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***Dedicated to Professor Luminița Silaghi-Dumitrescu***
***on the occasion of her 65th anniversary***

# HYDROGEN PEROXIDE ELECTROSYNTHESIS AND DETECTION IN SULPHATE MEDIA

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**ABSTRACT.** The increase of the graphite electrocatalytic activity toward hydrogen peroxide (HP) electrosynthesis (HPE) by the partial electroreduction of $O_2$ can be achieved by *in-situ* electroactivation (EA). Our previous studies completed in strong alkaline media (1 M NaOH) by galvanostatic multi-sequence EA techniques (MSETs) revealed that an adequate graphite EA can improve HPE current efficiency (CE) up to 35 % compared to the unmodified graphite. In order to implement the optimised operational parameters to a micro-pilot scale electrochemical reactor, in a first step, several systems for the on-line HP concentration monitoring were designed and tested. Unfortunately, the preliminary test, even in moderate alkaline media (0.1 M NaOH) revealed that, at concentrations greater that 50 ppm, the HP decomposes intensively in contact with the setup components, disallowing the HP accumulation. As a consequence, for all further experiments, the alkaline supporting electrolyte was replaced with 0.1 M $Na_2SO_4$. In these new conditions, two models of HP on-line detectors (spectrophotometrical and amperometrical) were designed and tested, presenting adequate limit of detection (L.O.D. = 10 ppm and L.O.D. = 0.23 ppm, respectively). Also, the HPE process was studied in sulphate media, using a Pt/graphite wall-jet ring disk electrode system, revealed that the CE can reach a 46 % value for the unmodified electrode and increases up to 52 % when the auto-adaptive galvanostatic MSETs protocol is used.

***Keywords:*** *hydrogen peroxide electrosynthesis, graphite electroactivation, hydrogen peroxide on-line monitoring, wall-jet ring disk electrode, auto-adaptive techniques*

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## INTRODUCTION

Hydrogen peroxide (HP) is widely used in many industrial areas, like chemical industry and environmental protection, but represents also a potential energy carrier. During the last decades, in order to counteract the main drawbacks of the consecrated anthraquinone based process for the HP production [1], significant efforts have been dedicated to develop efficient and *on-site/in-situ* HP production technologies, which can reduce considerably the cost for synthesis, separation, transport, storage and handling [2]. The methods based on the direct HP synthesis from $H_2$ and $O_2$ in plasma assisted [3] or catalytic [4] reactors allow the decentralized production of HP in continuous mode but still present the potential risk of $H_2/O_2$ gas mixture explosion. The HP electrosynthesis (HPE) by the partial electroreduction of $O_2$ represents another extremely studied alternative. In spite of the fact that, in special conditions, the concentration of the accumulated HP can reach values up to 3.6 M (~ 122 g/L) [5], in almost all other studies, final concentrations between 3 ppm [6] and 700 ppm [7] were reported. Even at low HP accumulated concentrations, below 50 ppm, the interest for the HPE remains high due to the fact that, at this reduced level, HP allows the direct degradation of certain pollutants [8] and the generation of the electro-Fenton reagent, a more powerful and versatile depolluting agent [9 - 13]. Irrespective to the design of the electrochemical reactor used for the HPE process (*i.e.* divided or undivided batch reactors, filter-press, flow-through or wall-jet micro-reactors [14]), in almost all studies, the modified or unmodified carbonaceous materials, in 2D or 3D shapes, were used as cathode. Among them, the compact graphite electrodes present major advantages (*i.e.* inexpensive and facile production, high selectivity and conductivity), recommending them for the design of reliable small scale plants for *on-site* and/or *in-situ* HPE. Unfortunately, the low specific surface of the compact graphite requires consistent studies dedicated to the increase of its electrocatalytic activity toward HPE by chemical, physical or electrochemical activation (EA).

In this context, the results of our previous studies [14] accomplished in strong alkaline media (1 M NaOH) by auto-adaptive galvanostatic multi-sequence electroactivation techniques (MSETs) revealed that the adequate graphite EA can improve HPE current efficiency (CE) up to 35 % compared to the unmodified compact graphite. In consequence, we decided to implement the optimal operational parameters at a micro-pilot scale electrochemical reactor with recirculation and HP accumulation capability. In order to accomplish this goal and better understand the influence of the new experimental parameters on the HPE process, we found out that is mandatory to design and validate an accurate and reliable flow-through detector able to monitor, *on-line* and *in-situ*, the concentration of accumulated HP.

Unfortunately, the preliminary test, accomplished in a moderate alkaline media (0.1 M NaOH) revealed that, at HP concentration over 50 ppm, it decomposes intensively in contact with the setup components (PTFE and PVC tubes and cells), disallowing the HP accumulation. As a consequence, for all further experiments, the alkaline supporting electrolyte was replaced with a weakly acidic one consisting in 0.1 M $Na_2SO_4$ (pH ~ 4.2). In these new conditions, to models of HP *on-line* detectors (a spectrophotometrical and an amperometrical one) were designed and tested, presenting adequate sensitivity and limit of detection. Also, the HPE process was studies in sulphate media, using a Pt/spectral graphite (Pt/SG) wall-jet ring disk electrode (WJRDE) system, revealing that the CE can be improved using an auto-adaptive galvanostatic MSETs protocol. Additional tests indicate that a symmetrical divided reactor with periodic inversion of the electrodes cannot be used for sulphate media.

## RESULTS AND DISCUSSION

### Design and validation of the flow-through HP detectors

Our previous results revealed that, even in optimal conditions, the increase of the electrosynthesized HP concentration during each passage of the electrolyte through the electrochemical reactor can reach a maximum value of 0.07 ppm (~ $2*10^{-6}$ M). In these conditions, in order to evaluate rigorously the influence of the EA parameters on the HPE efficiency and also the kinetic of the accumulation process, a very sensitive method of HP detection must be used. Many consecrated techniques (*i.e.* the Iodometric-molybdate, Titanium oxalate, Peroxidase enzyme-DPD or Copper-DMP method) [15] accomplish this requirements but are inadequate for flow analysis, especially if the accumulation process is envisaged due to the requirement of permanent addition of specific reagents. In order to overcome this problem, we decided to evaluate the possibility to estimate the HP concentration by spectrophotometry without addition of specific reagents, exploiting the ability of HP to present an intense absorption in the UV range. The preliminary tests were accomplished, at a wavelength ($\lambda$) of 225 nm, in a flow-through spectrometric cell with an optical path length of 10 mm, at a flow rate ($V_f$) of 10 mL/min, using dilute standard solution of HP (10, 20, 50, 100, 250 and 500 ppm) prepared in bi-distilled water. As indicated in Figure 1 and Table 1, if a second order polynomial fitting function ($Y = A + B1*X + B2*X^2$) is used, this method presents acceptable analytical parameters in the studied concentrations range (R = 0.9999 and L.O.D. = 6.5 ppm for a signal to noise ratio (S:N) of 3:1), but the accuracy is poor at concentrations less than 20 ppm.

In the next step, we tried to repeat the same set of measurements in the presence of 0.1 M NaOH in the standard solutions. Unfortunately, during the measurements, we observed, for the standard solutions having concentrations equal to or higher than 50 ppm, an intense HP decomposition, indicated by the gaseous oxygen evolution. This phenomenon, that appeared at the contact between the concentrated standard solutions and the setup elements (PVC and PTFE tubes, spectrophotometric cell), indicates that the available components and materials included in the structure of the designed micro-pilot scale electrochemical reactor are not compatible with the alkaline HP solutions, making, practically, impossible the accumulation of the electrosynthesized HP. In these conditions and based on literature data [9-13], we decided to replace, for all the further experiments, the alkaline supporting electrolyte with a weakly acidic one, consisting in a 0.1 M $Na_2SO_4$ solutions, having a intrinsic pH of around 4.2.

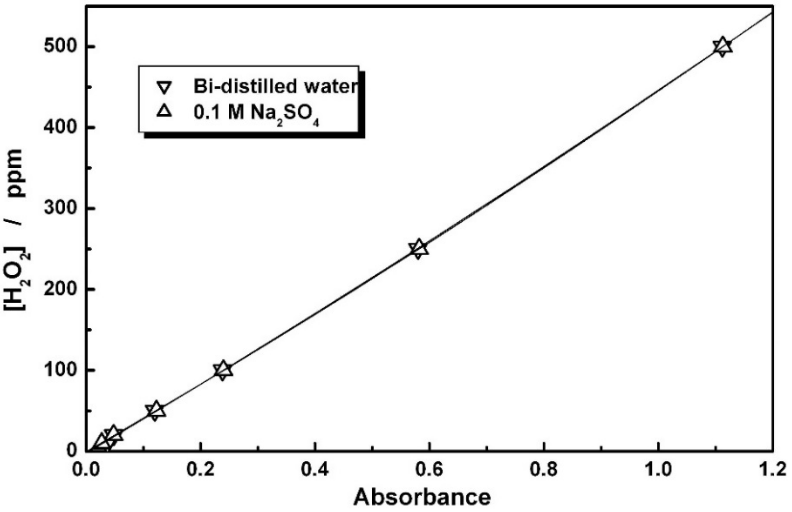

**Figure 1.** Spectrophotometric calibration curves for HP recorded in flow conditions in bi-distilled water and 0.1 M $Na_2SO_4$. ($\lambda$= 225 nm, $V_f$ = 10 mL/min.)

**Table 1.** Analytical parameters evaluated for the UV spectrophotometric detection of HP in flow conditions in bi-distilled water and 0.1 M $Na_2SO_4$.

| Solution | A | B1 | B2 | R | L.O.D. |
|---|---|---|---|---|---|
| Bi-distilled water | -2.3±1.7 | 420±11 | 28±9 | 0.99995 | 6.5 ppm |
| 0.1 M $Na_2SO_4$ | -0.5±0.4 | 410±3 | 36±2 | 0.99999 | 10 ppm |

At this point, in order to verify that the new supporting electrolyte does not interact with the HP in the investigated concentrations range, the previous measurements were repeated in the presence of 0.1 M $Na_2SO_4$. As it can be seen from Figure 1 and Table 1, the new calibration curve is quasi-identical with that recorded in bi-distilled water and the analytical parameters preserved very similar values, excepting the L.O.D. that degraded slightly. In these conditions, we conclude that de designed HP detection method can be used successfully during the accumulation experiments, but only at concentration greater that 10 ppm. Moreover, the detector is, practically, insensitive to the electrolyte flow rate, but presents failures risk if gaseous bubbles remain entrapped inside of the optical path.

As pointed before, in order to quantify rigorously the increase of the electrosynthesized HP concentration after each passage of the electrolyte through the electrochemical reactor, a more sensitive detector must be used. In order to fulfil this requirement, an original dedicated 3-electrodes flow-through amperometric detector (described in the EXPERIMENTAL SECTION) was designed and tested. Using this new detector, 5 calibration curves were recorded at flow rates of 2, 5, 10, 15 and 20 mL/min., in an extended range of standard HP solutions (5, 10, 20, 50, 75, 100, 250 and 500 ppm) prepared in 0.1 M $Na_2SO_4$. As indicated in Figure 2 and Table 2, if a similar second order polynomial fitting function is used, this new method presents excellent analytical parameters in the studied concentrations and flow rates ranges: R between 0.99996 and 0.99999 and L.O.D. between 0.15 and 0.23 ppm for a S:N of 3:1.

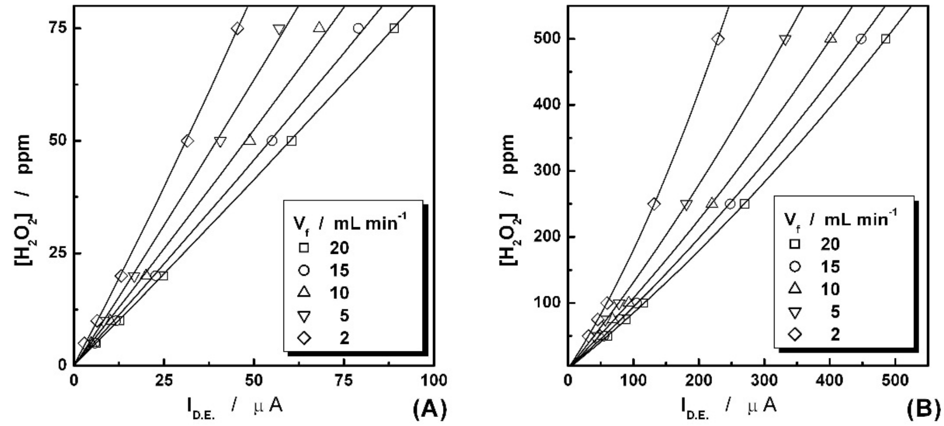

**Figure 2.** Amperometric calibration curves for HP recorded in 0.1 M $Na_2SO_4$ at different flow rates in the domain of reduced (A) and increased (B) concentrations ($\varepsilon_{D.E.}$ = 0.7 V vs. Ag/AgCl/$KCl_{SAT}$)

**Table 2.** Analytical parameters evaluated for the amperometric detection of HP in flow conditions in 0.1 M $Na_2SO_4$.

| $V_f$ [mL/min.] | A | B1 | B2*$10^4$ | R | L.O.D. [ppm] |
|---|---|---|---|---|---|
| 2 | 0.003±0.3 | 1.512±0.010 | 29±0.44 | 0.99999 | 0.23 |
| 5 | -0.22±0.8 | 1.233±0.016 | 8.2±0.50 | 0.99997 | 0.18 |
| 10 | 0.17±0.9 | 1.016±0.017 | 5.7±0.42 | 0.99996 | 0.15 |
| 15 | 0.07±0.7 | 0.887±0.011 | 5.1±0.24 | 0.99998 | 0.14 |
| 20 | 0.005±0.5 | 0.803±0.007 | 4.6±0.13 | 0.99999 | 0.15 |

Based on the obtained result, we conclude that de designed HP amperometric detector can be used successfully during the HPE experiments, with or without accumulation. Obviously, the detector response depends on the flow rate, but the HP concentration can be easily calculated based on the corresponding calibration curve. Also, the vertical position of the detecting electrode reduces the failures risk due to the gaseous bubbles fixation on the electrode surface.

### HPE tests using 0.1 M $Na_2SO_4$ as supporting electrolyte

Prior to the HPE experiments, the collecting efficiency (N) of the WJRDE system was evaluated by hydrodynamic voltammetry with linear scan of the potential (HVLSP), at flow rates of 1, 2.5, 5 and 10 mL/min, using the fero/feri redox system. Based on the calculated N values, the CE values for the HPE process in sulphate media were evaluated by HVLSP at the same flow rates, the obtained results being presented in Figure 3.

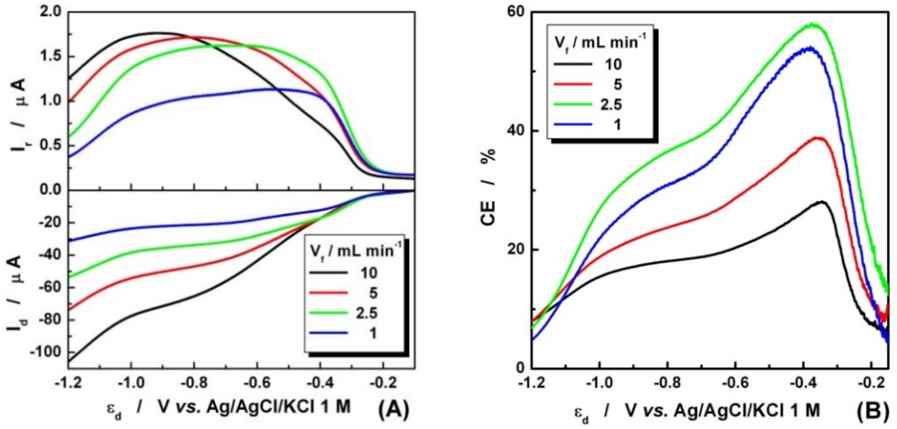

**Figure 3.** Voltamograms recorded by HVLSP on the Pt/SG WJRDE at different $V_f$ in 0.1 M $Na_2SO_4$ air saturated solution (A) and the corresponding CE evolution (B). (v = 5 mV/s, $\varepsilon_r$ = 0.7 V vs. Ag/AgCl/KCl 1 M)

As it can seen from Figure 3, a maximal CE value of ~ 58 % can be obtained at a flow rate of 2.5 mL/min. and a disc potential ($\varepsilon_d$) of -0.38 V, corresponding to a disc current ($I_d$) of -16 μA. Supplementary, these evolutions of the ring currents ($I_r$) and the CE values suggest that, in sulphate media, the adsorption of the dissolved $O_2$ on the electrode surface and desorption of the HPE products is considerable slower than in alkaline media, requiring additional studies able to elucidate the corresponding mechanism.

Based on the promising results obtained by HVLSP, we decided to test if the EA protocols optimised in alkaline media can be applied in sulphate media. After several preliminary measurements (results not shown), we found that the best results can be obtained following the auto-adaptive galvanostatic MSETs protocol, the corresponding results and the optimised parameters being presented in Figure 4, where the invoked terms are explained in our previous work [14].

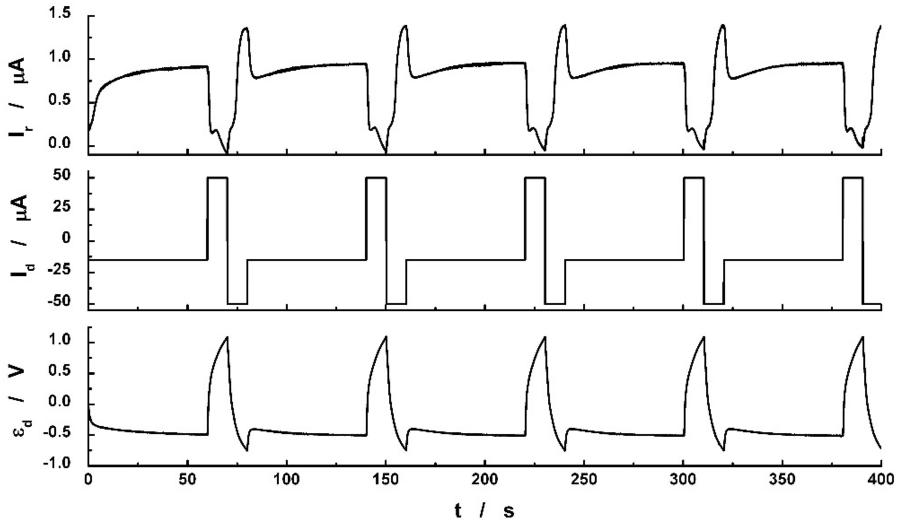

**Figure 4.** The evolution of $I_r$, $I_d$ and $\varepsilon_d$ during 5 cycles of galvanostatic auto-adaptive EA and HPE in 0.1 M $Na_2SO_4$ solution. ($V_f$ = 2.5 mL/min.; $\varepsilon_{AS,\,MAX}$ = +1.2 V; $\varepsilon_{PRS,\,MIN}$ = -0.8 V; $T_{PS}$ = 60 s; $I_{AS.}$= +50 μA; $I_{PRS.}$= -50 μA; $I_{PS.}$= -15 μA)

Based on the recorded data included in Figure 4, we found that, during the first cycle (corresponding to the inactivated graphite), the CE reached a global value of 46 % and increase to 52 % after 5 cycles of EA. These values are clearly superior to those of 28 % reported for a HPE continuous test accomplished using an unmodified graphite electrode, in very similar condition (0.05 M $Na_2SO_4$ as supporting electrolyte, pH = 3, j = 0.25 mA $cm^{-2}$) [16].

Finally, in order to check the possibility to use the sulphate media for HPE in a symmetrical divided reactor with periodic inversion of the electrodes, we made complementary measurements using rectangular asymmetrical or symmetrical current profiles. The comparison between the signals recorded in these conditions, presented in Figure 5, reveals that, if the symmetric profile current is imposed through the disc electrode, the recorded ring current decrease continuously, from cycle to cycle, indicating an advanced deactivation of the graphite electrode surface. In these conditions, we conclude that the idea of a symmetrical divided reactor with periodic inversion of the electrodes is not applicable when the sulphate media is used.

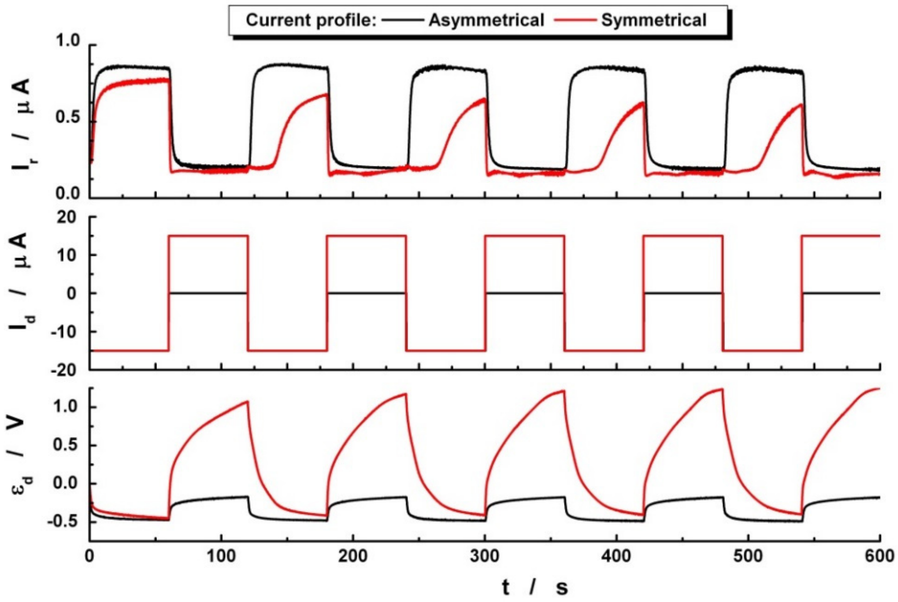

**Figure 5.** Comparison between the evolutions of $I_r$, $I_d$ and $\varepsilon_d$ recorded in 0.1 M $Na_2SO_4$ solution for asymmetrical and symmetrical current profiles. ($V_f$ = 2.5 mL/min., $\varepsilon_r$ = 0.7 V vs. Ag/AgCl/KCl 1 M)

## CONCLUSIONS

Obviously, HPE represents an attractive and eco-friendly alternative for *on-place* and/or *in-situ* production of HP and, consequently, extremely numerous researches are dedicated to this process. All these studies reveal that the evaluation of the HP concentration is a mandatory and essential task, accomplished mainly by periodic sampling and *ex-situ* analysis of the extracted samples using consecrated analytical techniques. In order to eliminate these complicated and time-consuming procedures, we decided to design and validate an accurate and reliable flow-through detector able to monitor *on-line* the concentration of electrosynthesized and accumulated HP. In a first attempt, exploiting the ability of HP to present an intense absorption in the UV range, we proposed a spectrophotometrical flow-through HP detector that works without addition of specific reagents. The preliminary tests, accomplished at a wavelength of 225 nm and using HP standard solutions prepared in bi-distilled water, revealed that, implementing a second order polynomial fitting function, the original designed method presents, for concentrations between 10 and 500 ppm, acceptable analytical parameters (R = 0.9995 and L.O.D. = 6.5 ppm at S:N = 3:1), but the accuracy is unsatisfactory at concentrations less than 20 ppm. The subsequent test, accomplished in a moderate alkaline media (0.1 M NaOH) revealed that, for HP concentrations over 50 ppm, it decomposes intensively in contact with the setup components (PTFE and PVC tubes and cells), compromising the HP accumulation tests. As a consequence, for all further experiments, we decided to replace the alkaline supporting electrolyte with a weakly acidic one consisting in 0.1 M $Na_2SO_4$ with an intrinsic pH of ~ 4.2. In these new conditions, the proposed original detection method presents very similar analytical parameters (R = 0.9999 and L.O.D. = 10 ppm at S:N = 3:1).

In order to improve the L.O.D. value, another original amperometric flow-through HP detector was designed and tested. In the studied concentrations and flow rates ranges, the new detection method presents excellent analytical parameters: R between 0.99996 and 0.99999 and L.O.D. between 0.15 and 0.23 ppm evaluated for a S:N of 3:1.

Finally, using the Pt/SG WJRDE system, the HPE process was studied in sulphate media, using different protocols. The experiments revealed that, for the unmodified electrode, the CE of HPE can reach a value of 46 %, but increases up to 52 % when the auto-adaptive galvanostatic MSETs protocol is used. Unfortunately, additional measurements lead to the conclusion that the idea of a symmetrical divided reactor with periodic inversion of the electrodes cannot be applied when the sulphate media is used as supporting electrolyte.

For future developments, in order to validate the very promising obtained results, the best experimental parameters will be implemented and tested at a micro-pilot scale electrochemical reactor.

## EXPERIMENTAL SECTION

For the spectrophotometric studies, a modular spectrometer (model UV-VIS USB4000), a miniature UV-VIS-NIR light source (model DT-MINI-2-GS), 2 UV optical fibres (model QP600-025-SR) and a flow spectrometric cell (model FIA-Z-SMA-ML-PE), all from Ocean Optics (SUA), were used.

The amperometric detector consists in a cylindrical PTFE flow channel of 3 mm inner diameter in which is fixed a coil (10 turns, 2.5 mm external diameter) of 0.1 mm diameter Pt wire as counter-electrode and, perpendicular to the flow direction, another Pt wire (0.8 mm diameter and 0.5 mm length) as detecting electrode (D.E.). Supplementary, in the superior wall of the channel is fixed a VYCOR® pill that inter-connects the flow channel with an external chamber for the reference electrode, of $Ag/AgCl/KCl_{SAT}$ type.

All the electrochemical measurements, including the calibration of the amperometric HP detector, were carried out in controlled hydrodynamic conditions, using the experimental setup described in detail in our previous work [14, 17]. In the wall-jet cell (WJC), the injector to disc electrode distance was fixed at 1 mm in order to achieve a planar laminar flow. For the HPE experiments, an air saturated ($[O_2]$ ~ 8 ppm) 0.1 M $Na_2SO_4$ aqueous solution was pumped in the WJC at $V_F$ of 1, 2.5, 5 or 10 mL/min. Before each set of HPE experiments, the RDE surface was polished on waterproof emery paper of 1200 grit (Struers, Denmark) and intensively washed with doubly distilled water. All measurements were performed at room temperature (25 ± 1 $^{o}$C).

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