

Synergy of Electrochemical/O₃ Process with Aluminum Electrodes in Industrial Wastewater Treatment

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ABSTRACT: This study aimed to evaluate the effects of pH (3–9) and current density (16–66 mA/cm²) on the removal of COD, color, and turbidity with electrochemical, ozonation, and combined electrochemical/ozonation processes. Regarding the electrochemical process, under optimal conditions of pH 9 and a current density of 66 mA/cm², the chemical oxygen demand (COD) was reduced by 44% after 30 min. The ozonation treatment was found to be more effective at pH 9 and reduced 63% of the original COD after only 12.5 min of treatment. Combining the electrochemical and ozonation processes resulted in a synergy that enhanced the removal of all three contaminants (COD, color, and turbidity). A COD removal of 79% (170 mg/L) was attained after only 12.5 min and at relatively low current density. Thus, the combination of the electrochemical and ozonation processes is able to noticeably improve wastewater quality.

1. INTRODUCTION

Industrial effluents are very difficult to treat satisfactorily because of significant variations in their compositions. Also, industrial wastewaters have high polluting powers as a result of their high organic loadings, pH values, and color intensities. Industrial wastewaters contain compounds such as aromatic amines, azo dyes, fats, and peptic substances, as well as many different macromolecules (mainly lignins, tannins, and humic acid) that are all highly structured compounds and are responsible for the wastewater color.^{1–4} Many processes developed to treat this type of effluent, including physical processes and physicochemical treatments such as coagulation/flocculation, filtration, and membrane adsorption, are used to remove organic compounds.⁵ These methods, however, offer only a partial solution and must be followed by a secondary treatment to comply with legal requirements. It is worth mentioning that they produce large quantities of sludge that cause other environmental problems,⁶ so it is necessary to develop technologies for water and wastewater treatments that destroy or immobilize toxic compounds, where the treatment of contaminants is the most effective and economical. Chemical oxidation treatments using photocatalytic oxidation,⁷ wet oxidation,⁸ or advanced oxidation processes (AOPs) are some alternative technologies.^{9–12} These advanced oxidative processes are based on the generation of hydroxyl radicals (OH), which have a high oxidation potential and can promote the degradation of a wide range of contaminants in minutes. In this context, the oxidation of organic compounds in water can be increased by combining ozone (O₃), hydrogen peroxide (H₂O₂), the semiconductors titanium dioxide (TiO₂) and zinc oxide (ZnO), ultraviolet (UV) light, Fenton's reagent, and/or electrochemical/O₃ processes.^{13–17} These processes can eliminate toxic substances and increase the biodegradability of organic pollutants because they are highly efficient treatments for recalcitrant wastewater and their combination

has a synergistic effect because of the intensified production of very reactive hydroxyl radicals. The hydroxyl radicals attack organic pollutants and initiate a series of oxidation reactions that ultimately lead to the total mineralization of the pollutants.¹⁸

In this work, the efficiency of the combination of electrocoagulation and ozonation processes is evaluated in the treatment of industrial wastewater. Electrocoagulation is a complex and interdependent process, in which the generation of coagulants takes place in situ by the dissolution of a sacrificial anode,¹⁹ such that electrocoagulation removes metallic, colloidal solid and particulate, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and results in their separation from the aqueous phase. This treatment prompts the precipitation of certain metals and salts.^{20–22} On the other hand, ozonation is an efficient and powerful oxidizing process well-known for its potential in the degradation of organic compounds. In wastewater treatment, ozone application is often limited by the cost of in situ ozone production and by high ozone consumption on account of high concentrations of oxidizable compounds.^{23–25} Moreover, the degree and rate of oxidation by ozonation is limited by the chemical structure; that is, amines, linear chain alcohols, and ketones are harder to oxidize with ozone than some aromatic compounds.²⁶ Thus, this study aimed to improve both the ozonation and electrocoagulation processes by combining them. In consequence, the efficiency, in terms of reductions in color, turbidity,

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and chemical oxygen demand (COD), of a treatment system consisting of a combined process of electrocoagulation and ozonation was established. The effects of operating parameters such as time of treatment, current density, and initial pH are also presented.

2. MATERIALS AND METHODS

2.1. Wastewater Samples. Wastewater samples were collected from a treatment plant at an industrial park that receives the discharge of 144 different facilities. Therefore, the chemical composition of this effluent is rather complex. Samples were collected in plastic containers and cooled to 4 °C, after which they were transported to laboratory for analysis and treatment. The quality parameters of the wastewater (raw water) were as follows: COD of 800 mg/L, BOD₅ of 397 mg/L, color of 2270 Pt–Co, turbidity of 110, pH of 7.8 (± 0.2), total solids of 4970 mg/L, and fecal coliforms of 59000 MPN/100 mL.

2.2. Electrocoagulation Reactor. A batch electrochemical reactor was set up for the electrochemical process. The reactor contained an array of four parallel monopolar aluminum electrodes. Two of them were anodes, and the other two were cathodes. The total area surface (A_a) of the electrodes was 60 cm². Each electrode was 5.0 cm \times 3.0 cm with a surface area of 15 cm², as shown in Figure 1a. Although the capacity of the reactor vessel was 1.5 L, only 1.0 L was used in all of the trials. A direct-current power source supplied the system with 1, 2, 3, and 4 A, corresponding to current densities of 16, 33, 50, and 66 mA/cm², in accordance with previous work.¹⁷

2.3. Ozonation Reactor. Ozone experiments were conducted in a 1.5-L glass reactor, although only 1.0 L of wastewater was used for the reaction. All experiments were carried out at 18 °C. Ozone was supplied at a flow rate of 60 mL/min by a model LAB212 Pacific Ozone Technology generator, at 10 standard cubic feet per hour of air at standard temperature and pressure and 3 psi pressure. The gas was fed into the reactor through a porous plate situated at the reactor bottom, as shown in Figure 1b. The ozone concentrations at the gas inlet and outlet of the reactor were measured by redirecting the flow to a series of flasks containing 0.1 M potassium iodide.²⁷ The mean concentration of ozone in the gas phase at the reactor inlet was 5 ± 0.5 mg/L and was measured immediately before each run. Ozonation experiments were carried out at pH 3, 5, 7 and 9, and samples were taken at regular intervals to determine COD, color, and turbidity.

2.4. Synergy of Electrocoagulation/O₃ Process. Aluminum electrodes were installed in the ozonation reactor as shown in Figure 1c. Although the capacity of the reactor vessel was 1.5 L, only 1.0 L was used in all of the trials. The reactor cell contains an array of four parallel monopolar aluminum electrodes as mentioned in section 2.2. Experiments were carried out at pH values of 3, 5, 7, and 9 with samples taken at regular intervals to measure COD, color, and turbidity.

2.5. Methods of Analysis. The initial evaluations of the electrochemical, ozonation, and integrated treatments were determined by analysis of the COD (mg/L). This parameter was determined by the open reflux method according to the standard methods of the American Public Health Association (APHA). According to this method, the sample was refluxed with potassium dichromate and sulfuric acid for 2 h. Before color (Pt–Co scale) and turbidity (NTU scale) analyses, samples were centrifuged at 10000 rpm for 15 min to remove all suspended matter. However, once the optimal conditions

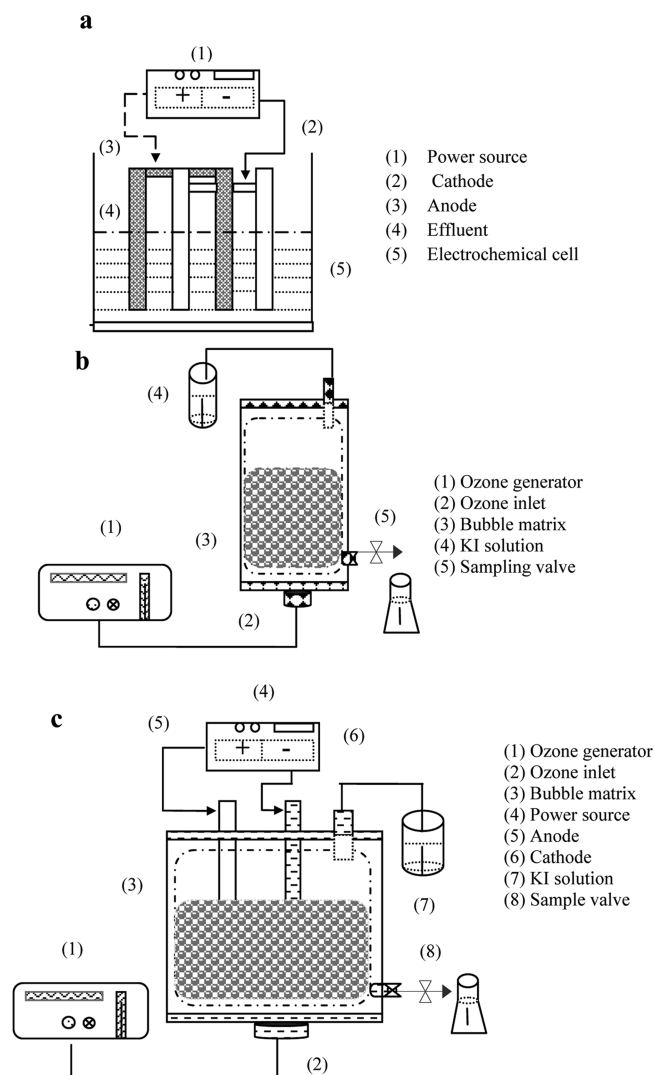


Figure 1. Experimental setup of (a) electrochemical, (b) ozonation, and (c) combined electrochemical/O₃ processes. Reaction volume = 1.0 L.

were found the raw and treated wastewater samples were analyzed using the procedures in *Standard Methods for the Examination of Water and Wastewater*.²⁸

Note that all experiments and measurements were carried out in duplicate and that the plotted values are the average of the obtained results. This allowed an error calculation of 2%.

3. RESULTS AND DISCUSSION

3.1. Electrocoagulation Treatment. **3.1.1. Effects of pH.** pH has a considerable effect on the efficiency of an electrocoagulation treatment. In this study, pH was varied between 3 and 9 (3, 5, 7, and 9). The COD (mg/L) changed as a function of treatment time at different initial pH values, as shown in Figure 2a. The maximum COD reduction was observed after 30 min of treatment at a pH of 9. Under these conditions, the removal was 44% (446 mg/L). Then, at a pH of 7, the maximum removal was 43%, whereas at pH values of 5 and 3, the removals were 39% and 41%, respectively. The low COD removal efficiency of the electrocoagulation process is largely due to the change in pH with time. Indeed, the results showed that, depending on the activities of the anode and cathode, the pH gradually increased because of the dominant

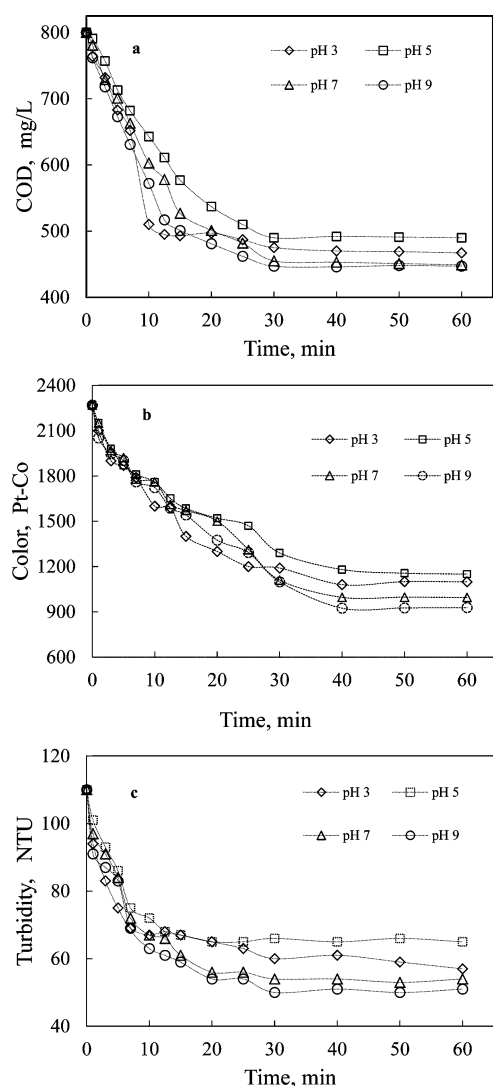
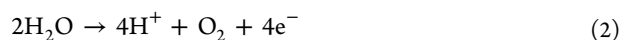


Figure 2. Electrochemical treatment. Effects of time and pH on (a) COD, (b) color, and (c) turbidity. Current density = 66 mA/cm².

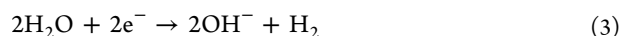
activity of the cathode. Thus, the increase in pH is a consequence of the cathodic reaction (eq 3). This trend has also been observed by other research groups.^{29,30} In the case of color removal, shown in Figure 2b, the maximum color reduction was observed after 40 min of treatment at pH 9 (59%), followed by 56% (996 Pt–Co) at pH 7, 48% (1180 Pt–Co) at pH 5, and 52% (1080 Pt–Co) at pH 3. Figure 2c shows the correlation between turbidity, pH, and time. The maximum turbidity reduction (54%) was observed after 30 min of treatment at pH 9 and was followed by 51% (54 NTU) at pH 7, 40% (65 NTU) at pH 5, and 45% (61 NTU) at pH 3. In Figure 2a–c, it can be observed that the percentage COD, color, and turbidity removals increased as the pH increased 7, as a result of sweep-floc electrocoagulation, in which colloidal particles are swept out of suspension by becoming enmeshed in the aluminum hydroxide precipitate. The single most determining factor in the electrocoagulation process is undoubtedly the pH, because pH affects all of the hydrolysis equilibria resulting from the addition of the metal cation. At low pH and low aluminum dose, the predominant mechanism is charge adsorption–neutralization, and at high pH and high aluminum dose, it is sweep-floc electrocoagulation.³¹ This

behavior can be attributed to the capability of aluminum to form different species depending on solution pH and the presence of other chemical species. That is, upon hydrolysis, Al³⁺ ions can generate the aqueous complex Al(H₂O)₆³⁺, which is predominant at pH < 4. Between pH 5 and 6, the predominant hydrolysis products are Al(OH)₂²⁺ and Al(OH)₂⁺; between pH 5.2 and 8.8, the solid Al(OH)₃ is most prevalent; above pH 9, the soluble species Al(OH)₄[−] is predominant; and above pH 10, Al(OH)₄[−] is the only species present.³² Therefore, the electrolytic dissolution of the aluminum anode produces cationic monomeric species such as Al³⁺ and Al(OH)₂⁺ at low pH that, at basic pH values, are initially transformed into Al(OH)₃ and finally polymerized to Al_n(OH)_{3n} according to eqs 1 and 5.

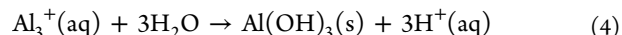
The processes occurring at the anode are



and those occurring at the cathode (in alkaline solutions) are



The metal ions generated in eq 1 are hydrolyzed in the electrochemical cell to produce metal hydroxide ions, and the solubility of the formed metal hydroxide complexes depends on pH and ionic strength of the solution. For instance



According to the literature,³³ during electrocoagulation treatments, the species can interact in solution in several stages: (a) electrophoresis and aggregation due to charge neutralization, (b) formation of a precipitate between the cation or hydroxyl ion (OH[−]) and the pollutant, (c) formation of a hydroxide when the aluminum cation interacts with OH[−], (d) formation of larger lattice-like structures from the hydroxides that are swept through the water (coagulation), and (e) removal by electroflotation and adhesion to bubbles.



However, depending on the pH of the aqueous medium, other ionic species such as Al(OH)₂²⁺, Al₂(OH)₂⁴⁺, and Al(OH)₄[−] might also be present in the system.²⁰

3.1.2. Current Density. An experimental study was performed to determine the effect of changing the current density on the COD removal efficiency at pH 7. The results after 40 min of treatment are shown in Figure 3a. The treatment efficiency seems to have increased slightly with increasing current density. Specifically, when the current density was changed from 16 to 66 mA/cm², the efficiency of COD removal also increased from 35% (518 mg/L) to 43% (453 mg/L). In Figure 3b, the reduction of color and turbidity with increasing current density at pH 7 after 40 min of treatment are presented. The color removal percentage is not highly correlated with the current density because it varied only from 54% (1032 Pt–Co) to 57% (996 Pt–Co). On the contrary, the turbidity removal percentage increased from 40% (65 NTU) at 16 mA/cm² up to 48% (57 NTU) at 55 mA/cm² and 51% (54 NTU) at 66 mA/cm².

The increase in COD removal with current density can be explained in terms of an increase in flocs in solution. Similar results have been reported for the treatment of paper mill wastewater using electrochemical methods with aluminum electrodes in which the treatment efficiency remained

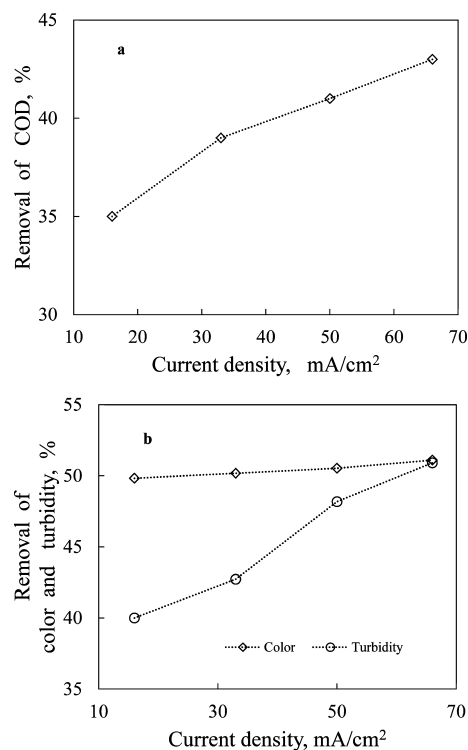


Figure 3. Electrochemical treatment at pH 7. Effects of current density (16, 33, 50, and 66 mA/cm²) on removal of (a) COD, (b) color and turbidity.

approximately constant with current density up to 70 mA/cm².^{34,35}

The amount of aluminum released into solution by electrolytic oxidation of the anode material as a function of current density and time and can be calculated using the following form of Faraday's law:³⁴

$$w = itM/(zF) \quad (6)$$

where w is the mass of dissolved metal (g), i is the current (A), t is the contact time (s), M is the molecular weight of Al, z is the number of electrons involved in the redox reaction ($z_{\text{Al}} = 3$), and F is Faraday's constant (96500 C/mol). It is also evident that higher current density implies lower electrode lifetime. This can be ascribed to the fact that, at high current density, the amount of metal oxidation increases. This also results in a greater amount of precipitate for the removal of pollutants.

3.2. Ozonation Treatment. 3.2.1. Effects of pH. The study was carried out with an ozone concentration of 5 ± 0.5 mg/L. The evolution of the COD, color, and turbidity removal efficiency was studied as a function of ozonation time at different initial pH values (3, 5, 7, and 9). Figure 4a shows COD removal as a function of ozone supplied at different pH values. The COD reduction was observed to be 63% (290 mg/L) at pH 9, 59% (328 mg/L) at pH 7, 60% (321 mg/L) at pH 5, and 47% (426 mg/L) at pH 3. This behavior is a consequence of ozone degradation, which occurs by the consumption of hydroxyl ions and the formation of organic and inorganic acids (ozonation by products).^{36,37} According to Tomiyasu et al.,³⁷ ozonation treatment can be initiated by the reactions

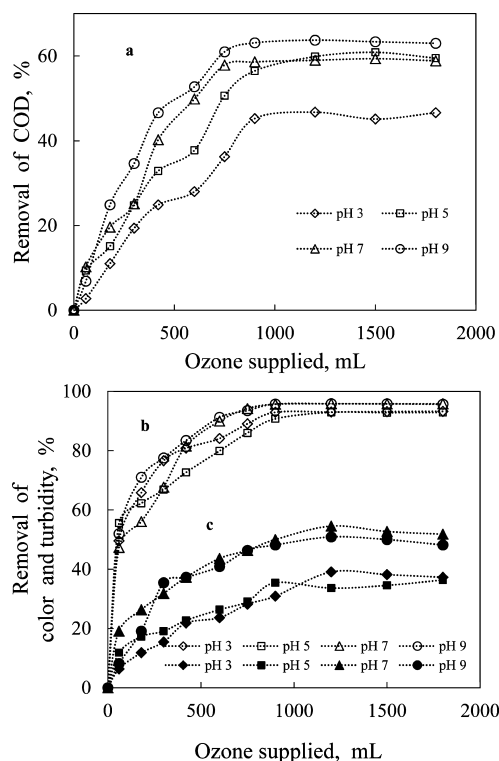
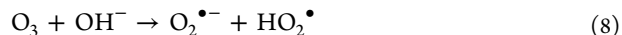


Figure 4. Ozonation treatment. Effects of pH (3, 5, 7, 9) and supplied ozone on the reduction of (a) COD, (b) color, and (c) turbidity.



According to the literature,³⁸ the pH value of the solution significantly influences ozone decomposition in water because basic pH causes an increase in ozone decomposition (eq 8). At $\text{pH} < 3$, hydroxyl radicals do not influence the decomposition of ozone. In the range $7 < \text{pH} < 10$, the typical half-life of ozone is 15–25 min.³⁸

Figure 4b clearly shows that total color removal was achieved under both alkaline and acid conditions. The maximum color reduction was observed after 750 mL of ozone had been supplied (20 min) at pH 9 and 7 (95%, 94 Pt-Co), followed by 92% (160 Pt-Co) and 93% (158 Pt-Co) at pH 5 and 3, respectively. These results confirm that ozonation is a very efficient process for color removal and that, under the reaction conditions employed in this study, color removal did not depend on pH. Regarding turbidity, Figure 4c shows that a maximum reduction was attained also after 750 mL of ozone had been supplied, being 51% at pH 9, 54% (50 NTU) at pH 7, 34% (73 NTU) at pH 5, and 39% (67 NTU) at pH 3. Therefore, it can be concluded that ozonation only partially reduces COD and turbidity but almost completely eliminates color. This can be attributed to the presence in water of several compounds capable of initiating, promoting, or inhibiting the radical chain reaction process. Hydroxyl anions, hydrogen peroxide, perhydroxyl radical, ferrous ion, formate, and humic substances are recognized as initiators and are capable of inducing the formation of superoxide ion $\text{O}_2^{\bullet-}$ from an ozone molecule. The promoters [$\text{R}_2\text{-CH-OH}$, formate, humic substances, ozone] are responsible for the generation of the $\text{O}_2^{\bullet-}$ ion from hydroxyl radicals. The inhibitors [$\text{CH}_3\text{-COO}^-$, alkyl-(R), bicarbonate ion, carbonate ion, humic substances]

are compounds capable of consuming hydroxyl radicals without regenerating the superoxide anion.³⁹ In addition, it should be kept in mind that the treated wastewater is a mixture of effluents of several industries (pharmaceuticals, textiles, food, and chemicals), and therefore, the presence of several compounds and functional groups is expected. Some of these compounds might be responsible for the color of the effluent, and from the results, it can be inferred that such molecules are preferentially oxidized. On the other hand, the COD removal results suggest that such an oxidation is only partial and leads to species that are more stable and cannot be mineralized solely by ozone. Actually, this ozone limitation has been observed and reported for amines, halogenated aromatics, and melanoidins.²⁵

3.3. Synergy of Electrocoagulation/O₃ Process.

3.3.1. Effects of pH. The effects of pH (3, 5, 7, and 9) on the COD, color, and turbidity removal efficiencies were studied through a series of experiments using the coupling of two treatment systems, namely, electrocoagulation and ozonation. The COD change as a function of treatment time for the aforementioned pH values is shown in Figure 5a. The COD maximum removal occurred after a reaction time of 12.5 min at pH 7. Under these conditions, a COD reduction of 79% was achieved. After the same reaction time but at a pH of 3, a 78% COD reduction was observed, and the corresponding values for pH 9 and 5 were 76% and 69%, respectively. Although the difference in COD removals at pH 3 and 7 is not significant, it is worth mentioning that neutral pH offers the advantage of eliminating the use of additional chemicals to reach an acidic pH, thereby reducing costs and environmental and operational risks. It is also noticeable that the combined electrocoagulation/ozonation process enhanced both the degradation rate and the maximum COD removal when compared to the electrocoagulation and ozonation processes alone. This could be due to a combination of the electrochemical (eqs 1–5) and ozonation (eq 7–9) mechanisms. At acidic pH, the pollutant removal occurs through complexation with flocs (electrochemically produced) and direct and indirect ozonation, where the last, unlike ozonation alone, is catalyzed at acidic pH. In such a process, the decomposition of ozone (eq 8) can be catalyzed by the hydroxide species produced through the electrocoagulation process. The catalysis of ozonation by such species has been previously reported;^{38,40} however, the novelty in this study is that such catalytic species were produced in situ. At basic pH, the formation of different aluminum hydroxide species, mainly $\text{Al}(\text{OH})_3$, is expected.² Rather than catalyzing ozonation, these species would favor pollutant removal through adsorption followed by coagulation. At the same time, however, pollutant removal by ozonation is higher at basic pH than at acidic pH because eq 9 might no longer be limited by the OH^- anion concentration, thus increasing the presence of $\cdot\text{OH}$ radicals. Therefore, under both acidic and basic pH conditions, the higher COD removal attained with the combined electrochemical/ozonation can mainly be ascribed to the enhancement of eq 9 either by catalysis (acid pH) or by stoichiometry (basic pH). In the case of color removal shown in Figure 5b, it can be concluded that pH does not have a significant influence because the maximum color reduction after 12.5 min of treatment was practically the same at all investigated pH values (~97%). In contrast, turbidity was significantly affected by pH (see Figure 5c). The maximum turbidity reduction was achieved at pH 3 (77%), followed by 72% (30 NTU) at pH 7, 63% (65 NTU) at pH 9, and 56% (48 NTU) at pH 5. These results show that the efficiency of the ozonation process strongly depends on the pH

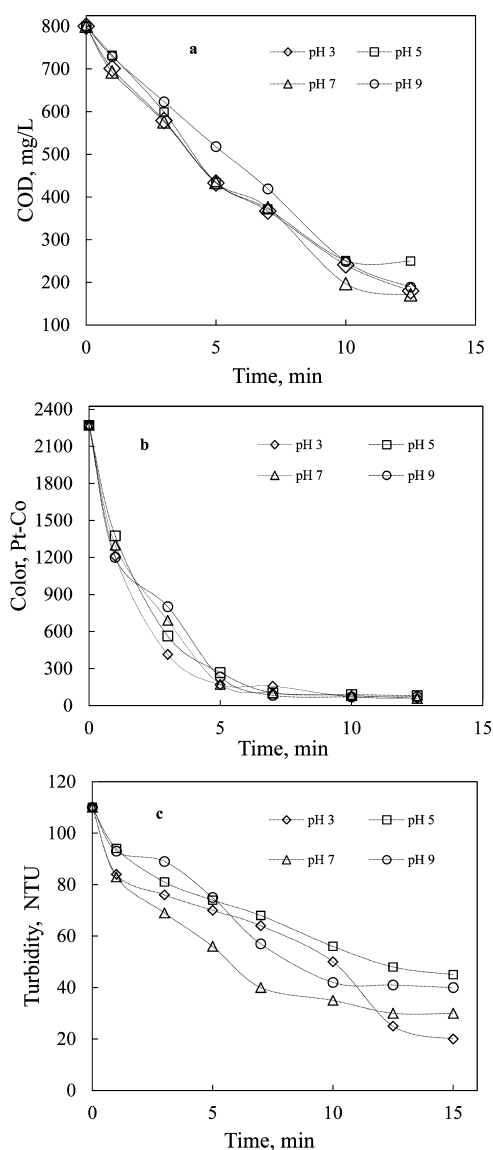


Figure 5. Combined electrochemical/O₃ process. Effects of pH and time on the reduction of (a) COD, (b) color, and (c) turbidity. Current density = 66 mA/cm².

of the solution, which influences the presence of active sites and the occurrence of ozone decomposition reactions in aqueous solutions.

Figure 6 shows a comparison of the effects of pH on the COD removal percentage achieved by the three different treatments, namely, electrocoagulation, ozonation, and combined electrocoagulation/O₃, after 12.5 min of reaction at a current density of 66 mA/cm². These conditions were chosen because they were the ones for which the maximum removal of COD was achieved with the combined electrocoagulation/O₃ process. For the electrochemical treatment, it can be observed that the percentage removal of COD increased from pH 5 to 9, because of the interaction between Al^{3+} and OH^- forming aluminum hydroxides and thus producing monomeric and polymeric species capable of adsorbing contaminants present in the wastewater (eqs 4 and 5). Likewise, a high $\cdot\text{OH}$ concentration also favors the ozonation process through the enhancement of eq 8. For the electrocoagulation/O₃ process, it can be seen that the pH value plays an important and

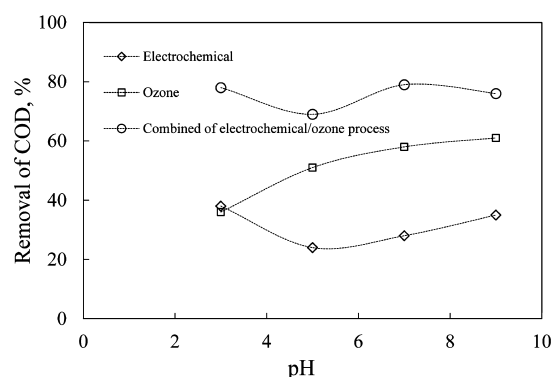


Figure 6. Effects of pH on the COD percentage removal by the three different treatments (electrochemical, ozone, and combined electrochemical/ O_3 processes) at 12.5 min.

interesting role, as already discussed herein. It is worth noticing that, for the integrated process, neutral pH was also found to lead to the highest removal efficiency, and because the effluent pH is 7, this increases the sustainability of the combined electrocoagulation/ O_3 process.

3.3.2. Current Density. The treatment efficiency seemed to increase slightly with increasing current density; see Table 1. The COD as a function of time for current densities of 16, 33, 50, and 66 mA/cm² at pH 7 is shown in Figure 7a. The COD removals were 68% (258 mg/L), 75% (200 mg/L), 78% (180 mg/L), and 79% (171 mg/L) at current densities of 16, 33, 50, and 66 mA/cm², respectively, after 12.5 min of reaction time. Figure 7b shows that the color removal for 66 mA/cm² was 97% (58 Pt–Co), and that for 16, 33, and 50 mA/cm² was 96% (82 Pt–Co). At 16 mA/cm², the turbidity removal was 54% (51 NTU); at 33 mA/cm², it was 60% (44 NTU); at 33 mA/cm², it was 63% (40 NTU); and at 60 mA/cm², it was 72% (30 NTU). These percentages were calculated from the turbidity data shown in Figure 7c. It is also worth mentioning that this process (electrocoagulation/ O_3) produced lower amount of sludge than the electrochemical treatment alone. Table 2 summarizes the characteristics of the treated wastewater after electrocoagulation, ozone, and combined electrocoagulation/ O_3 process treatment. The initial characteristics of the wastewater are described in section 2.1.

It is worth mentioning that the amount of total solids was significantly lower at the end of the combined process than at the end of the electrochemical process alone. This parameter consists of organic material in the solid state and generated sludge. Therefore, it can be concluded that another advantage of the combined process is its low sludge generation.

4. CONCLUSIONS

The combination of electrocoagulation and ozonation processes results in a synergy that greatly enhances the extents and rates of removal of COD, color, and turbidity from a

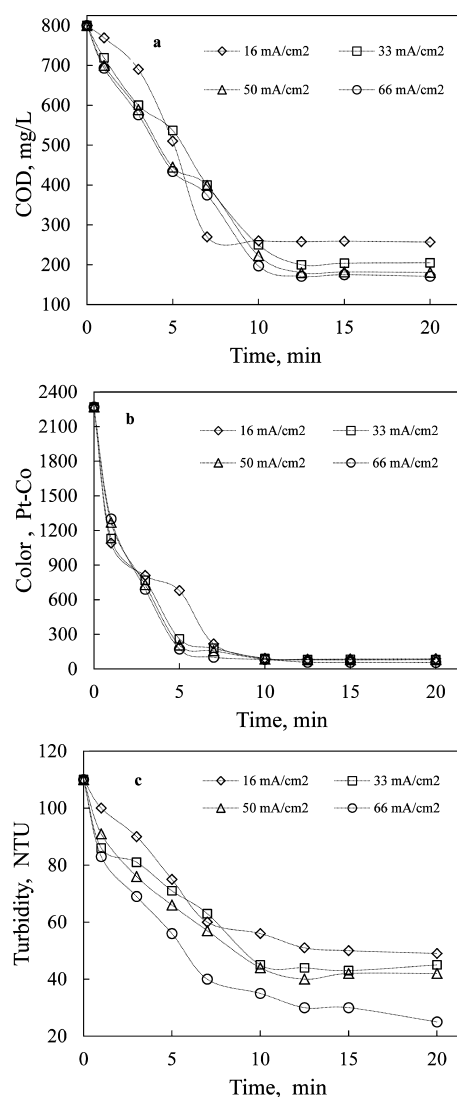


Figure 7. Effects of current density (16, 33, 50, and 66 mA/cm²) and treatment time on the reduction of (a) COD, (b) color, and (c) turbidity during the combined electrochemical/ O_3 process at pH 7.

chemically complex industrial effluent. A maximum of 79% COD removal was achieved by the combined process at pH 7 and 50 mA/cm². Ozonation alone is effective for reducing color, but it is not as effective at completely oxidizing persistent organic compounds and thus reducing COD in industrial effluents. Additionally, by combining ozonation and electrochemical processes, the optimum pH is reduced from 9 to 7, bringing it closer to that of the original wastewater. Whereas electrocoagulation efficiency usually increases with increasing current density, the coupled process is more efficient at a relatively low (50 mA/cm²) current density.

Table 1. Effects of Current Density on the Removal of COD as a Consequence of the Combined Electrochemical/ O_3 Process

current density (mA/cm ²)	pH 3		pH 5		pH 7		pH 9	
	COD (mg/L)	removal (%)	COD (mg/L)	removal (%)	COD (mg/L)	removal (%)	COD (mg/L)	removal (%)
16	256	68	275	66	258	68	234	71
33	250	69	260	68	200	75	218	73
50	235	71	255	68	180	78	208	74
66	180	78	250	69	171	79	189	76

Table 2. Physicochemical and Microbiological Parameters of Electrochemical (at 40 min), Ozonation (at 20 min), and Combined Electrochemical/O₃ (at 12.5 min) Treatments

parameter	electrochemical	ozone	combined electrochemical/O ₃ process
COD (mg/L)	453	290	171
BOD ₅ (mg/L)	219	149	81
color (Pt–Co)	996	94	58
turbidity (NTU)	54	54	30
pH	7 (±0.2)	9 (±0.2)	7 (±0.2)
total solids (mg/L)	1005	765	39
fecal coliforms (MPN/100 mL)	>3	>1	>1

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Notes

The authors declare no competing financial interest.

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