



A combined electrocoagulation–electrooxidation treatment for industrial wastewater

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ABSTRACT

This study addresses the elimination of persistent organic compounds in industrial wastewater using a synergistic combination of electrocoagulation and electrooxidation. Electrocoagulation is a relatively quick process (30 min), which is very effective in removing colloidal and suspended particles, as seen in changes in coliforms, turbidity, and color and in the general absorbance by UV–vis spectroscopy. However, it is relatively ineffective in eliminating stable persistent organic compounds—in this work, only half of the COD was eliminated from wastewater and an oxidation peak in the cyclic voltammetry scan remained. Electrooxidation is very effective in breaking down organic compounds through oxidation as reflected in the elimination of COD, BOD₅, and oxidative peak in cyclic voltammetry, but requires so much time (21 h) that it has very limited practicality, especially when colloidal and suspended particles are present. Electrooxidative mineralization of electrocoagulated wastewater, in which most of the colloids and charged species have been removed, takes less than 2 h. In the coupled technique, electrocoagulation quickly coagulates and removes the colloidal and suspended particles, as well as many charged species, then electrooxidation oxidizes the remaining organics. The coupled process eliminates COD, BOD₅, color, turbidity, and coliforms in a practical amount of time (2 h).

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1. Introduction

Industrial effluents contain a wide variety of pollutants, including biorefractory organic compounds which resist conventional treatment techniques. In addition to their potential toxicity, biorefractive compounds can cause taste and odor problems in water. They are not completely removed by biological treatment, so additional physical and/or chemical treatments are necessary to improve the water quality and enhance the biodegradability of the wastewater [1–4].

Electrocoagulation (EC) involves the generation of coagulants *in situ* by electrically dissolving either aluminum or iron ions from the respective metal electrodes. The metal ion generation takes place at the anode, while hydrogen gas is produced at the cathode. The metal ions form flocculates which trap contaminants while the hydrogen gas floats these particles. This process is sometimes

called electroflocculation [5–7]. EC has been applied successfully to remove phenolic compounds [8], decolorize reactive dye solutions [9,10], clarify suspended clay solutions [11], treat textile wastewater [12] and remove heavy metals [13–15]. The advantages of EC include high particulate removal efficiency, compact treatment facility, and relatively low cost of complete automation [16,17].

Recently, there has been great interest in the development of practical electrochemical methods for the destruction of biorefractory organic compounds present in industrial wastewater. Electrooxidation (EO) of these pollutants can be fulfilled through different ways. For example, indirect electrooxidation process use chlorine and hypochlorite generated anodically to destroy organic pollutants. Contaminants can also be degraded by electrochemically generated hydrogen peroxide. Direct anodic oxidation of pollutants can also occur directly on anodes by generating physically adsorbed “active oxygen” (oxygen in the oxide lattice, MO_{x+1}) through a process called anodic or direct oxidation. Anodic oxidation does not require added chemicals or oxygen and does not produce secondary pollutants or require complicated accessories. The most important component in the anodic oxidation process is the anode. The most common anode materials for EO are glassy

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carbon, Ti/RuO₂, Ti/Pt-Ir, carbon fiber and stainless steel. However, none of these materials have the combination of both activity and stability necessary for effectiveness and durability to be practical. Recently, boron-doped conductive diamond anodes have been used in EO and appear to be one of the most promising technologies in the treatment of organics in industrial wastes [18]. Compared with other electrode materials, conductive diamond has shown a higher stability, efficiency and overpotential for both oxygen and hydrogen evolution [19,20]. These properties have led to the application of diamond electrodes in electrosynthesis [21], oxidation of organic pollutants [22,23], degradation of surfactant [24], decolorization of solutions [25–28], oxidation of benzoic and carboxylic acids [29,30], breakdown of phenolic aqueous wastes [31], treatment of olive-oil mills wastewater [32] and degradation of triazines [33]. It is important to point out that this method achieves the complete mineralization of organics contained in wastewater.

In this study, we present the results of the application of EC and EO over industrial wastewater. The main goal of this study is to compare the effectiveness of each electrochemical method in the pollutant removal from wastewater. Once the optimal conditions of each method have been identified we combine them to reach synergistic effects and to obtain the best conditions for complete pollutant removal.

2. Experimental

2.1. Wastewater samples

Samples of wastewater were collected from a treatment plant located at the end of an industrial park. This facility receives the industrial discharge of 144 different factories, specifically 39 chemical, 34 metal finishing, 22 textile, and 11 food processing factories, along with various pharmaceutical, automotive, leather, and other facilities. All of the industrial effluents enter the wastewater treatment plant together. The actual wastewater treatment plant consists of shredders, sand separators, oil and grease separators, primary clarifiers, biological activated sludge reactors, secondary clarifiers and a chlorine disinfecting unit. The COD and BOD₅ values of the mixed influent are high, as shown in Table 1, but are reduced by 60% through the current treatment. However, this reduction still does not comply with environmental discharge standards. Thus, additional techniques are needed to improve the quality of the water. The industrial wastewater samples were collected at the inlet of the biological activated sludge reactor in plastic containers

Table 1
Physicochemical characteristics of industrial wastewater.

Parameter	Inlet value	Outlet value
Color/(Pt-Co)	2500–3700	1500–2500
Turbidity/(NTU)	1400	900
COD/(mg L ⁻¹)	1700–2500	800–1200
BOD ₅ /(mg L ⁻¹)	930	350–450
Total coliforms/(MPN mL ⁻¹)	1.1 × 10 ⁵	5.5 × 10 ⁴
Total solids/(mg L ⁻¹)	5500	4820
Conductivity/(mS cm ⁻¹)	7.0	6.0

and cooled to 4 °C, then transported to the laboratory for analysis and electrochemical treatments.

2.2. Electrocoagulation reactor

As shown in Fig. 1, a batch monopolar electrochemical reactor was constructed with iron electrodes for the electrocoagulation step. Each electrode was 0.05 m long and 0.05 m wide for an area of 0.0025 m² each and a total combined area, A_a of 0.0050 m². Each 0.05 L batch of wastewater was treated in a bucket which served as the supply vessel for the reactor. A dc power source supplied the system with different current density values (200–800 A m⁻²). The electrolysis was carried out without additional electrolyte. After various elapsed times, samples were taken and filtered for analysis.

2.3. Electrooxidation process

The EO was carried out in batch mode using a boron-doped diamond (BDD) anode and an iron cathode. Both electrodes were rectangular plates with an area of 0.0050 cm² each. The anode consisted of a BDD film synthesized by hot filament chemical vapor deposition on a single-crystal p-type Si (1 0 0) wafer, provided by CSEM (Switzerland). The wastewater was stored in a glass tank (0.05 L), a dc power source supplied the system with 1–4 A at 3 V, corresponding to a current density of 200–800 A m⁻² applied at a range of pH values between 2 and 12; however the pH of the sample was not controlled during the treatment. The electrolysis was carried out without additional electrolyte.

2.4. Methods of analysis

The evaluation of the treatments was determined by analysis of the chemical oxygen demand (COD), biochemical oxygen demand

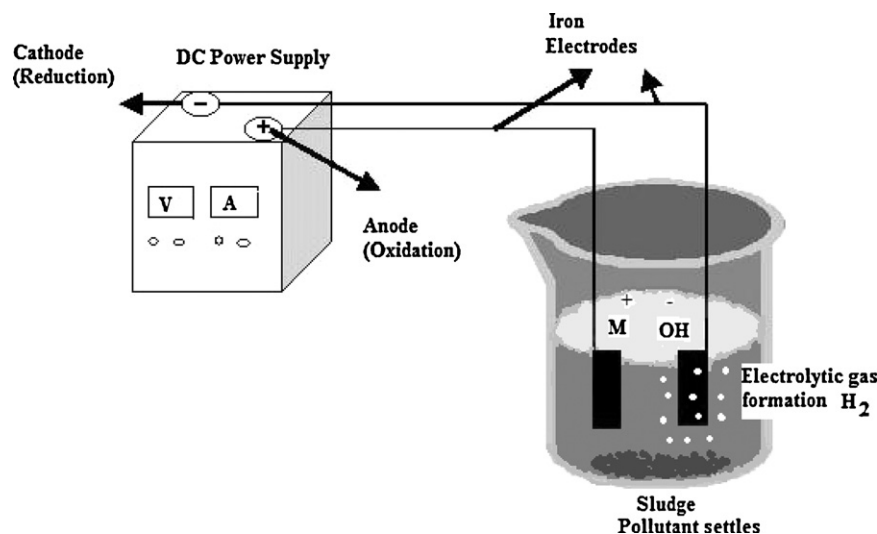


Fig. 1. A schematic diagram of the electrochemical reactor.

(BOD₅), color (Pt/Co scale), turbidity, and pH, as indicated in the Standard Methods procedures [34].

2.4.1. Thermodynamic analysis

The existence of iron complexes in aqueous solution has been reported [35,36]. Using this information the distribution diagrams of chemical species were calculated using the MEDUSA program [37].

2.5. Cyclic voltammetric measurements

Cyclic voltammetry of crude and treated wastewater was performed using a standard three-electrode cell. The waveforms were generated by a potentiostat model Epsilon BAS. The carbon paste electrodes (CPE) were circular and prepared from a 1:1 mixture of 99.99% pure single-crystal graphite (Alfa AESAR) and nujol oil (Fluka). The paste was transferred into a PVC tube and compacted to eliminate trapped air then a copper conductor was inserted before the paste set. The surface of the electrode was renovated after each potential scan. The scan rate was 100 mV s⁻¹ with an Ag/AgCl reference electrode and a platinum wire counter electrode [38].

2.6. UV-vis spectrometry

UV-vis spectra were obtained from samples of raw and treated wastewater using a double beam PerkinElmer 25 spectrophotometer. The scan rate was 960 nm s⁻¹ within 200–900 nm wavelength range. The samples were scanned in quartz cells with a 1 cm optical path.

2.7. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

After the experiments, the sludge samples were characterized by SEM. The samples mounted directly onto metal studs were analyzed in a JEOL JSM-5900 LV microscope to obtain information regarding the surface morphology. The secondary electron images of the material depict approximate sizes in the range of a few microns. A DX-4 analyzer was coupled to the microscope to perform the energy dispersive X-ray spectroscopy, which offers *in situ* elemental analysis.

3. Results and discussion

The wastewater treatment plant from which the samples were taken uses a traditional biological process. However, as shown in Table 1, a large part (about 50%) of the organic load persists. Much of this is likely due to complex persistent organic compounds produced in the industrial processes.

To address the problem of the high organic load and persistent organic compounds, electrocoagulation and electrooxidation were evaluated both separately and in a coupled process on the raw wastewater collected from the outlet of the biological system of the treatment plant.

3.1. Electrocoagulation

To optimize the electrocoagulation operating conditions, the COD was measured as a function of treatment time for different values of pH and current density. As shown in Fig. 2, the COD reduction increases with increasing pH from 2 to 8, but decreases for higher values. These results agree with previous research where COD removal dropped dramatically at pH values larger than 10 [38].

The effect of the variation in the current density is shown in Fig. 3. The COD reduction improves with increasing current density. However, the degree of improvement diminishes at higher current

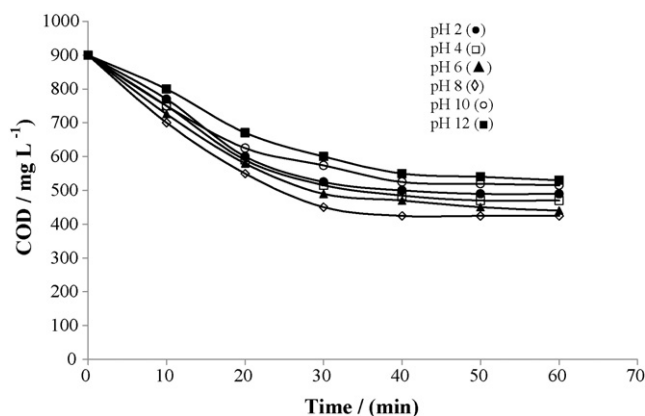


Fig. 2. Electrocoagulation process shows COD reduction as a function of treatment time, at different values of pH. Current density was 800 A m⁻².

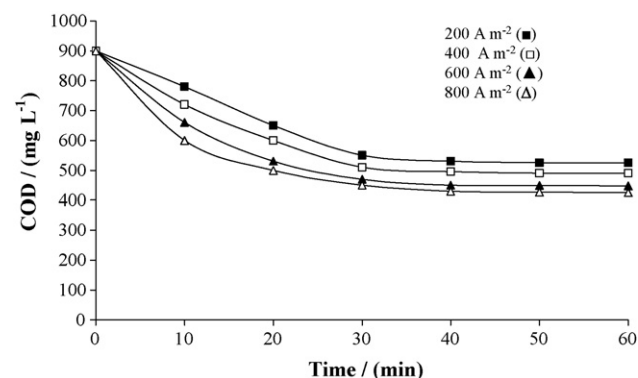


Fig. 3. Electrocoagulation process shows COD reduction as a function of treatment time, at various current densities. The pH of the water sample was adjusted to 8.

densities, i.e. the difference between 600 and 800 A m⁻² is much smaller than that between 200 and 400 A m⁻².

The reduction of the COD as a function of treatment time under optimum conditions of pH 8 and current density 800 A m⁻² is shown in Fig. 4. There is a rapid drop in the COD for the first 30 min of treatment then a limiting value is reached with no further improvement.

3.2. Electrooxidation

The reduction in COD as a function of time of a wastewater sample (at the outlet of the biological system) subjected to

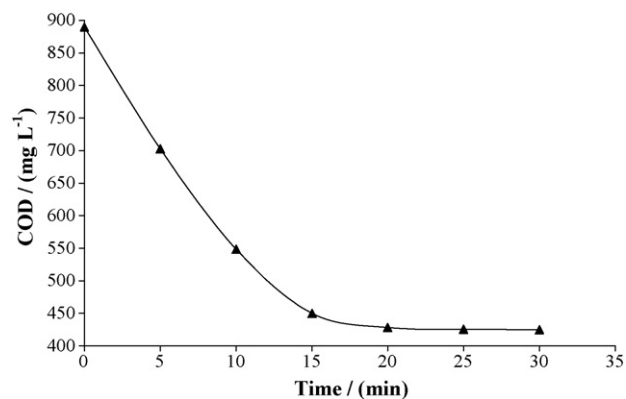


Fig. 4. COD reduction when electrocoagulation is applied at pH of 8 and a current density of 800 A m⁻².

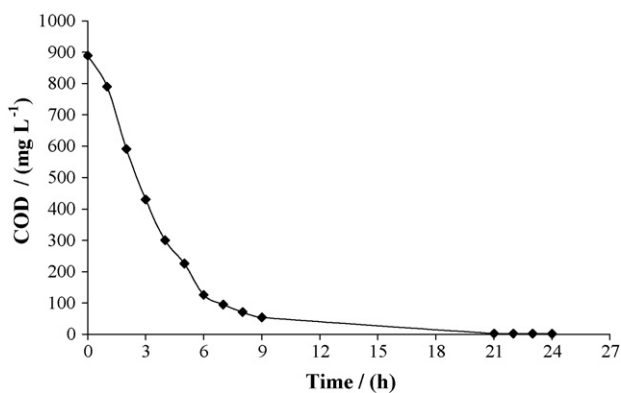


Fig. 5. Direct electrooxidation into wastewater at pH 7.2. The current density used was 800 A m^{-2} .

electrooxidation without any adjustments to the pH is shown in Fig. 5. The sample is completely mineralized after 21 h of treatment, although the rate is much slower than electrocoagulation. The time to reduce the COD to about half ($900\text{--}425 \text{ mg L}^{-1}$) with electrooxidation takes about 3 h, while electrocoagulation (Fig. 4) takes less than 30 min. Since electrocoagulation is a fast but incomplete process and electrooxidation is a complete but slow process, coupling the two processes offers a practical hybrid.

Since electrooxidation alone is not practical due to the time required, we focused optimization efforts on the coupled technique, i.e. the starting material for electrooxidation was electrocoagulated wastewater ($\text{COD} = 425 \text{ mg L}^{-1}$ and $\text{pH} 8$). The COD as a function of electrooxidation treatment time at various pH values is shown in Fig. 6. The fastest rate for complete mineralization by electrooxidation occurred at pH 8, which is fortuitous since that is also the optimum pH for electrocoagulation.

To evaluate the effect of current density, the COD as a function of treatment time for various current densities is shown in Fig. 7. Higher current densities result in a faster rate of COD reduction. However, the difference is smaller for higher current densities, i.e. the difference between 600 and 800 A m^{-2} is much smaller than between 200 and 400.

3.3. Kinetics

To determine whether the reaction was first or second order, $-\log(C/C_0)$ and $1/C$ versus t were plotted based on the data shown in Figs. 4 and 8. Since the plot of $-\log(C/C_0)$ versus t was linear; the

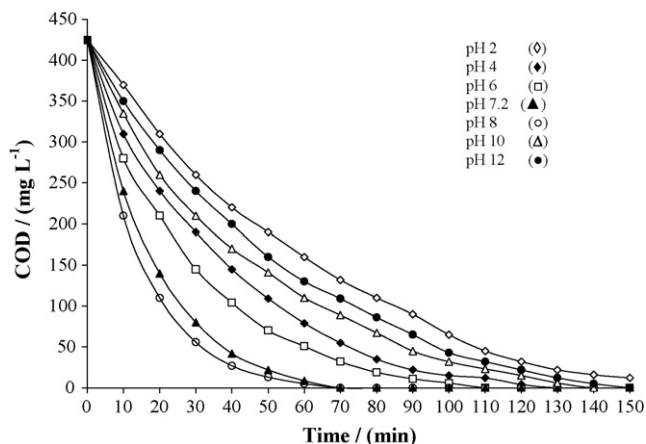


Fig. 6. COD reduction as a function of treatment time at different values of pH in electrooxidation process using pre-treated water. The current density used was 800 A m^{-2} .

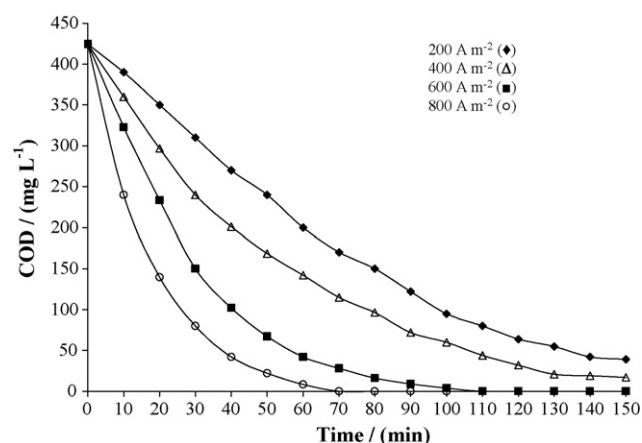


Fig. 7. COD reduction as a function of treatment time at various current densities in electrooxidation process.

reaction was determined to be first order. The first order kinetic model is given in Eq. (1):

$$\frac{dC_{\text{COD}}}{dt} = -k[C_{\text{COD}}] \quad (1)$$

where C_{COD} indicates the concentration of COD (mg L^{-1}), t indicates electrolysis time (h) and k is the velocity constant (h^{-1}). In the case of electrocoagulation k is 2.71 h^{-1} and for electrooxidation k is 4.35 h^{-1} .

3.4. Combined electrocoagulation–electrooxidation

Once the optimal conditions for the electrocoagulation and electrooxidation processes were determined, the coupled treatment was applied and the COD reduction as a function of treatment time was monitored, as shown in Fig. 9. The total time required to achieve the complete elimination of COD was 90 min, which is less than 10% of the time required using electrooxidation alone. Table 2 summarizes the results of the treatments. Note that in addition to reducing COD, it also greatly reduced the BOD_5 , color, turbidity and total coliforms.

3.5. Electrochemical mechanisms

Electrocoagulation of wastewater using iron electrodes takes place according to the following reactions [39]:

Anodic reaction:

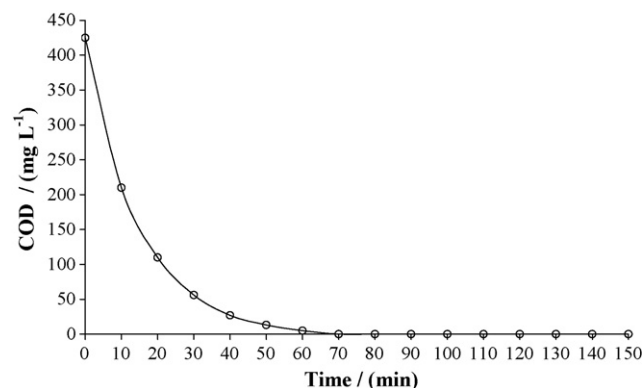
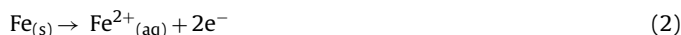


Fig. 8. COD reduction as a function of treatment time at pH 8 and a current density of 800 A m^{-2} using pre-treated water.

Table 2
Physicochemical characteristics of treated wastewater.

Wastewater	Color/(Pt-Co)	Turbidity/(NTU)	COD/(mg L ⁻¹)	BOD ₅ /(mg L ⁻¹)	Total coliforms/(MPN mL ⁻¹)
Raw	2160	926	890	373	5.5 × 10 ⁴
Electrocoagulation	310	150	425	200	<1
Electrocoagulation–electrooxidation	0	0	<1	<1	<1
%Reduction efficiency	100	100	>99	>99	>99

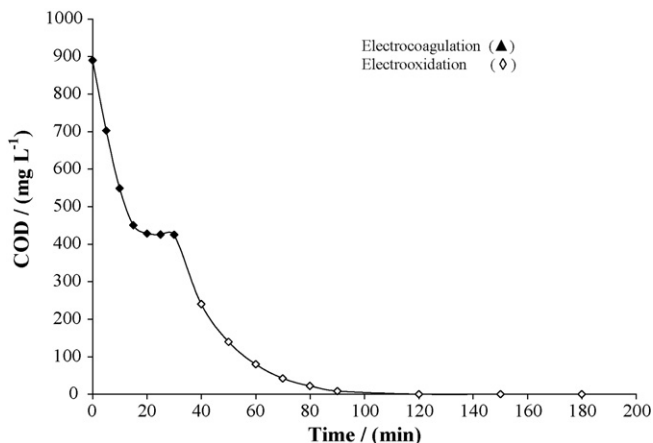
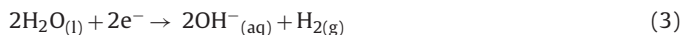
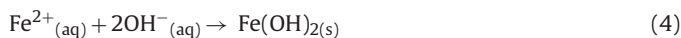


Fig. 9. Combined treatment: electrocoagulation and electrooxidation processes. The current density used was 800 A m⁻² and the pH of the water sample was 8.

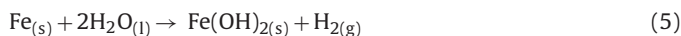
Cathodic reaction:



Solution reaction:



Overall reaction:



Once the iron has been dissolved it acts as a coagulant. Iron ions hydrolyze and mononuclear complexes are formed (as shown in Fig. 10). The presence of iron ions and iron complexes destabilize the colloidal particles, breaking the emulsion. This process leads to flocculation, which generates bigger particles. The flocs settle and form a sludge at the bottom of the reactor.

Earlier reports indicate that wastewaters containing several carboxylic acids (formic, oxalic and maleic) were oxidized using BDD electrodes. In all cases, the only product generated was carbon dioxide with no other intermediates detected by HPLC [40,41].

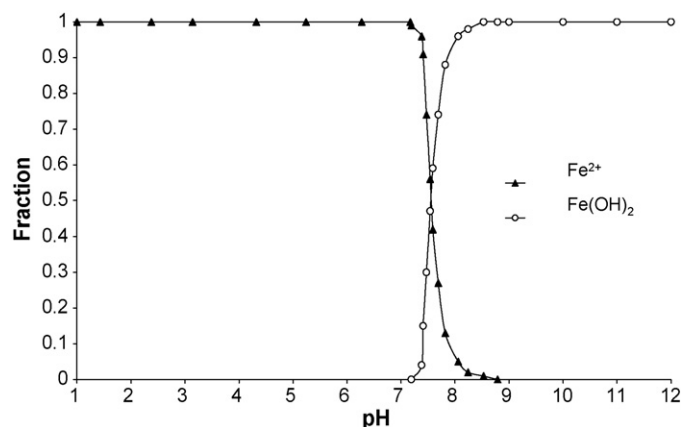
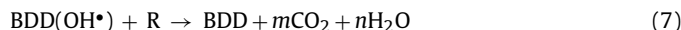
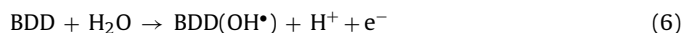
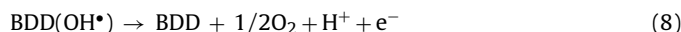


Fig. 10. Iron (II) species distribution diagram in wastewater as a function of pH. The concentration of iron is $[\text{Fe}^{2+}]_{\text{TOT}} = 74 \text{ mM}$.

Previous research [19] indicates that the oxidation of organics with concomitant oxygen evolution assumes that both organic oxidation and oxygen evolution take place on a BDD anode surface via intermediation of hydroxyl radicals, generated from the reaction with water shown in Eqs. (6) and (7):



Reaction (7) is in competition with the side reaction of hydroxyl radical conversion to O₂ without any participation of the anode surface as indicated in Eq. (8):



Two mechanisms are involved in the removal of total coliforms. The first one is related to reaction (5) in which green colloids of Fe(OH)_{2(s)} form, indicating some adsorption of organic matter and coliforms to the colloidal particles. The other mechanism occurs when the applied current creates a potential difference across the cell membrane due to its electrical resistance. This potential difference modifies the transmembrane potential disrupting the cell membrane [42]. On the other hand, ion motion is restricted in a limited area. Near the charged area, ions cannot pass through the membrane due to electrostatic repulsion and vital physiological functions are hindered in the cell. For biomacromolecules such as enzymes, their conformations are transformed by the charging which changes their bioactivity and physiological function [43].

This mechanism implies that the oxidation of the compounds take place on the electrode surface. However, in the case of industrial wastewater that contains colloidal material along with the dissolved organics, this process becomes extremely slow. Therefore, the use of electrocoagulation eliminates the colloids and leaves only dissolved compounds.

3.6. Cyclic voltammetry

To obtain further information on the electrochemical processes occurring at the electrodes, a series of cyclic voltammetric experiments were performed using a CPE as the working electrode. Cyclic voltammetry results indicate that a chemically irreversible oxida-

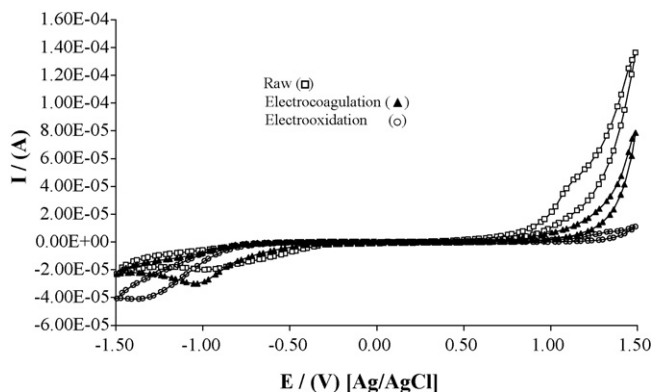


Fig. 11. Cyclic voltammograms recorded at the CPE over the potential window from -1.5 to 1.5 V of the samples at a scan rate of 0.1 V s⁻¹.

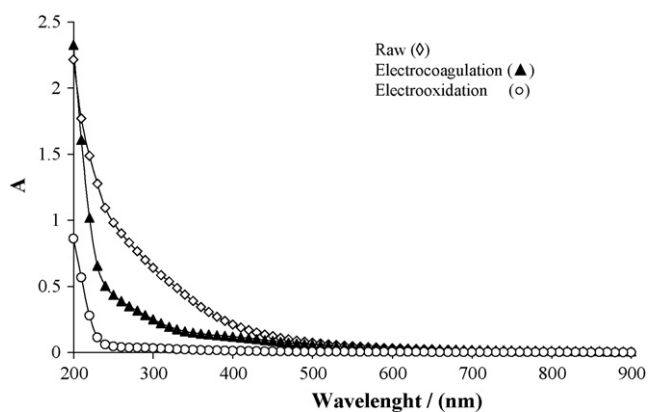


Fig. 12. UV-vis spectra of the samples. The scan rate was 960 nm s^{-1} within the 200–900 nm wavelength range. The samples were scanned in quartz cells with a 1 cm optical path.

tion peak in the wastewater is detectable at potentials lower than those corresponding to oxygen evolution, as shown in Fig. 11. This peak corresponds to the direct electrochemical oxidation of pollutants present in the wastewater. It is important to note that when cyclic voltammetry is applied after wastewater is electrochemically treated, the peak does not appear, indicating that pollutants in the solution have already been oxidized. On the other hand, the voltammetric curves of reduction present similar behavior before and after the electrochemical treatment, possibly due to anions, such as Cl^- and SO_4^{2-} in the wastewater.

3.7. UV-vis spectra

The UV-vis spectra of the raw, electrocoagulated, and coupled electrocoagulation–electrooxidation-treated wastewater are shown in Fig. 12. There are no peaks in the spectra corresponding to components of the raw and treated wastewater; there is only a continuous rise over the range of 240–300 nm. However, it is interesting to note that the overall absorbance of the curve decreases when the electrochemical treatments are applied, likely due to colloidal and suspended particles.

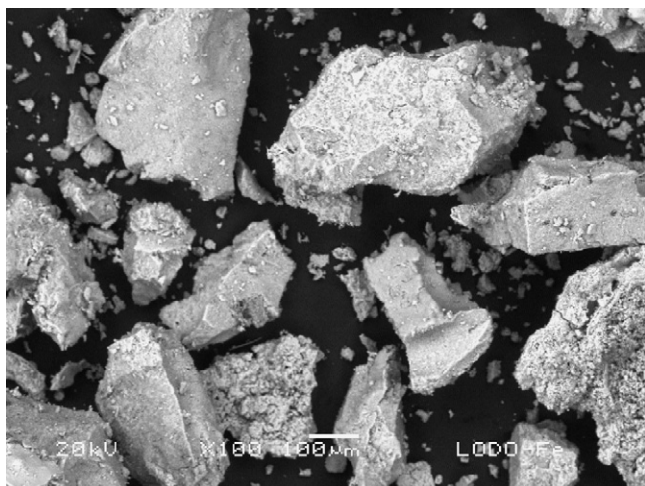


Fig. 13. Micrograph of the sludge produced in the electrocoagulation process. The photograph was recorded at $100\times$ and the marker is $100 \mu\text{m}$.

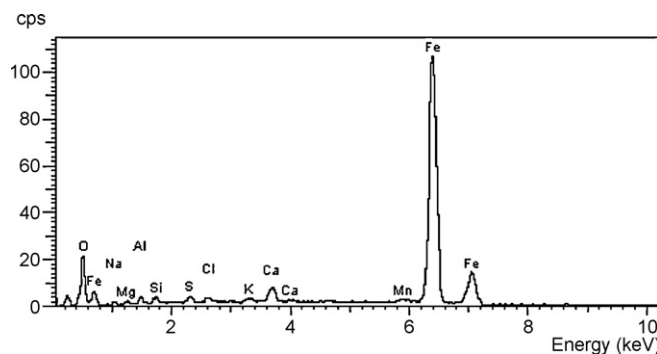


Fig. 14. Energy dispersion spectra of the sludge produced in the electrocoagulation process showing the presence of the elements: Fe and O, confirming the mechanism discussed earlier.

3.8. Scanning electron micrographs

To evaluate the structural features of the sludge that was generated by the electrocoagulation process, a series scanning electron microscopy experiments were performed. The micrograph in Fig. 13 shows continuous flake-shaped aggregates with diameters of around $50 \mu\text{m}$. This technique also allows elemental analysis of the sample by energy dispersive X-ray spectroscopy (EDS), as shown in Fig. 14. The peaks indicate that carbon, oxygen, iron, calcium and sulfur are present in the sludge. This information confirms that once the colloidal matter is destabilized, it can be separated from the wastewater and that the iron generated by the electrolysis forms insoluble complexes.

4. Conclusions

Electrocoagulation and electrooxidation each has advantages and disadvantages and neither alone is completely effective and practical in the removal of organic industrial pollutants, but coupling the two produces a synergistic process which does completely mineralize the organic components in a reasonable time. Electrocoagulation is a relatively quick process, which is very effective in removing colloidal and suspended particles, as well as charged species. However, it is relatively ineffective in eliminating stable persistent organic compounds—in this work, only half of the COD was eliminated from the industrial wastewater. Electrooxidation is very effective in breaking down organic compounds through oxidation, but requires so much time that it has very limited practicality, especially when colloidal and suspended particles are present. In the coupled technique, electrocoagulation quickly coagulates and removes the colloidal and suspended particles, as well as many charged species, then electrooxidation oxidizes the remaining organics. The coupled process eliminates COD, BOD_5 , color, turbidity, and coliforms in a practical amount of time (2 h).

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