁻¹)	0.2824	0.9409	0.0237	0.897	0.0023	0.8123
	DOC (mg·L ⁻¹)	0.0695	0.7998	0.0015	0.8098	3.0×10^{-5}	0.8194
33.3 A·m ⁻² /O ₃	DFZ ₄₃₆ (m ⁻¹)	0.2668	0.5815	0.0425	0.8275	0.0115	0.9813
	DOC (mg·L ⁻¹)	0.1595	0.7921	0.0038	0.7983	9.0 × 10 ⁻⁵	0.804
$66.6 \mathrm{A} \cdot \mathrm{m}^{-2}$	DFZ ₄₃₆ (m ⁻¹)	0.2967	0.971	0.0298	0.9744	0.0036	0.9248
	DOC (mg·L ⁻¹)	0.1886	0.9173	0.0043	0.9249	1.0×10^{-4}	0.9302
$(((h))^{-2})$	DFZ ₄₃₆ (m ⁻¹)	0.2163	0.6148	0.0379	0.8338	0.0102	0.965
66.6 A·m ⁻² /O ₃	DOC (mg·L ⁻¹)	0.2168	0.7634	0.0055	0.8019	0.0001	0.8354
133.3 A·m ⁻²	DFZ ₄₃₆ (m ⁻¹)	0.2341	0.9078	0.0271	0.9845	0.0037	0.9756
	DOC (mg·L ⁻¹)	0.276	0.8822	0.0065	0.9106	0.0002	0.9334
133.3 A·m ⁻² /O ₃	DFZ ₄₃₆ (m ⁻¹)	0.2286	0.6477	0.0614	0.8834	0.0404	0.959
	DOC (mg·L ⁻¹)	0.1451	0.6873	0.0036	0.7196	9.0 × 10 ⁻⁵	0.7519
O ₃	DFZ_{436} (m ⁻¹)	0.1969	0.9145	0.0222	0.9466	0.0028	0.9395
	DOC (mg·L ⁻¹)	0.0847	0.6207	0.0018	0.6201	4.0×10^{-5}	0.6193

Table 3

Electrical energy consumption values

	33.3 A⋅m ⁻²	33.3 A·m ⁻² /O ₃	66.6 A·m ⁻²	66.6 A·m ⁻² /O ₃	133.3 A·m ⁻²	133.3 A·m ⁻² /O ₃	O ₃
EEC (kWh⋅m⁻³)	1.02	18.66	3.53	21.03	7.48	25.18	17.50
EEC (kWh·m)	2.64×10^{-4}	3.71×10^{-3}	8.44×10^{-4}	5.26 × 10 ⁻³	2.17×10^{-3}	6.37×10^{-3}	6.33×10^{-3}

ozone was applied behaved as a first-order process, showing an indirect oxidation behavior. Regarding DOC removal, the experiments using only EO and those adding ozone to the EO followed a second-order model. The ozonation-only experiment followed a first-order DOC mechanism.

3.3. Electrical energy consumption

In addition to the effluent treatment efficiency, electrical energy consumption is an essential parameter due to the costs associated with the treatment plant operation and maintenance. The electrical energy consumption per volume (kWh·m⁻³) and electrical energy consumption per DFZ removed (kWh·m) are presented in Table 3. The values show that the increase in current density and the use of ozone promoted an increase in energy consumption. Saleh et al. [15] obtained 34.90 kWh·m⁻³ in textile effluent treatment using graphite electrodes and 150 A·m⁻².

4. Conclusion

The study enabled the evaluation of the efficiency of the association of EO and ozonation in the post-treatment of the textile effluent. The current density slightly influenced the color removal and the applications using ozone alone had the lowest color removal. However, the association of techniques promoted the best removal of color, DOC, and turbidity, which better results were observed by applying 66.6 A·m⁻² combined with O₃ presented removals of 91.77%, 33.02%, and 91.09%, respectively. The removal of color (DFZ₄₃₆) by EO/ozonation corresponded to the second-order kinetic model and the electrical energy consumption values ranged from 1.02 to 25.18 kWh·m⁻³. Therefore, the application of polishing in textile effluents with the combined techniques of electro-oxidation and ozonation can be an excellent alternative for their remediation.

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