



Degradation of Dipyrone by Electrogenerated H₂O₂ Combined with Fe²⁺ Using a Modified Gas Diffusion Electrode

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The aim of the present study was to investigate the electrochemical degradation of dipyrone in a single compartment electrochemical cell equipped with a gas diffusion electrode (GDE) modified with cobalt (II) phthalocyanine. Degradations were performed under conditions of anodic oxidation (GDE pressurized with N₂) and under conditions promoting the electrogeneration of H₂O₂ (GDE pressurized with O₂) both in the absence and presence of 1 mmol FeSO₄·7H₂O (electro-Fenton conditions). The efficiency of the electro-Fenton process was satisfactory at all studied potentials, and achieved a maximum reduction of 67% in electrolyte absorbance at 262 nm after 90 min electrolysis at -0.7 V (vs. Ag/AgCl). The reduction in dipyrone concentration attained 95% after 90 min of reaction with electrogenerated H₂O₂ in the absence or presence of Fe²⁺ ions at all potentials except -0.5 V (vs. Ag/AgCl). The removal of total organic carbon (TOC) was most efficient under electro-Fenton conditions with a decrease of 54.4% in organic load attained at -0.9 V (vs. Ag/AgCl) and energy consumption (EC) of 270 kWh per kg of TOC removed.

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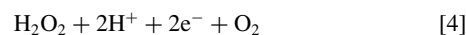
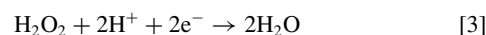
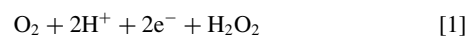
The increase in levels of human and veterinary drugs and metabolites detected in urban sewage represents an issue of growing concern. Pollution of surface and ground water by pharmaceutical products can occur via a number of mechanisms including incorrect disposal of expired drugs, metabolic excretion of medications, or the discharge of effluent from the cleaning and decontamination of machinery and equipment involved in drug production.¹⁻⁸ Although the effects of drugs on the organisms to which they are administered have been widely studied, the undesirable consequences of the presence of these molecules and their corresponding metabolites in the environment remain poorly understood.⁹⁻¹¹ It is, therefore, essential to minimize the pollution of the environment by such compounds.

The pharmaceuticals most commonly encountered as contaminants in wastewater systems are non-steroidal anti-inflammatories, such as acetylsalicylic acid, diclofenac and dipyrone (DIP), since these medications are consumed in the largest quantities by the general population.^{6,11} Dipyrone (*syn.* metamizole), for example, is used widely as an analgesic and antipyretic in various countries in Europe, Africa and South America, although it has been banned in North America and some European countries because of its potential collateral effects.^{2,12-16}

In view of the reported increase in the level of pharmaceutical pollution, it is clearly of paramount importance to develop methodologies that could prevent contact between these biologically active compounds and the environment. Unfortunately, the techniques currently employed in the treatment of public sewage are not able to remove completely these types of compounds from aqueous medium. A number of alternative methods are available for the removal of drugs from wastewaters,¹⁷ but straightforward approaches such as incineration generally involve high operating costs, while the more complex biological strategies depend on the continued survival of a microbial colony without genetic alteration. Given these serious limitations, advanced oxidation processes (AOPs) would appear to offer an important alternative for the removal of pharmaceutical contaminants.¹⁸ Such processes depend on the in situ production of the metastable hydroxyl radical (*OH), the high oxidizing potential of which promotes the non-selective oxidation of a wide range of organic compounds in an aqueous matrix.¹⁹⁻²¹ The reactive radicals may be formed from a primary oxidant such as oxygen, ozone or hydrogen peroxide (H₂O₂), generally in the presence of UV light or a catalyst.²²⁻²⁷ However, oxidation processes involving H₂O₂ are limited by the relatively low rate of formation of *OH, which implies decreased treatment efficiency. In the Fenton reaction, Fe²⁺ ions are employed as catalyst in order

to increase *OH production and, thereby, improve the efficiency of degradation of organic compounds.²²

The use of the Fenton reagent is described in the literature for the treatment of organic compounds in wastewater, but the traditional process suffers from two specific difficulties.^{22,23} Firstly, the reaction must be performed in acidic medium in order to prevent precipitation of the catalyst, and secondly H₂O₂ is a powerful oxidizing agent, the transport and storage of which can be dangerous under certain conditions. However, application of the gas diffusion electrode (GDE) allows the production of high levels (hundreds of mg per liter) of H₂O₂ directly in the acidic reaction medium, thereby eliminating the need for transport, storage and manipulation of the primary oxidant.²⁴⁻²⁸ In this system, H₂O₂ is electrogenerated in an O₂-pressurized GDE by an oxygen reduction reaction (ORR) involving a two-electron transfer (equation 1) which, in acidic medium, may be accompanied by a number of parallel reactions (equations 2 to 5).²⁹⁻³⁴



In this context, the use of GDE for the in situ generation of H₂O₂ in the electro-Fenton (e-Fenton) process appears to be a viable possibility for the oxidation of organic compounds, and reports are available concerning the degradation of ranitidine and sodium diclofenac by this route.^{35,36} The aim of the present study was to evaluate the e-Fenton degradation of DIP in acidic medium with H₂O₂ electrogenerated in situ in an electrochemical cell comprising a GDE modified with 5.0% cobalt (II) phthalocyanine (CoPc).

Experimental

Configuration and components of the electrochemical cell.— Experiments were carried out in a cylindrical single compartment electrochemical cell (total capacity 450 mL) constructed of polypropylene. The working electrode was a modified GDE prepared by the hot pressing method using a catalytic mass composed of Printex 6L carbon (Degussa Brazil) with 5.0% of CoPc (97% dye content; Sigma-Aldrich,

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St Louis, MO, USA; cat. # 307696) and a 60% PTFE dispersion (DuPont Teflon PTFE DISP 30) as hydrophobic binder. The preparation of the catalytic mass and the construction of the modified GDE followed published procedures.^{11,35,36} The counter electrode comprised a 30.0 mm diameter screen fabricated from platinum wire (99.95% pure; wire diameter 0.25 mm; space between wires 4.0 mm), and an Ag/AgCl electrode served as the reference electrode.

Electrochemical conditions.— Electrochemical reactions were performed with an aqueous electrolyte (400 mL) containing DIP (50 mg L⁻¹), H₂SO₄ (0.1 mol L⁻¹) and K₂SO₄ (0.1 mol L⁻¹). In experiments involving the anodic oxidation of DIP, the GDE was pressurized with N₂ (0.2 bar) and a constant potential in the range $-0.5 \text{ V} \leq E \leq -0.9 \text{ V}$ (vs. Ag/AgCl) was applied for 90 min with the electrolyte maintained at 20°C. The degradation of DIP by H₂O₂ electrogenerated in situ was investigated under similar conditions but with the GDE pressurized with O₂ (0.2 bar), whereas in the e-Fenton experiments, the electrolyte was supplemented with 1 mmol FeSO₄·7H₂O.

Electrogeneration of H₂O₂.— The amount of H₂O₂ electrogenerated as a function of time during electrolysis was determined using the peroxymolybdate complex method. Briefly, a sample (0.5 mL) of electrolyte was added to 4.0 mL of solution containing 2.4×10^{-3} mol L⁻¹ (NH₄)₆Mo₇O₂₄ and the absorbance at 350 nm of the yellow solution so-formed was measured using an Agilent Varian Cary 50 spectrometer.

Electrochemical degradation of DIP.— For each series of experiments, samples of electrolyte were collected at appropriate time intervals and the UV-Vis spectra recorded in the range 200–800 nm using an Agilent Varian Cary 50 spectrometer. The degradation of DIP was monitored in terms of the change in absorbance of the electrolyte at 262 nm.

The quantitative evaluation of DIP at each time interval was carried out by high performance liquid chromatography (HPLC) using a Shimadzu model LC-20AT chromatograph equipped with a SPD-20A UV detector and a Phenomenex Luna C₁₈ column (250 × 4.6 mm i.d.; 5 μm). The mobile phase comprised a 30:70 (v/v) mixture of methanol and phosphate buffer (pH 7), elution was isocratic at a flow rate of 1.0 mL min⁻¹, and the UV detector was set at 262 nm. The quantification of DIP was performed with the aid of a calibration curve constructed using analytical grade reference standard drug. Total organic carbon (TOC) in electrolyte samples was determined using a Shimadzu model TOC-VCPN analyzer.

Results and Discussion

Electrogeneration of H₂O₂.— In an earlier investigation concerning the electrogeneration of H₂O₂ at GDEs modified with different amounts of CoPc,³⁷ we demonstrated that the addition of 5.0% of modifier produced the highest concentrations of H₂O₂. On this basis, the present study of the electrodegradation of DIP in acidic medium was carried out using a single compartment electrochemical cell comprising a GDE modified with 5.0% of CoPc as the working electrode.

A plot of H₂O₂ concentration vs applied potential obtained using this system (Figure 1) revealed that the maximum concentration of H₂O₂ (331 mg L⁻¹) was produced after 90 min of electrolysis at a constant potential of -0.7 V (vs. Ag/AgCl).³⁷ However, the amount of H₂O₂ used in a degradation process should be proportional to the quantity of organic matter present, since excess of oxidant in the reaction medium may promote the sequestration of •OH.^{22,35,36} In consideration of this limitation, it was important to evaluate the best potential for the degradation of DIP associated with the largest amount of electrogenerated H₂O₂, thus experiments were performed at five different potentials, namely -0.5 V (corresponding to a final concentration of 136 mg L⁻¹ H₂O₂), -0.6 V (202 mg L⁻¹ H₂O₂), -0.7 V (331 mg L⁻¹ H₂O₂), -0.8 V (112 mg L⁻¹ H₂O₂) and -0.9 V (147 mg L⁻¹ H₂O₂).³⁷

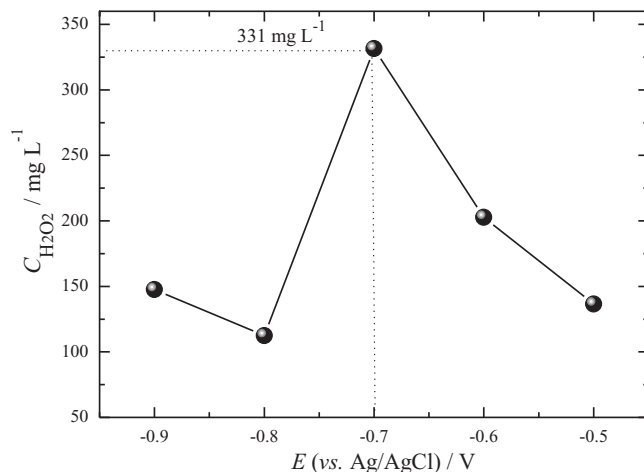


Figure 1. Final concentration of electrogenerated H₂O₂ ($C_{\text{H}_2\text{O}_2}$) as a function of the potential applied to a GDE modified with 5.0% CoPc and pressurized with O₂ (0.2 bar). The supporting electrolyte comprised an aqueous solution of H₂SO₄ (0.1 mol L⁻¹) and K₂SO₄ (0.1 mol L⁻¹). (Adapted from Barros et al.).³⁷

Electrochemical degradation of DIP.— Since the degradation experiments were performed in a single compartment electrochemical cell, all species present in the electrolyte were in contact with both electrodes, thus allowing reduction reactions to occur at the cathode and oxidation reactions at the anode. Three series of experiments were performed at each potential studied in which: (i) the GDE was pressurized with N₂ in order to evaluate the degradation of DIP by anodic oxidation in the absence of H₂O₂; (ii) the GDE was pressurized with O₂ such that the degradation of DIP was through oxidation by H₂O₂ together with anodic oxidation; and (iii) the experiments were conducted under the same conditions as series (ii) but with 1 mmol of FeSO₄·7H₂O added to the electrolyte such that DIP degradation was through H₂O₂/•OH oxidation together with anodic oxidation.

Figure 2 shows the decrease in absorbance of DIP at 262 nm during electrodegradation experiments under the three different reaction conditions and at five different applied potentials. When the GDE was pressurized with N₂, the reductions in absorbance at 262 nm were extremely small under all applied potentials, and attained a maximum of only ≈ 4.0% after 90 min of electrolysis. In contrast, the reductions in absorbance achieved in experiments involving the generation of H₂O₂ in the absence or presence of FeSO₄·7H₂O were associated with the participation of •OH in the oxidation of organic matter present and were, therefore, much greater than those obtained with anodic degradation. The greatest decreases in absorbance occurred in experiments involving the generation of H₂O₂ in the presence of Fe²⁺, i.e. the e-Fenton process, where a reduction of 67% in absorbance at 262 nm was attained at -0.7 V (vs. Ag/AgCl) after 90 min of electrolysis.

The results obtained in the experiments involving electrogeneration of H₂O₂ in the presence of FeSO₄·7H₂O are consistent with published reports.^{38,39} According to Batista and Nogueira,⁴⁰ degradation by the Fenton process is more efficient than degradation by H₂O₂ alone because the Fe²⁺ ions catalyze the formation of •OH from H₂O₂ present in solution. The results shown in Figure 2 verify that the changes in absorbance of the electrolyte followed the profile of electrogenerated H₂O₂, and that increasing the applied potential from -0.5 to -0.7 V (vs. Ag/AgCl) promoted an increase in the generation of H₂O₂ and a reduction in total absorbance of the electrolyte. However, at more negative potentials, the decrease in absorbance was diminished, thereby confirming the dependency of the degradation of DIP on the electrogeneration of H₂O₂.

The observation of a significant decrease in the absorbance of the aqueous electrolyte during electrolysis may be indicative of the degradation of DIP but did not provide conclusive evidence that the concentration of organic matter had also been reduced. Quantitative

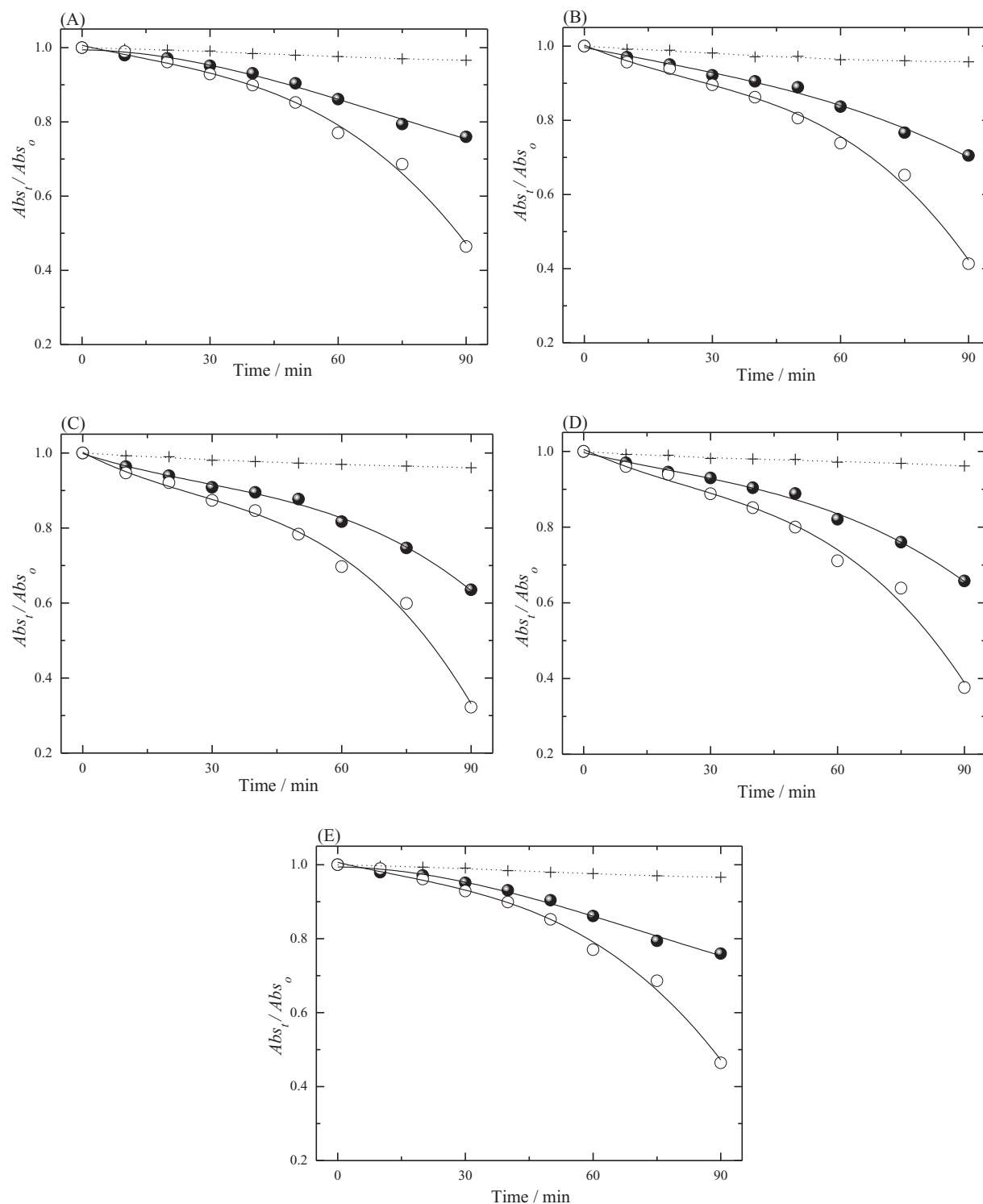


Figure 2. Decrease in normalized absorbance (Abs_t/Abs_0) at 262 nm of an aqueous solution of DIP as a function of time of electrolysis performed at applied potentials of (A) -0.5 V, (B) -0.6 V, (C) -0.7 V, (D) -0.8 V and (E) -0.9 V under three different experimental conditions, namely anodic oxidation ($\cdots + \cdots$), electrogenerated H_2O_2 ($-\bullet-$) and e-Fenton ($-o-$).

HPLC analysis of DIP during electrolysis (Figure 3) revealed that the decrease in concentration of analyte was minimal under conditions of anodic oxidation, i.e. in the absence of H_2O_2 (GDE pressurized with N_2), with only 5.0% of DIP being degraded after 90 min at a potential -0.9 V (vs. Ag/AgCl). Such low levels of drug removal are also associated with small current densities under experimental conditions that promote degradation by the electrochemical process alone.¹⁷ In contrast, experiments involving the generation of H_2O_2

in the absence or presence of $FeSO_4 \cdot 7H_2O$ achieved reductions of 96% in the concentration of DIP at an applied potential -0.9 V (vs. Ag/AgCl). While both of these procedures were able to remove the analyte almost completely, the rate of degradation was greater under e-Fenton conditions. Thus, at the optimal applied potential for the electrogeneration of H_2O_2 (-0.7 V vs. Ag/AgCl), 88% of DIP was removed in 40 min by the e-Fenton process compared with 66% of DIP removed in the same time when Fe^{2+} was absent. At more negative

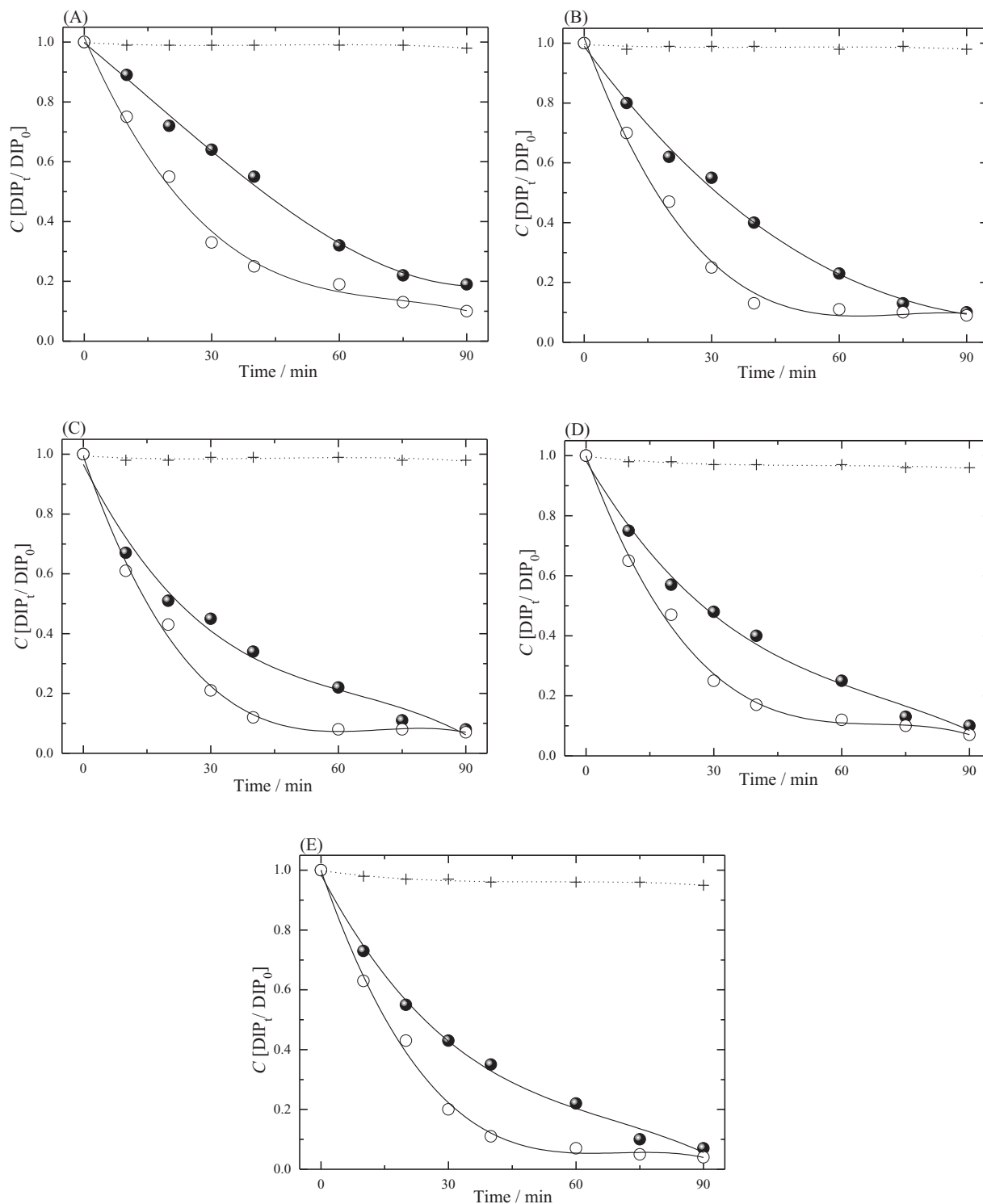


Figure 3. Decay in normalized concentration (as determined by HPLC) of an aqueous solution of DIP [$C(DIP_t/DIP_0)$] as a function of time of electrolysis performed at applied potentials of (A) -0.5 V, (B) -0.6 V, (C) -0.7 V, (D) -0.8 V and (E) -0.9 V under three different experimental conditions, namely anodic oxidation ($\cdots + \cdots$), electrogenerated H_2O_2 (\bullet) and e-Fenton (\circ).

potentials, the removal of DIP was less efficient showing that the degradation process was associated directly with H_2O_2 generation.

The profiles of plots of concentration of DIP with respect to time obtained under all experimental conditions indicated that the reaction followed first-order kinetics.^{22,35,36} The rate constant (k_{app}) for the degradation of DIP was determined from the slope of the function $\ln[DIP]$ ($mg\ L^{-1}$) vs. time (min) for each experiment, and the values are displayed in Figure 4. Under conditions of anodic oxidation, i.e.

in the absence of H_2O_2 , the k_{app} at -0.9 V (vs. Ag/AgCl) was $4.0 \times 10^{-4}\ min^{-1}$, with the lower values established at less negative potentials being associated with smaller current densities. Degradation experiments conducted in the presence of H_2O_2 showed much higher values for k_{app} , attaining a maximum of $4.0 \times 10^{-2}\ min^{-1}$ under e-Fenton conditions at -0.7 V (vs. Ag/AgCl). It is noteworthy, however, that in the e-Fenton process, the values of k_{app} were reduced at the most negative potentials, decreasing to $3.6 \times 10^{-2}\ min^{-1}$ at -0.9 V

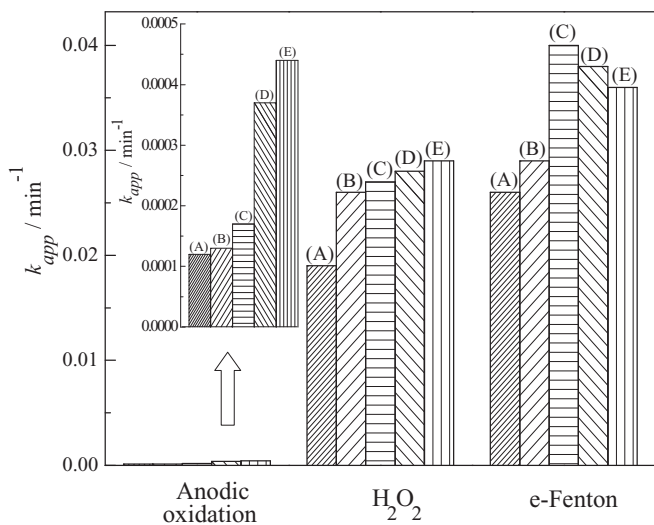
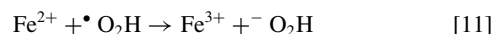
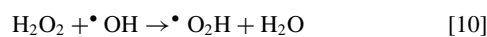
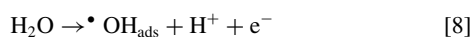
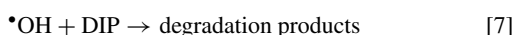
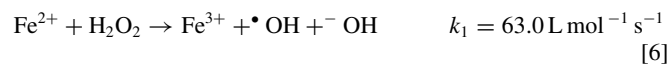


Figure 4. Values of the apparent rate constant (k_{app}) obtained from a plot of $\ln[DIP]$ (mg L^{-1}) vs. $time$ (min) (determined by HPLC) for the electrodegradation of DIP performed at applied potentials of (A) -0.5 V, (B) -0.6 V, (C) -0.7 V, (D) -0.8 V and (E) -0.9 V under three different experimental conditions, namely anodic oxidation, electrogenerated H_2O_2 and e-Fenton.

(vs. Ag/AgCl). The mechanism of degradation associated with the e-Fenton process is described in equations 6 and 7 in which a DIP molecule reacts with $\bullet\text{OH}$ formed by decomposition of H_2O_2 in the presence of Fe^{2+} ions to yield degradation products. However, in the e-Fenton process other reactions may occur such as those shown in equations 8–10 involving the formation of $\bullet\text{OH}_{ads}$, the recombination of $\bullet\text{OH}$ to produce H_2O_2 and the generation of hydroperoxyl radicals ($\bullet\text{O}_2\text{H}$). In addition, the $\bullet\text{O}_2\text{H}$ radical can oxidize Fe^{2+} (equation 11) promoting a deficiency in the production of $\bullet\text{OH}$.^{20,41}



The observed reduction in k_{app} values under e-Fenton conditions at more negative potentials is, therefore, associated with the decrease in generation of H_2O_2 at such potentials (Figure 1), resulting in a decline in the formation of $\bullet\text{OH}$ and a lower degradation rate, as shown in Figure 4.

Although the results presented in Figures 3 and 4 demonstrate removal of DIP from the electrolyte, they do not provide proof of reduction in the amount of organic matter present. The level of TOC in samples was monitored directly, and the results are shown in Figure 5. Under conditions of anodic degradation, the removal of organic matter was small, reaching only 2.7% after 90 min at an applied potential of -0.9 V (vs. Ag/AgCl). Reduction of TOC was much greater in degradation experiments involving the electrogeneration of H_2O_2 in the absence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, with 13.8% of organic matter removed at the end of electrolysis at -0.9 V (vs. Ag/AgCl). However, the highest

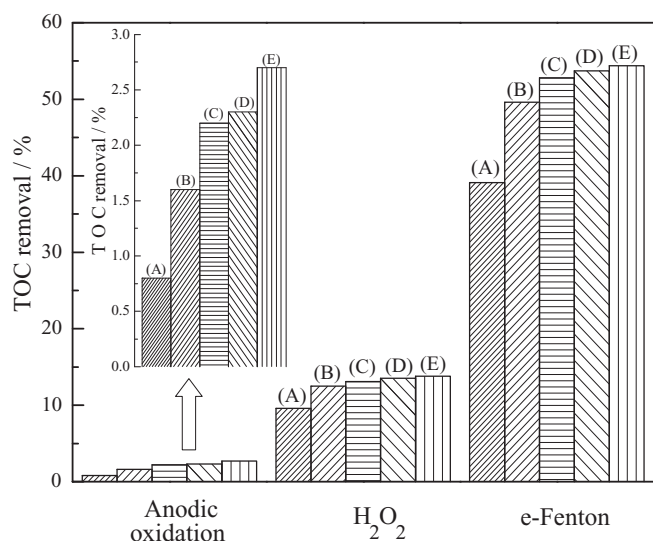


Figure 5. TOC removal (%) after 90 min of electrolysis of an aqueous solution of DIP performed at applied potentials of (A) -0.5 V, (B) -0.6 V, (C) -0.7 V, (D) -0.8 V and (E) -0.9 V under three different experimental conditions, namely anodic oxidation, electrogenerated H_2O_2 and e-Fenton.

levels of TOC removal were observed with the e-Fenton process, under which conditions a maximum decrease of 54.4% in organic load was recorded at the end of electrolysis at -0.9 V (vs. Ag/AgCl).

The profiles of DIP decay, established by UV/Vis (Figure 2), HPLC (Figure 3) and TOC (Figure 5) analyses, revealed large differences between degradative processes carried out with and without H_2O_2 , whereby the presence of H_2O_2 promoted a greater removal of analyte and other organic matter at all potentials studied. This difference in behavior may be attributed to the type of catalysis involved. Degradation in the absence of H_2O_2 is a heterogeneous anodic catalysis in which reactions occur on the surface of the anode. Under such conditions, DIP molecules present in solution have to reach the surface of the anode and, therefore, the reaction is controlled by the mechanisms of mass transport. In contrast, in degradative processes carried out in the presence of H_2O_2 (with or without $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), catalysis occurs in a homogeneous phase in which $\bullet\text{OH}$ radicals (derived from H_2O_2 electrogenerated in the GDE) promote the degradation of DIP. Since both $\bullet\text{OH}$ and DIP are present in solution, reaction occurs without the limitation of mass transport and higher removal values are achieved.

The evaluation of energy consumption (EC ; kWh kg^{-1}) during the process of electrochemical degradation is of fundamental importance because the technique is based on electron flow. In the present study, the amount of energy required to remove 1 kg of DIP was evaluated according to equation 12:

$$EC = \frac{i \cdot E_{cel} \cdot t}{\Delta \text{TOC} \cdot 1000} \quad [12]$$

where i is the current (A), E_{cel} is the cell potential (V), and ΔTOC is the mass of TOC removed (kg) in time t (min). Figure 6 shows the values of EC determined after 90 min of electrolysis under the three degradation conditions studied. Anodic oxidation, which produced the smallest reductions in TOC, was associated with the highest values of EC , attaining 1750 kWh kg^{-1} at an applied potential of -0.9 V (vs. Ag/AgCl). Compared with anodic degradation, reactions involving the electrogeneration of H_2O_2 in the absence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ exhibited lower EC values, attaining a maximum of 532 kWh kg^{-1} at an applied potential of -0.9 V (vs. Ag/AgCl). According to equation 12, the decrease in EC values obtained in these experiments in comparison with those involving anodic oxidation is related directly to TOC removal and not to the values of potential and current, since the latter showed little variation [3.7 ± 0.1 A and 7.8 ± 0.1 V, respectively,

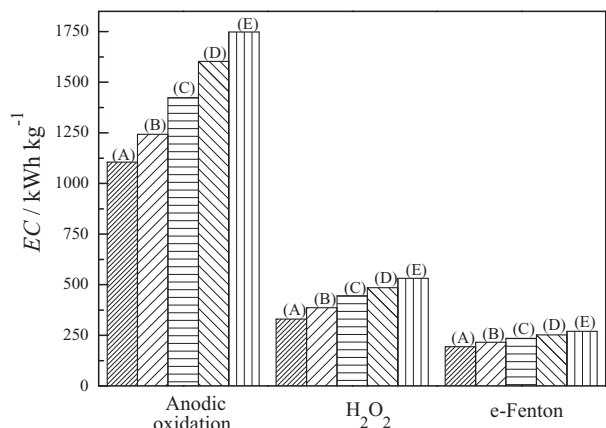


Figure 6. Energy consumption (EC) for the removal of 1 kg of TOC evaluated after 90 min of electrolysis of an aqueous solution of DIP performed at applied potentials of (A) -0.5 V, (B) -0.6 V, (C) -0.7 V, (D) -0.8 V and (E) -0.9 V under three different experimental conditions, namely anodic oxidation, electrogenerated H_2O_2 and e-Fenton.

at -0.9 V (vs. Ag/AgCl)] in the series of experiments performed at different potentials.

The lowest levels of energy consumed for the degradation of DIP were obtained under e-Fenton conditions, with an EC value of 270 $kWh\ kg^{-1}$ being recorded at an applied potential of -0.9 V (vs. Ag/AgCl) and values of 3.6 ± 0.1 A and 7.9 ± 0.1 V for current and cell potential, respectively. Consideration of these findings revealed that the e-Fenton process promoted a reduction in energy involved in the degradation of DIP of approximately 547% in comparison with anodic degradation and of 97% compared with H_2O_2 degradation in the absence of Fe^{2+} ions.

Although the e-Fenton process produced a decrease in TOC of 54% after 90 min of reaction at -0.9 V (vs. Ag/AgCl), the overall process did not comply with Brazilian legislation for the disposal of treated wastewater, which demands 80% removal of organic matter prior to discharge into class III water bodies.⁴² In order to determine the conditions required for the complete removal of TOC, the degradation of DIP under e-Fenton conditions was monitored over a period of 8 h. For this experiment, an applied potential of -0.7 V (vs. Ag/AgCl) was chosen based on the higher amount of electrogenerated H_2O_2 in 90 min as compared with the other potentials studied. As shown in Figure 7, 99% of the original TOC was removed after 8 h of reaction,

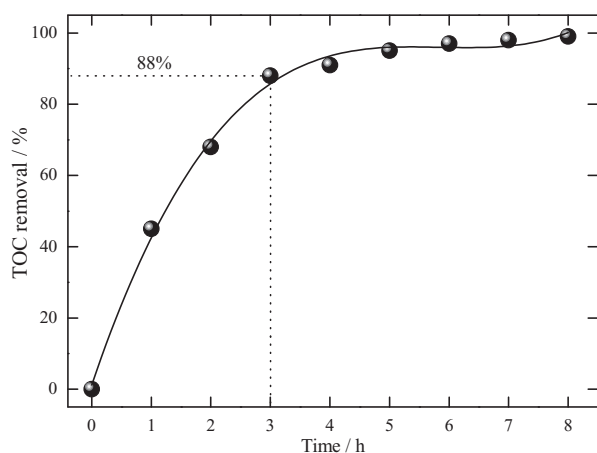


Figure 7. TOC removal (%) after 8 h of electrolysis of an aqueous solution of DIP performed at an applied potential of -0.7 V (vs. Ag/AgCl) under e-Fenton conditions. The electrolyte contained DIP ($50\ mg\ L^{-1}$), H_2SO_4 ($0.1\ mol\ L^{-1}$) and K_2SO_4 ($0.1\ mol\ L^{-1}$).

while the 80% reduction in organic load required by Brazilian law was achieved in less than 3 h. These findings verify that the e-Fenton process with H_2O_2 generated in a GDE modified with 5.0% CoPc is efficient in eliminating DIP from aqueous solution to the level required by Brazilian legislation.

Conclusions

The electrogeneration of H_2O_2 in acidic medium using a single compartment electrochemical cell equipped with a GDE modified with 5.0% CoPc and pressurized with O_2 was most effective when a potential of -0.7 V (vs. Ag/AgCl) was applied. Under these conditions, 95% of DIP and 13.8% of TOC could be removed in 90 min. The process was more efficient when H_2O_2 was electrogenerated in the presence of $FeSO_4 \cdot 7H_2O$ and, at an applied potential of -0.9 V (vs. Ag/AgCl), 96% of DIP was degraded ($k_{app} = 4.0 \times 10^{-2}\ min^{-1}$) and 54.4% of TOC removed ($EC\ 270\ kWh\ kg^{-1}$). In an extended experiment conducted under e-Fenton conditions, a reduction of 88% in organic matter was achieved within 3 h of electrolysis, a level of removal that was well within the 80% limit required by Brazilian legislation, while after 8 h of reaction the reduction in TOC attained 99%. In contrast, conditions that promoted anodic oxidation were ineffective in the removal of DIP and organic matter, being limited by low current density and mass transport of DIP to the electrode surface. It is concluded that e-Fenton conditions are the most appropriate for DIP degradation, although process parameters must be selected in order to comply with local legislation relating to the removal of organic load from drug-contaminated waters.

Acknowledgments

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