

## Degradation of Dipyrone by the Electro-Fenton Process in an Electrochemical Flow Reactor with a Modified Gas Diffusion Electrode

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A crescente ocorrência de antibióticos e seus metabólitos estão cada vez maiores em águas superficiais e subterrâneas, causando impactos significativos no meio ambiente e necessitando de desenvolvimento de novos tratamentos para a remoção completa de tais contaminantes. Este trabalho apresenta o estudo da eletrogeração de peróxido de hidrogênio ( $H_2O_2$ ) em meio ácido e a degradação do analgésico dipirona em um reator de fluxo eletroquímico usando um eletrodo de difusão gasosa (GDE) modificado com 5,0% ftalocianina de cobalto (II) (CoPc) e pressurizado com  $O_2$ . A maior produção de  $H_2O_2$  alcançada foi de  $133\text{ mg L}^{-1}$  a um potencial aplicado de  $-2,1\text{ V}$  (vs. Pt//Ag/AgCl/KCl<sup>1</sup>) e os melhores resultados para a degradação da dipirona foram obtidos sob condições eletro-Fenton, em que o carbono orgânico total (TOC) foi reduzido 62,8% após 90 min de reação e 49,1 kW h de energia foi consumida per kg de dipirona degradada.

The increasing occurrence of antibiotics and their metabolites in surface and ground waters is causing a significant impact on the environment and needing of developing novel treatments for the complete removal of such contaminants. This paper presents the study of the electrogeneration of hydrogen peroxide ( $H_2O_2$ ) in acidic medium and the degradation of the analgesic dipyrone in an electrochemical flow reactor using a gas diffusion electrode (GDE) modified with 5.0% cobalt (II) phthalocyanine (CoPc) and pressurized with  $O_2$ . The highest yield of  $H_2O_2$  ( $133\text{ mg L}^{-1}$ ) was achieved after 90 min of electrolysis at an applied potential of  $-2.1\text{ V}$  (vs. Pt//Ag/AgCl/KCl<sup>1</sup>) and the best results for degradation of dipyrone were obtained under electro-Fenton conditions, where the total organic carbon (TOC) was reduced 62.8% after 90 min of reaction and 49.1 kW h of energy was consumed per kg of dipyrone degraded.

**Keywords:** gas diffusion electrode, electrochemical reactor, dipyrone, Fenton process

### Introduction

Drugs that have been administered to humans are excreted either unchanged or in the form of metabolites. Conventional treatments of sewage water are not able to remove these compounds completely,<sup>1,2</sup> and contamination of surface and ground water by pharmaceutical products has been reported in a number of countries.<sup>3-8</sup> Various classes of drugs have been implicated as sources of environmental pollution, but non-steroidal anti-inflammatory drugs (NSAIDs) such as acetylsalicylic acid, diclofenac and dipyrone (DP) are generally detected in the largest quantities

mainly because of their high level of consumption.<sup>7,9</sup> In this context, DP (also known as metamizole) is of particular interest since in some European, African and South American countries it is widely available as an over-the-counter analgesic and antipyretic, although in others its use is restricted or even banned because of its potential side effects and the possibility of environmental contamination.<sup>10-15</sup>

Recent concerns about environmental pollution have engendered renewed interest in the development of techniques that would promote the complete removal of recalcitrant contaminants from sewage waters. In the case of DP, the kinetics of photodegradation of metabolites of the drug in aqueous systems have been established

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and toxicities of the products so-formed determined.<sup>16</sup> Additionally, it has been shown that electrochemical degradation of DP using boron-doped diamond (BDD) electrodes under optimized conditions allows total removal of the drug within 20 min and 95.2% removal of total organic carbon (TOC) in 8 h.<sup>17</sup>

An alternative type of effluent treatment that has received considerable attention over the last few years is based on advanced oxidation processes (AOPs) in which the hydroxyl radical ( $\cdot\text{OH}$ ) is produced from oxidizing agents such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).<sup>18</sup> In this process, the  $\cdot\text{OH}$  plays a key role since its high oxidation potential promotes attack on organic substances by extracting hydrogen atoms and adding to double bonds.<sup>19</sup> The efficiency of production of  $\cdot\text{OH}$  from  $\text{H}_2\text{O}_2$  is enhanced by the presence of  $\text{Fe}^{2+}$ , as in the Fenton reaction, where iron acts as a reducing agent to oxidize the  $\text{H}_2\text{O}_2$  according to equation 1:<sup>19</sup>



A particular advantage of this type of process is that it does not require the presence of organic chlorine and, therefore, does not generate organochlorine compounds as undesirable by-products.<sup>20</sup>

The direct production of  $\text{H}_2\text{O}_2$  in the medium in which the AOP occurs represents a particularly attractive proposition since it removes the requirement of transport and storage of a reagent that is corrosive and inflammable.<sup>21,22</sup> Efficient electrogeneration of  $\text{H}_2\text{O}_2$  can be readily achieved using gas diffusion electrodes (GDEs) in which the oxygen reduction reaction (ORR) occurs at the triple interface between pressurized  $\text{O}_2$  gas, the electrolyte solution and the surface of the electrode.<sup>23,24</sup> The ORR occurs via a complex mechanism, the steps of which are described in equations 2–6:<sup>24–27</sup>



The complete reduction of  $\text{O}_2$  to water occurs via a reaction involving four electrons (equation 2), while partial reduction to produce  $\text{H}_2\text{O}_2$  involves a two electron transfer (equation 3). Electrogenerated  $\text{H}_2\text{O}_2$  can be reduced to water via a two electron transfer (equation 4) or it can be oxidized to regenerate molecular  $\text{O}_2$  (equation 5). Since the electrogeneration of  $\text{H}_2\text{O}_2$  takes place in acidic medium,

the involvement of the hydrogen evolution reaction (HER), as shown in equation 6, is also likely.

The aim of the present study was to investigate the electrogeneration of  $\text{H}_2\text{O}_2$  in acidic medium in an electrochemical flow reactor using a GDE modified with cobalt (II) phthalocyanine (CoPc), and to explore the application of this system to the degradation of DP by means of the Fenton reaction.

## Experimental

### Electrogeneration of $\text{H}_2\text{O}_2$

The production of  $\text{H}_2\text{O}_2$  was carried out in an electrochemical flow reactor, the construction of which has been described previously, comprising two parallel polypropylene plates fitted with a dimensionally stable anode type  $\text{Cl}_2$  (DSA- $\text{Cl}_2$ ®; geometric area  $20 \text{ cm}^2$ ) obtained from De Nora do Brasil (Sorocaba, SP, Brazil).<sup>17,21,22,24,28</sup> The cathode was a GDE (geometric area  $20 \text{ cm}^2$ ) that had been prepared by the hot pressing procedure using Carbon Printex 6L conductive black graphite (Degussa Brasil, Jardim Paulista, SP, Brazil) with 5.0% (m/m) of CoPc and 20% (m/m) of polytetrafluoroethylene (PTFE; Dyneon TF 5035, 3M do Brazil, Sumaré, SP, Brazil).<sup>24,28–30</sup> A pseudo-reference Pt//Ag/AgCl/KCl<sup>s</sup> electrode was positioned on the face of the GDE as the reference electrode.<sup>31</sup> The reactor was connected to a recirculation system (capacity 2 L) through which electrolyte could be supplied at a flow rate of  $50 \text{ L h}^{-1}$  (laminar flow; Reynolds number,  $Re = 290$ ).

Electrogeneration of  $\text{H}_2\text{O}_2$  in the electrochemical reactor was investigated in two stages. In the first step, the working GDE cathode was pressurized with  $\text{N}_2$  for 20 min, after which linear voltammetry (LV) was carried out in the range  $-0.5 \text{ V} \leq E \leq -2.8 \text{ V}$  (vs. Pt//Ag/AgCl/KCl<sup>s</sup>) at  $20 \text{ mV s}^{-1}$  with an electrolyte containing  $\text{H}_2\text{SO}_4$  ( $0.1 \text{ mol L}^{-1}$ ) and  $\text{K}_2\text{SO}_4$  ( $0.1 \text{ mol L}^{-1}$ ) supplied at a flow rate of  $50 \text{ L h}^{-1}$ . Subsequently, the GDE was pressurized with  $\text{O}_2$  for 30 min and LV measurements were recorded under the conditions stated above. Electrochemical analyses were carried out using a Metrohm Autolab (Utrecht, The Netherlands) model PGSTAT-302 potentiostat with a model BSTRA10A current booster, and the cell potential was measured using a high impedance digital multimeter connected in parallel to the working and counter electrodes. In the second step, electrolysis was performed at a constant applied potential in the range  $-0.3 \text{ V} \leq E \leq -2.4 \text{ V}$  (vs. Pt//Ag/AgCl/KCl<sup>s</sup>), and the amounts of  $\text{H}_2\text{O}_2$  present in samples of electrolyte collected during a 90 min reaction period were quantified spectrophotometrically using a standard method.<sup>17</sup>

### Electrodegradation of DP

For the electrodegradation of DP (50 mg L<sup>-1</sup>) was used the same electrochemical flow reactor used in the experiments of electrogeneration of H<sub>2</sub>O<sub>2</sub>. Aqueous electrolyte (1.5 L) containing H<sub>2</sub>SO<sub>4</sub> (0.1 mol L<sup>-1</sup>) and K<sub>2</sub>SO<sub>4</sub> (0.1 mol L<sup>-1</sup>) was employed in the electrodegradation of DP, while the electro-Fenton process was used the same electrolyte with 1.0 mmol L<sup>-1</sup> of FeSO<sub>4</sub>·7H<sub>2</sub>O. Electrolyses were carried out at constant applied potential of -2.1 V (vs. Pt//Ag/AgCl/KCl<sup>s</sup>) for 90 min with the electrolyte thermostated at 20 °C. The electrolyte was sampled at appropriate intervals throughout the experiment, and the ultraviolet-visible (UV-Vis; 200-800 nm) spectrum of each sample was measured using an Agilent (Santa Clara, CA, USA) Varian Cary 50 spectrometer. The removal of DP was monitored from the absorbance at 262 nm, which was determined to be the  $\lambda_{\text{max}}$  of the analytical-standard grade drug.

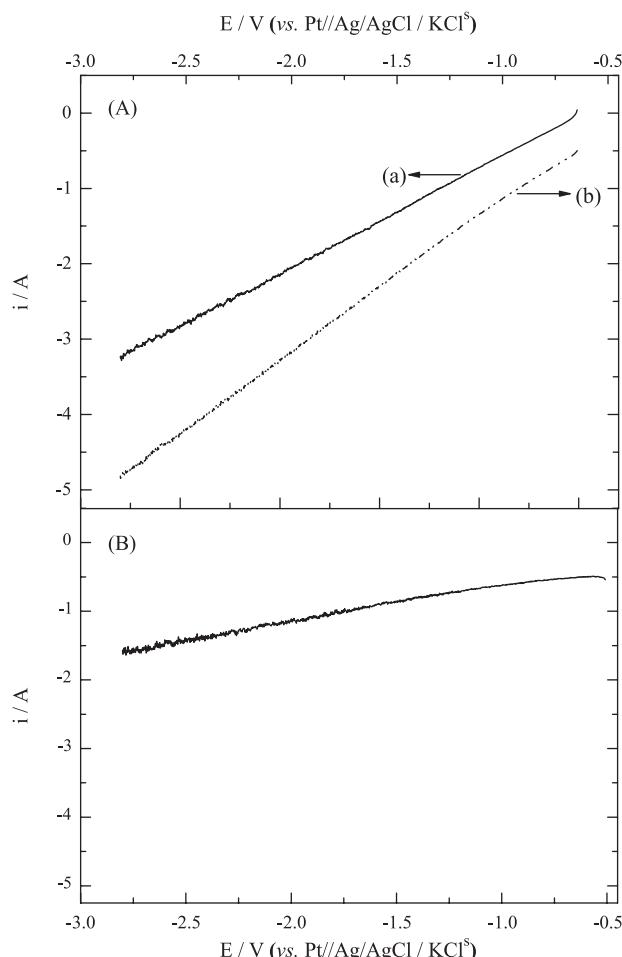
The amount of DP remaining in the electrolyte was determined by high performance liquid chromatography (HPLC) using a Shimadzu (Kyoto, Japan) model LC-20AT chromatograph equipped with a model SPD-20A UV detector and a Phenomenex (Torrance, CA, USA) Luna C<sub>18</sub> column (250 × 4.6 mm i.d.; 5 µm). Elution was isocratic with a 30:70 (v/v) mixture of methanol and phosphate buffer (pH 7) at a flow rate of 1.0 mL min<sup>-1</sup>, and detection was at 262 nm. Quantitative estimation of DP was performed with the aid of a calibration curve constructed using analytical-standard grade drug. The variation in TOC in samples of electrolyte was measured using a Shimadzu TOC-VCPN analyzer.

## Results and Discussion

### Electrogeneration of H<sub>2</sub>O<sub>2</sub>

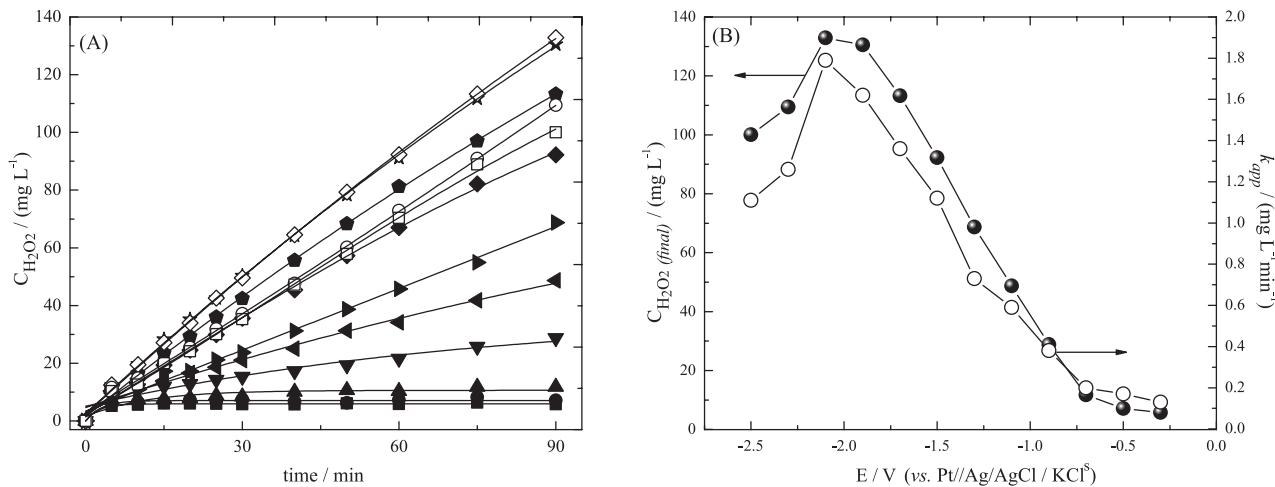
Linear voltammograms (LVs) recorded in the electrochemical reactor after the GDE had been pressurized with N<sub>2</sub> and, subsequently, with O<sub>2</sub> are shown in Figure 1. The variation in current observed when the GDE was pressurized with N<sub>2</sub> was likely associated with the reduction of H<sup>+</sup> ions in the acidic electrolyte to form H<sub>2</sub> (equation 6). On the other hand, the increased current observed when the GDE was pressurized with O<sub>2</sub> may be associated with the reduction of H<sup>+</sup> ions and O<sub>2</sub> to form H<sub>2</sub>O<sub>2</sub> (equation 3), although other reactions may occur in parallel under these conditions including the reduction of O<sub>2</sub> to water via a 4-electron transfer.<sup>22,24,29</sup> It appears that ORR is dependent on the applied potential, whereby potentials that are more negative tend to promote ORR via 4-electron transfer in parallel with the reduction of water.<sup>24</sup> A plot of the

difference between the LVs recorded under O<sub>2</sub> and N<sub>2</sub> pressurization (Figure 1B) revealed that, the ORR current increased with increasing applied potential and attained a value of -1.6 A at -2.8 V. These findings are very much in line with those established previously by our research group using the same modified GDE for the electrogeneration of H<sub>2</sub>O<sub>2</sub>.<sup>30</sup>



**Figure 1.** Linear voltammograms (LVs) obtained with an electrochemical reactor comprising a GDE modified with 5.0% of CoPc and supplied with 1.5 L of electrolyte containing 0.1 mol L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub> and 0.1 mol L<sup>-1</sup> of K<sub>2</sub>SO<sub>4</sub> at a flow rate of 50 L h<sup>-1</sup>, showing (A) LVs with the GDE pressurized with N<sub>2</sub> (a) or O<sub>2</sub> (b); and (B) LV with N<sub>2</sub> subtracted from LV with O<sub>2</sub>.

As displayed in Figure 2, the concentration of H<sub>2</sub>O<sub>2</sub> varied in a linear manner with respect to time of electrolysis under applied potentials within the range -0.3 V ≤ E ≤ -2.5 V (vs. Pt//Ag/AgCl/KCl<sup>s</sup>). The amount of H<sub>2</sub>O<sub>2</sub> formed during 90 min of electrolysis increased as the applied potential increased from -0.3 V (vs. Pt//Ag/AgCl/KCl<sup>s</sup>), and attained a maximum value of 133 mg L<sup>-1</sup> at -2.1 V (vs. Pt//Ag/AgCl/KCl<sup>s</sup>) (Figure 2B). This potential range is associated with an ORR involving 2-electron transfer and the consequent formation of H<sub>2</sub>O<sub>2</sub>. At potentials in the



**Figure 2.** (A) Variation of  $\text{H}_2\text{O}_2$  concentration vs. time of electrolysis, and (B) concentration of  $\text{H}_2\text{O}_2$  after 90 min of electrolysis and apparent rate constant ( $k_{app}$ ) for the formation of the oxidant during the first 30 min in an electrochemical reactor comprising a GDE modified with 5.0% of CoPc and supplied with 1.5 L of electrolyte containing 0.1 mol L $^{-1}$  of  $\text{H}_2\text{SO}_4$  and 0.1 mol L $^{-1}$  of  $\text{K}_2\text{SO}_4$  at a flow rate of 50 L h $^{-1}$ . -0.3 V (■), -0.5 V (●), -0.7 V (▲), -0.9 V (▼), -1.1 V (◀), -1.3 V (▶), -1.5 V (◆), -1.7 V (●), -1.9 V (★), -2.1 V (◇), -2.3 V (○) and -2.5 V (□).

range  $-2.1 \text{ V} < E \leq -2.5 \text{ V}$  (vs. Pt//Ag/AgCl/KCl $^{\circ}$ ), the final  $\text{H}_2\text{O}_2$  concentration gradually diminished, and a value of 100 mg L $^{-1}$  was recorded at -2.5 V (vs. Pt//Ag/AgCl/KCl $^{\circ}$ ). These more negative potentials tend to promote ORR via 4-electron transfer with a corresponding reduction in the generation of  $\text{H}_2\text{O}_2$ .<sup>24</sup>

It is of interest to note that the potential range employed in the present investigation involving an electrochemical reactor ( $-0.3 \text{ V} \leq E \leq -2.5 \text{ V}$  (vs. Pt//Ag/AgCl/KCl $^{\circ}$ )) was substantially greater than that reported in a previous study ( $-0.4 \text{ V} \leq E \leq -1.4 \text{ V}$  (vs. Ag/AgCl/KCl $^{\circ}$ )) by our group concerning the electrogeneration of  $\text{H}_2\text{O}_2$  in an electrochemical cell with a similar electrode and supporting electrolyte.<sup>30</sup> The reason for the apparent discrepancy in potential range is associated with differences between the electrochemical cell and the electrochemical reactor regarding the type and area of the counter electrode (platinum screen in the cell, DSA electrode in the reactor), the distance between the working and counter electrodes (ca. 1.5 cm in the cell, 2 mm in the reactor), the hydrodynamics of the system (simple stirring in the cell, laminar regime in the reactor), and the reference system employed (Ag/AgCl/KCl $^{\circ}$  in the cell, Pt//Ag/AgCl/KCl $^{\circ}$  in the reactor).<sup>22</sup>

The linear variation of  $\text{H}_2\text{O}_2$  concentration with time of electrolysis signifies that the electrogeneration of the oxidant followed zero-order kinetics. However, the variation observed derives from the summation of a number of different reactions (equations 2 to 6) that occurred in parallel with the formation of  $\text{H}_2\text{O}_2$  and, therefore, the kinetics of this reaction must be considered to be global pseudo zero-order. The apparent rate constant for the formation of  $\text{H}_2\text{O}_2$  ( $k_{app}$ ; mg L $^{-1}$  min $^{-1}$ ) was estimated from the slope of the plot of  $\text{H}_2\text{O}_2$  concentration vs. time,

considering the first 30 min of reaction. According to the  $k_{app}$  values shown in Figure 2B, the rate constant increased as the applied potential from -0.3 V (vs. Pt//Ag/AgCl/KCl $^{\circ}$ ), and attained a maximum value of 1.79 mg L $^{-1}$  min $^{-1}$  at -2.1 V (vs. Pt//Ag/AgCl/KCl $^{\circ}$ ). At more negative potentials, however, the rate constant showed a gradual reduction to 1.11 mg L $^{-1}$  min $^{-1}$  at -2.5 V. Overall, the values of the rate constants determined in the present study were lower than those reported previously because of the differences between the electrochemical cell and the corresponding reactor as outlined above.<sup>30</sup>

**Table 1.** Electrogeneration of  $\text{H}_2\text{O}_2$  during 90 min of electrolysis at different applied potentials and energy consumed (EC) in the generation of 1 kg of  $\text{H}_2\text{O}_2$  for each experiment

$E_{app}$ / (V vs. Pt//Ag/AgCl/KCl $^{\circ}$ )	$E_{cell}$ / V	$C_{\text{H}_2\text{O}_2}$ / (mg L $^{-1}$ )	EC / (kWh kg $^{-1}$ )
-0.3	-0.7	5.8	12.0
-0.5	-1.0	7.2	15.8
-0.7	-1.3	11.8	90.1
-0.9	-1.9	28.8	99.2
-1.1	-2.3	48.7	102.3
-1.3	-3.1	68.6	100.3
-1.5	-3.8	92.3	89.3
-1.7	-4.5	113.2	67.2
-1.9	-5.2	130.5	56.4
-2.1	-5.4	133.0	47.6
-2.3	-5.9	109.4	68.7
-2.5	-6.6	100.0	86.8

The energy consumed (EC, in kWh kg $^{-1}$ ) in the electrogeneration of 1 kg of  $\text{H}_2\text{O}_2$  was calculated according to equation 7:

$$EC = \frac{i \cdot E_{cell} \cdot t}{m \cdot 1000} \quad (7)$$

where  $i$  is the current (A),  $E_{cell}$  is the cell potential (V),  $t$  is the time (h) and  $m$  is the mass of  $H_2O_2$  (kg) generated during that time. As verified in Table 1, electrogeneration of  $H_2O_2$  at an applied potential of  $-2.1$  V (vs. Pt//Ag/AgCl/KCl<sup>s</sup>) not only gave the highest yield of  $H_2O_2$  during 90 min of reaction but also showed a very low  $EC$  value of  $47.6$  kWh kg<sup>-1</sup>. At more negative potentials, the  $EC$  increased quite sharply as energy was diverted away from  $H_2O_2$  and towards parallel ORR involving 4-electron transfer. The  $EC$  values obtained in the present study with the electrochemical reactor are similar to those reported previously for the electrochemical cell in which a consumption of  $30.8$  kWh kg<sup>-1</sup> was recorded under the experimental conditions that generated the highest yield of  $H_2O_2$ .<sup>30</sup>

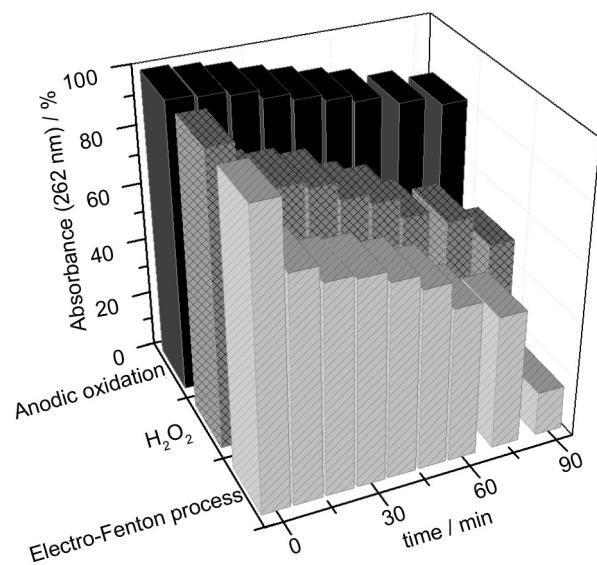
#### Electrodegradation of DP

The electrodegradation of DP was performed under three different reaction conditions. In the first experiment, the GDE was pressurized with  $N_2$  such that  $H_2O_2$  was not generated at the cathode and the observed degradation of DP occurred via anodic oxidation at the DSA. In the second experiment, the GDE was pressurized with  $O_2$ , leading to the formation of  $H_2O_2$  and  $\cdot OH$ , and the observed degradation of DP resulted from anodic oxidation and oxidation by  $\cdot OH$ . The final degradation was performed under electro-Fenton conditions with the GDE pressurized with  $O_2$  and  $Fe^{2+}$  present in the electrolyte. In this case, the formation of  $\cdot OH$  from  $H_2O_2$  was catalyzed by  $Fe^{2+}$ , and the observed degradation of DP resulted from anodic oxidation and oxidation by  $\cdot OH$ . Since it had already been established that the best potential for the generation of  $H_2O_2$  in the electrochemical reactor was  $-2.1$  V (vs. Pt//Ag/AgCl/KCl<sup>s</sup>), the degradation experiments were performed at this applied potential.

Figure 3 shows the reduction in absorbance at 262 nm recorded during the degradation of DP under the three different electrochemical conditions. After 90 min of electrolysis, the smallest decrease (18.5%) in absorbance occurred when the GDE was pressurized with  $N_2$ . The reduction in absorbance was considerably greater (51.6%) when  $O_2$  was used to pressurize the GDE, while the presence of  $Fe^{2+}$  ions in the electrolyte under these conditions promoted a decrease in absorbance of 84.7% after 90 min.

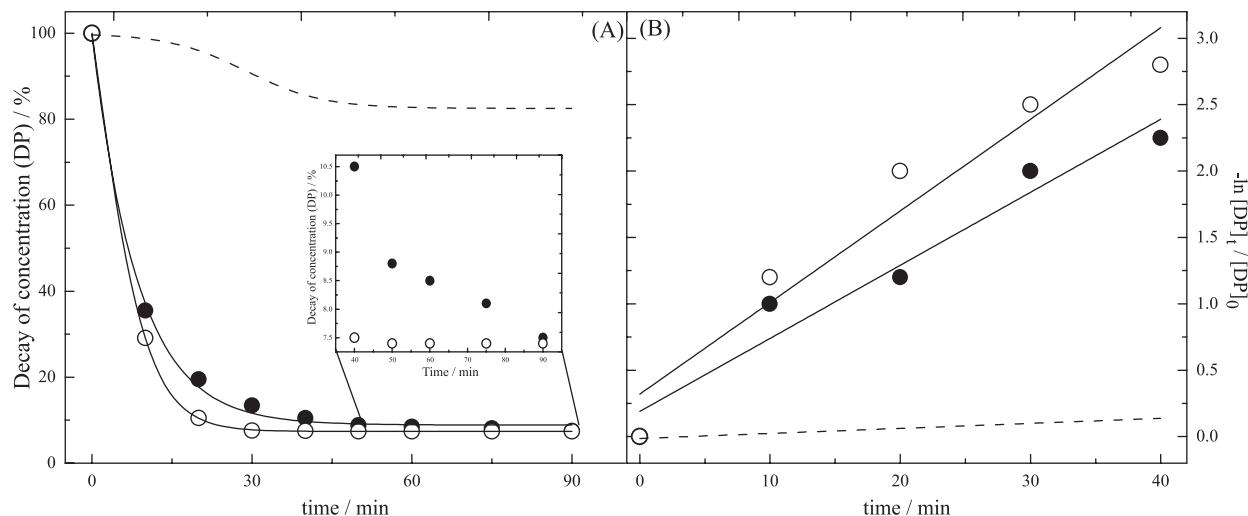
In order to verify that the observed reduction in absorbance at 262 nm accurately reflected the removal

of DP from the electrolyte, the variation in concentration of analyte during electrodegradation was monitored by HPLC. The results displayed in Figure 4 confirm that anodic oxidation accounted for a reduction in DP concentration of only 17.5% after 90 min. In contrast, when the GDE was pressurized with  $O_2$ , around 92.5% of the initial DP was removed after 90 min of reaction in the absence or presence of  $Fe^{2+}$  ions. However, while 90% of analyte was removed within 40 min of reaction in the absence of  $Fe^{2+}$  ions, the same level of removal could be achieved in 20 min in the presence of these ions. The increased rate of degradation of DP was associated with the augmented rate of formation of  $\cdot OH$  under Fenton reaction conditions.



**Figure 3.** Variation in absorbance of DP at 262 nm (expressed as a percentage of the initial absorbance) with respect to time of electrolysis performed in the electrochemical reactor under the conditions: anodic - GDE pressurized with  $N_2$ ;  $H_2O_2$  - GDE pressurized with  $O_2$  in the absence of catalyst; electro-Fenton process - GDE pressurized with  $O_2$  in the presence of  $1\text{ mmol L}^{-1}$  of  $FeSO_4 \cdot 7H_2O$ .

In all experiments, the reduction in concentration of DP was most rapid during the first 40 min of electrolysis (Figure 4), during which period the reaction presented first-order kinetics.<sup>21,22,32</sup> The rate constant for the degradation of DP was evaluated from the slope of the plot  $\ln$  (DP concentration / mg L<sup>-1</sup>) vs. time (min) for each experiment, and the respective values of  $3.8 \times 10^{-3}$ ,  $5.5 \times 10^{-2}$  and  $7.0 \times 10^{-2}$  min<sup>-1</sup> (Figure 4B) were obtained for anodic degradation, reaction by electrogenerated  $H_2O_2$ , and electrodegradation under electro-Fenton conditions, respectively. The difference these values is due (*i*) in the degradation process of direct anodic oxidation, that is, using higher oxides formed on the surface of the anode,<sup>32</sup> occurs less yields in the percentage of degradation and (*ii*) in electro-Fenton process of degradation of DP occurs



**Figure 4:** (A) Decay of concentration of DP (determined by HPLC and expressed as a percentage of the initial concentration) and (B) plot linear *versus* time of experiment during the first 40 min with respect to time of electrolysis performed in the electrochemical reactor under the conditions: anodic - GDE pressurized with  $N_2$  (---);  $H_2O_2$  - GDE pressurized with  $O_2$  in the absence of catalyst (●); electro-Fenton process- GDE pressurized with  $O_2$  in the presence of 1 mmol  $L^{-1}$  of  $FeSO_4 \cdot 7H_2O$  (○).

the high forming  $\cdot OH$  radicals due to the rapid kinetics of the formation of these radicals, with a constant, as shown in equation 1.

Although almost complete removal of absorbance at 262 nm of DP concentration was achieved in experiments involving the electrogeneration of  $H_2O_2$ , such results cannot be considered as indicative of mineralization of organic matter in the electrolyte. The levels of TOC present at the start and final of each degradation experiment were measured directly, and the results (Table 2) showed that mineralization by  $H_2O_2$  electrogenerated was 4.4 times greater (5.3 mg  $L^{-1}$  TOC removed) and in the presence of ions  $Fe^{2+}$  was 13.3 times greater (15.9 mg  $L^{-1}$  TOC removed), both compared to anodic degradation with 1.2 mg  $L^{-1}$  TOC removal. Moreover, the *EC* value for the removal of 1 kg of TOC under electro-Fenton conditions was 2.9- and 12.9-fold lower than those relating, respectively, to anodic oxidation and electrogeneration of  $H_2O_2$  alone.

Pressurization of the GDE with  $N_2$  promoted degradation of organic materials at the anode surface by processes associated with the anodic current density in the DSA. However, since the current density was low (130 mA  $cm^{-2}$ ),

the anodic degradation of DP was compromised.<sup>32</sup> When the GDE was pressurized with  $O_2$ ,  $H_2O_2$  was generated *in situ* but, in the absence of  $Fe^{2+}$ , the degradation process was effectuated by  $\cdot OH$  and other oxidizing species, such as radical anions ( $O_2^{\cdot -}$ ), hydroperoxyl radicals ( $HO_2^{\cdot}$ ), triplet oxygen ( $^3O_2$ ) and organic peroxy radicals ( $R-O-O^{\cdot}$ ), with less potential than the  $\cdot OH$ .<sup>33</sup> Thus, although this experiment showed better results in comparison with anodic degradation, the process was less efficient than that involving generation of  $H_2O_2$  in the presence of  $Fe^{2+}$ , which presented higher formation of  $\cdot OH$  greater removal of DP and TOC, and lower power consumption.<sup>16,19,34,35</sup>

The results of TOC removal are in agreement with the literature, Giri *et al.*<sup>36</sup> reached 56% of TOC removal at 45 min, but the authors used a photo-assisted system with addition of  $H_2O_2$  in the presence of  $Fe^{2+}$ .<sup>36</sup> Considering the *in situ* electrogeneration of  $H_2O_2$  for the degradation of dipyrone, Assumpção *et al.*<sup>37</sup> reached 57% of TOC removal using electro-Fenton and 75% for the same system but photo-assisted.<sup>37</sup> Using electrochemical reactor with parallel plate, Reis *et al.*<sup>17</sup> studied the anodic degradation using boron-doped diamond, reached 44% of TOC removal after 120 min at 50 L  $h^{-1}$  by 5.0 V (*vs.* Pt//Ag/AgCl/KCl<sup>10</sup>).

**Table 2.** Percentage of total organic carbon (TOC) removed after 90 min of electrolysis and energy consumed (*EC*) in the removal of 1 kg of TOC during the degradation of DP in an electrochemical reactor operated at a flow rate of 50 L  $h^{-1}$  under different reaction conditions

Parameter	Anodic oxidation	Electrogenerated $H_2O_2$	Electro-Fenton process
Initial TOC / (mg $L^{-1}$ )	24.6	25.6	25.3
Final TOC / (mg $L^{-1}$ )	23.4	20.3	9.4
TOC removed / %	5.0	20.1	62.8
EC / (kWh $kg^{-1}$ )	635.5	143.9	49.1

In comparison with the results presented in the literature, the use of electrochemical reactor for  $\text{H}_2\text{O}_2$  generation for dipyrone degradation was efficient for this process, but with the advantage of generating a specific  $\text{H}_2\text{O}_2$  amount depending the characteristics of wastewater to be treated.

## Conclusions

Hydrogen peroxide could be generated efficiently in an electrochemical reactor comprising a GDE modified with 5.0% of CoPc and pressurized with  $\text{O}_2$ . The highest yield of  $\text{H}_2\text{O}_2$  ( $133 \text{ mg L}^{-1}$ ) was achieved after 90 min of electrolysis at an applied potential of  $-2.1 \text{ V}$  (vs. Pt//Ag/AgCl/KCl<sup>s</sup>), under which conditions the reaction rate was  $1.79 \text{ mg}^{-1} \text{ min}^{-1}$  and the energy consumption was  $47.6 \text{ kWh per kg}$  of  $\text{H}_2\text{O}_2$  generated.

Degradation of DP in the electrochemical reactor was investigated with the GDE pressurized with  $\text{N}_2$  (conditions for anodic oxidation), and with  $\text{O}_2$  in the absence of catalyst (conditions for  $\text{H}_2\text{O}_2$  generation) and in the presence of  $\text{Fe}^{2+}$  (conditions for the electro-Fenton process). The best results were obtained under electro-Fenton conditions, whereby absorbance at 262 nm was decreased by 84.7%, the concentration of DP was diminished by 92.5%, and TOC was reduced by 62.8% after 90 min of reaction. These results were associated with the increased formation of  $\cdot\text{OH}$  from  $\text{H}_2\text{O}_2$  catalyzed by  $\text{Fe}^{2+}$ , and this gave rise to a reduction in energy consumption for TOC removal of 92.3% compared with anodic degradation, and of 65.8% compared with  $\text{H}_2\text{O}_2$  electrodegradation without catalyst. The findings reported herein confirm the importance of using  $\text{Fe}^{2+}$  in electrodegradation reactions involving the *in situ* generation of  $\text{H}_2\text{O}_2$ .

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