The jet aerator as oxygen supplier for the electrochemical generation of H₂O₂

Pérez, J.F; Llanos, J.; Sáez, C.*; López, C.; Cañizares, P.; Rodrigo, M.A.

Chemical Engineering Department, Facultad de Ciencias y Tecnologías Químicas.

University of Castilla-La Mancha, Edificio Enrique Costa Novella. Av. Camilo José

Cela nº 12, 13071 Ciudad Real, Spain

*Corresponding author: Cristina.saez@uclm.es

Graphical Abstract

Abstract

The hydrogen peroxide is a key and versatile compound that can be readily produced in one-pot electrochemical reactors via the $2e^-$ oxygen reduction reaction. In all the electrolyzers studied up to date, the external aeration is carried out by means of a compressor. In this work, the compressor is substituted by a device based on the Venturi effect to minimize the acquisition, maintenance and operating costs associated to the aeration of the reactor. Interestingly, it was found that this aerator can super saturate in oxygen the solution thanks to the formation of air bubbles. The catalytic effect of carbon black (CB) and/or polytetrafluoroethylene (PTFE) to increase the production of H₂O₂ was studied, observing a synergistic effect

when the CB/PTFE mixture was deposited on the carbon felt cathode. Efficient hydrogen peroxide generation was obtained at 15 mA cm^{-2} : instantaneous production rate of around $9.2 \text{ mg H}_2\text{O}_2 \text{ h}^{-1} \text{ cm}^{-2}$ and a corresponding current efficiency in the order of 90%. The limiting current density increased when the jet aerator was used thanks to *i*) the super saturation of the solution (dissolved oxygen + air bubbles) and *ii*) the ability of the CB/PTFE modified carbon felt to use them as oxygen source. The jet aerator is rather promising for the electrochemical generation of hydrogen peroxide.

Keywords: electrogeneration, hydrogen peroxide, jet aerator, flow-through, carbon felt

1. Introduction

The hydrogen peroxide (H_2O_2) is a versatile and interesting compound with many different domestic and industrial applications [1]. At present, this compound is mainly obtained industrially by the anthraquinone oxidation process with a significant environmental impact derived from the use of organic solvents, metal catalysts and considerable amounts of energy [2, 3]. Because of this, novel and cleaner methods are of great interest.

An interesting alternative is the electro-synthesis by means of the two-electron pathway oxygen reduction reaction (ORR). The ORR is a multi-step reaction following a complex mechanism which, despite its importance in different areas of the electrochemistry, has not been fully understood yet [4, 5]. In a simplified way, the reaction can proceed directly via $4 e^-$ (Equation 1) to water or via $2 + 2 e^-$ also to water, but yielding hydrogen peroxide as stable intermediate (Equation 2) [5]:

Carbonaceous materials exhibit a high overpotential for the $4 e^-$ pathway, probably because of the difficulties in breaking down the strong $O=O$ bond (498 kJ mol^{-1}) [4, 5], and the ORR reaction proceeds mainly via $2 e^-$ pathway in those materials [6]. Different carbonaceous cathodes have already been tested for the electro-generation of hydrogen peroxide from ORR, namely graphite [6-8], carbon cloth [9], carbon sponge [9, 10], reticulated vitreous carbon [6, 11, 12] or carbon felt [6, 9, 13]. It is worth mentioning that an interesting catalytic effect have been obtained in those electrodes fabricated by mixtures of carbon and polytetrafluoroethylene [13-16].

For an adequate performance of the cathodic material, oxygen has to be adequately supplied to its surface. In fact, one of the major limitations of the reduction of

oxygen to produce hydrogen peroxide is the low solubility of the oxygen in water, around 8 mg dm⁻³ under room conditions [6, 8, 17]. Because of this, the way in which the oxygen is supplied to the system is critical in the development of H₂O₂ electrolyzers.

The most straightforward solution is the bubbling of atmospheric air directly to saturate the solution. Those systems may suffer from important mass transfer limitations, normally leading to low limiting current densities. An increase in the saturation level can be obtained, according to Henry's Law [18, 19], by increasing the pressure of the system [8]. Nevertheless, both strategies would lead to an increase in the operating and investment costs of the technology.

Another interesting and widely applied approach for the electro-generation of H₂O₂ are the so-called gas diffusion electrodes (GDEs) [15, 20, 21]. In this aeration system, the electrode (solid) is placed in between the electrolyte (aqueous) and the air inlet (gaseous) acting as a three-phase contactor. This way, the oxygen is supplied directly to the triple interphase without the need for it to be dissolved in the electrolyte, so that, mass transfer resistance is minimized [22]. Thus, moderate-to-high current densities with acceptable current efficiencies are achieved, even using atmospheric air as oxygen source [23]. However, the generous air flow needed to prevent percolation of water through the electrode surface utilization efficiencies lead to very low oxygen utilization efficiency (< 1 % [24]) which results in a waste of energy and over-sizing of compressors in the event of potential industrial application [25, 26].

In any case, all the previous reactor designs for electro-generation of hydrogen peroxide with external aeration include a compressor/compressed air. In a previous work [25], we introduced an aeration device based on the Venturi effect to eliminate this need and minimize the costs related to the acquisition, operation and maintenance of the compression system. The jet aerator (JA), interestingly, is able to generate air bubbles

and super-saturate in oxygen the electrolyte, thus, potentially enabling the electro-generation of hydrogen peroxide at higher current densities. Because of this positive prospect, the electro-generation of hydrogen peroxide using the JA deserves attention.

In this work, the global objective is the study of the JA as a way to provide the oxygen necessary for the electro-generation of hydrogen peroxide. To do this, the catalytic activity of the flow-through cathode is studied in detail and the effect of the current density is evaluated to find out if the jet aerator can certainly increase the limiting current density for the production of hydrogen peroxide in an electrochemical system.

2. Materials and methods

2.1 Experimental set-up

A schematic representation of the experimental set-up is shown in the Figure 1. A picture and a video clip showing the real experimental set up together can be found as supplementary material in Appendix A.

The installation is operated under discontinuous mode. The electrolyte (0.05 M Na_2SO_4 at constant 25 °C) is stored in the tank (filled with 1 dm³) and pumped at a fixed flow rate of 64 dm³ h⁻¹ to the jet aerator. In this device, the air enters into the system due to a pressure difference. A flow-meter connected to the suction point of the jet aerator enables the measurement of the air-flow. The bi-phasic electrolyte-air mixture is fed to the electrochemical cell which is equipped with a funnel-like piece to distribute the flow along the cathodic surface. Then, the flow goes through the CF cathode (circular-shape) supplied by the SGL Group (Wiesbaden, Germany) with a geometric active area of 50 cm² and a geometric active volume of 20 cm³ (0.4 cm thickness). After, the electrolyte reaches the anode (IrO_2 -coated titanium electrode with 50 cm² of active area supplied by Tianode, India) and leaves the cell by an exit located in its upper part. The current is fed by means of titanium and steel plates acting as current collector in the case of the cathode

and the anode, respectively. These current collectors are not in contact with the electrolyte.

2.2 Modification of the carbonaceous materials

Two different procedures were used to add the CB/PTFE mixture to the carbonaceous materials: ultrasonic immersion and hot dripping.

i) Ultrasonic immersion

In this procedure, the electrode is modified following a similar to the one described originally by Yu [13]. This procedure consists of three steps: 1) Pretreatment: 15 minutes of ultrasound washing in acetone + water + water, followed by drying at 80 °C for 24 hours; 2) Immersion: the electrode is soaked for 30 minutes in an ultrasound bath containing an ink with 10 mg/mL-ink of carbon black (Vulcan ® XC72R), 50 mg/mL-ink of polytetrafluoroethylene (from a 60% Teflon ® emulsion solution supplied by ElectroChem, Inc.) and 20 mL/L-ink of *n*-butanol, and 3) Post-treatment: drying at 80 °C for 24 hours and annealing at 360 °C for 1 hour.

ii) Hot dripping

For the study of the CB/PTFE mass added to the cathode, the following procedure was used: 1) Pretreatment: 3 hours in boiling NaOH 1 M and subsequently rinsed with deionized water up to neutrality and dried at 80 °C for °C; 2) Hot dripping: the carbon felt is weighted and put on top of a house-made hot plate at 100 °C. Then, the CB/PTFE mixture is added slowly by dripping; and 3) Post-treatment: drying at 80 °C for 24 hours and annealing at 360 °C for 1 hour. The weight increment was calculated as the difference between the initial and after-annealing mass of each carbon felt piece.

2.3 H₂O₂ measurement

Hydrogen peroxide concentration was measured by the potassium titanium (IV) oxalate method [27] according to standard DIN 38 409, part 15, DEV-18. Titanium solution was supplied by Fluka and absorbance was determined at $\lambda = 407$ nm by means of an Agilent 300 Cary series UV-Vis spectrophotometer.

2.4 O₂ measurement

The concentration of dissolved oxygen is measured using an oxy-meter sensIONtm + supplied by HACH with two calibration points (0% and 100%). The equipment was calibrated immersing the sensor in the same electrolyte solution at the same temperature and pressure of the experiments. The 0% point is obtained after bubbling N₂ in the electrolyte for 30 minutes at a high flow rate. The 100% point is obtained after bubbling air for 30 minutes.

2.5 SEM pictures and EDAX analysis

The pictures of the surface were obtained by means of a Scanning Electron Microscope (SEM) FEI model QUANTA 250 working under low vacuum. The EDAX analyses were performed with an Apollo X (Ametek, U.S.A.) coupled to the previous SEM system.

3. Results

3.1 Aeration capacity of the jet cell

Firstly, the aeration capacity of the jet aerator system was estimated. This device consists in a pipeline with a nozzle opened to the atmosphere in the constriction, and thanks to the Venturi effect is able to supply air to a reactor in the absence of a compressor. Because of the high liquid velocity in the Venturi throat, the bubbles are broken into smaller pieces by the consequently high shear rates, favoring the oxygen saturation of the solution [28]. Once the saturation is achieved, the air introduced in the system must remain in the form of bubbles, super-saturating the solution. This way, a

concentration of oxygen higher than the equilibrium described by Henry's law would be achieved.

In order to determine the aeration capacity, the solution in the tank (1 dm³) was bubbled with N₂ to strip all the oxygen. After 15 minutes, the pump was connected and the jet aerator started to supply oxygen. After just 1 minute, 75 % of saturation was measured and the 99% saturation level was reached after 5 minutes (Figure 2).

Equation 3 presents an oxygen mass balance in a discontinuous system as the one used in the present work. In this Equation, C_{O_2} stands for the concentration of oxygen (mg dm⁻³), $C^*_{O_2}$ for the saturation concentration (maximum solubility, 8 mg dm⁻³), K_La for the volumetric mass transfer coefficient (h⁻¹) and V for the volume of the system (dm³). By fitting experimental data to the mass balance of oxygen shown in Eq. 3,) the mass transfer coefficient can be obtained [29] and related to the real oxygenation capacity (OC, g O₂ h⁻¹) by Eq. 4:

$$\frac{dC_{O_2}(t)}{dt} = K_La \cdot (C^*_{O_2} - C_{O_2}(t)) \quad (3)$$

$$OC = K_La \cdot V \cdot C^*_{O_2} \quad (4)$$

Considering the aforementioned equations, the mass transfer coefficient (K_La) is 43.2 h⁻¹ and the value of the OC is 0.35 g O₂ h⁻¹. According to the measurement of the flow meter in the inlet of the jet aerator, an oxygen flow of 4.13 g O₂ h⁻¹ is supplied in the absence of an external compressor. This means that the efficiency (percentage of oxygen that is transferred into the liquid) of the jet aerator is 8.5 % and the rest of it remains in the form of bubbles, supersaturating the solution without increasing the pressure using a simple and cheap device.

3.2 Study of the catalytic effect of carbon black and PTFE on the cathode performance

Carbon felt electrode was selected as cathode because of its high 3D surface area, chemical and mechanical resistance, low cost and commercial availability [30]. The cathode was fed in a flow-through configuration in which the electrolyte is forced to circulate across the cathode to achieve an intimate contact between solid-liquid-gas interphase and, therefore, a high mass transport rate of oxygen to the cathode surface is expected [25, 31]. Figure 3 shows the evolution of H_2O_2 concentration conducted in the jet cell under a given current density of 20 mA cm^{-2} (1 A) using both modified and unmodified CFs.

As can be seen, the maximum concentration of hydrogen peroxide using the unmodified CF was as low as 33 mg dm^{-3} after 45 minutes of experiment. Previous studies showed that the efficiency of CF towards the generation of hydrogen peroxide can be greatly enhanced by adding a mixture of carbon black and polytetrafluorethylene [13, 32]. The material tagged as CB/PTFE/CF was modified by ultrasonic immersion, according to the procedure proposed by Yu [13] using an ink containing CB/PTFE 1:5 (best ratio in Yu's work). In the case of CB/CF, the concentration of hydrogen peroxide slightly increases at the beginning, probably due to an increase in the surface area. After 30 minutes of experiment, the concentration started to decrease. It was also observed that the set-up (especially the pipelines) was gradually covered by a black dust. Therefore, the decreasing in the concentration may be explained by the detachment of the carbon black particles from the carbon felt fibers. The PTFE/CF performed poorly at the beginning, probably due to the surface coverage of the PTFE, but the concentration increased progressively up to 63 mg dm^{-3} . This improvement is attributed to an increase in the hydrophobicity, preventing the wettability of the pores.

On the other hand, when the electrode CB/PTFE/CF was employed, the concentration of hydrogen peroxide dramatically increased. It can be seen in Figure 3 that

this modification clearly outperforms the rest of the electrodes, achieving an instantaneous (after 15 min) current efficiency of approximately 70%. In this case, no black dust was observed in the set-up, because of the binding effect of the PTFE. This way, it was demonstrated that it is necessary the simultaneous addition of CB and PTFE to increase the production of hydrogen peroxide in carbon felt electrodes. Previous studies also observed a better performance in the production of hydrogen peroxide, directly by measuring H_2O_2 concentration [13, 32, 33] or indirectly by obtaining better organic removal in an Electro-Fenton process [34].

Next parameter to be studied is the CB/PTFE loading at a fixed ratio CB/PTFE of 1:5. Using the ultrasonic immersion, it is difficult to control the total amount of CB/PTFE added to the carbon felt support. Because of that, an alternative methodology for the modification of the carbon felt (described in section 2.2) was applied: the hot dripping. In those experiments, the inks were prepared in every case with a fixed 1:5 ratio but a total volume of CB-PTFE so as to achieve 0.1 - 1.3 g CB-PTFE / g CF in each piece of carbon felt.

The electro-generation of hydrogen peroxide was evaluated under the same operating conditions of the previous experiments and the results are shown in Figure 4.

According to the Figure 4, the concentration of hydrogen peroxide increases with CB-PTFE loading. At low loadings (0.1 g CB-PTFE / g CF), the catalytic effect is certainly poor and the concentration obtained is similar to the one unmodified, thus, this loading is clearly insufficient. This fact may be caused by a poor coverage of the electrode fibers. At 0.5 and 0.7 g CB-PTFE / g CF the effect is already noticeable and the concentration is about one order of magnitude higher than in the case of the unmodified, achieving 240 and 345 $\text{mg H}_2\text{O}_2 \text{ dm}^{-3}$ after two hours. At high CB-PTFE loadings (1 and

1.3 g CB-PTFE / g CF), the concentration obtained after two hours is increasingly higher, achieving a maximum of 445 and 583 mg H₂O₂ dm⁻³, respectively. However, at smaller reaction times (and concentrations of hydrogen peroxide), the difference between 1 and 1.3 g CB-PTFE / g CF is not that significant. The reason behind this behavior is found in the kinetics of the destruction of H₂O₂ in the cathode (Eq. 5) and the anode (Eq. 6) [21, 35]:

A degradation test was performed adding 1,200 mg H₂O₂ dm⁻³ to the electrolyte at the beginning of the experiment using a bare carbon felt as cathode (Figure 5):

Three regions were identified in the kinetics of the destruction. At high concentration, the decay fits a straight line, indicating that the process is under current control (Region A in Figure 5). At approximately 200-300 mg H₂O₂ dm⁻³ appears the mixed control (Region B) and approximately and below 200 mg H₂O₂ dm⁻³ the destruction starts to be controlled by the mass transfer (Region C) of the hydrogen peroxide to the electrode surfaces.

Interestingly, the difference in the accumulation of hydrogen peroxide between 0.7, 1 and 1.3 g CB-PTFE / g CF in Figure 4 begins at 30 minutes approximately, when the concentration is around 200 mg H₂O₂ dm⁻³, that is to say, when the concentration is sufficiently high not to be controlled by mass transfer. It was hypothesized that the uneven distribution of the CB/PTFE along the thickness of the cathode would make that part of the fibers remain bare, without coverage, and this would also lead to a fast destruction of hydrogen peroxide. This is reasonable because the boiling of the solvent during the fabrication process lead to the accumulation of a bigger proportion of CB/PTFE in the surface of the cathode. This hypothesis was confirmed by observing different modified

materials under a SEM microscope. As an example, the Figure 6 shows SEM images and EDAX analysis of the upper part (A and B) and a transversal cut (C and D) of the electrode.

The fibers of the upper part are clearly coated with a rough crust with an average diameter in the order of 11 μm . A similar surface morphology was obtained by other authors using similar CB/PTFE deposition techniques [13, 32, 33]. The EDAX analysis indicates that this coverage is predominantly composed by carbon and fluorine, being the latter directly associated with PTFE content. On the other hand, the fibers of the core are predominantly uncovered, exhibiting a lower diameter (around 8 μm). Furthermore, the EDAX analysis confirms the absence of fluorine and, thus, PTFE in the fibers of the core. This way, the part uncovered fibers would lead predominantly to the destruction of hydrogen peroxide, affecting negatively to the accumulation of hydrogen peroxide.

Therefore, it is important to assure the uniform coverage or deposition of the CB/PTFE mixture throughout the electrode surface for the adequate design of a CB/PTFE/CF flow-through electrode.

3.3 Study of the current intensity

Current intensity is one of the most important parameters in any given electrochemical cell. In the particular case of an electrolyzer for the production of hydrogen peroxide, it is interesting to work with a current intensity as high as possible since higher current per time unit implies faster generation, lower reactor size for a given production and, therefore, lower investment costs.

The effect of current intensity was studied within the range 0.5 to 1.5 A, resulting in a current density from 10 to 30 mA cm^{-2} with respect to the geometrical area of the cathode. The concentration versus time curves obtained for two different electrodes

(synthesized under the same conditions but in different baths) are plotted in Figure 7.a and b.

In general terms, the higher the current density, the faster is the accumulation of hydrogen peroxide. In particular, there is an important improvement when the current density is shifted from 10 to 15 mA cm⁻². Further increase to 20, 25 and 30 mA cm⁻² does not lead to significantly better concentration of the product of interest. This behavior may be explained considering the limiting current intensity [26, 36]. If the electrode surface is provided with a sufficient flow of oxygen, the reaction that predominantly takes place over carbonaceous materials is the reduction of oxygen via 2 electrons to yield hydrogen peroxide (Equation 1). However, if there is an excess of current (working current density about the limiting one) with respect to oxygen in the cathode, its concentration would be zero and other reactions may take place [7]. Among them, the most important is the reduction of hydrogen peroxide to water (Equation 5). In this parasitic reaction, not only the charge is not used to generate the product of interest but is used in decomposing the already existing one. This way, current efficiency towards hydrogen peroxide is significantly reduced.

On the other hand, in Figures 7.c and d the same experiments are plotted versus the applied electric charge. In fact, when the current density is increased from 10 to 15 mA cm⁻² there is an improvement in both production rate and current efficiency, meaning that the process is under charge transfer control. That is, working below the limiting current intensity. However, when the current is increased up to 20 mA cm⁻² or higher, there is a slight increase in production rate because more current is passing through the system for a given period of time, but the current efficiency decreases in the order 20 > 25 > 30 mA cm⁻².

Considering the aforementioned results, the value that combines a high production rate and current efficiency turned out to be 15 mA cm^{-2} . At this current density, an instantaneous (concentration after 8 minutes) production rate of $8.48 - 9.84 \text{ mg H}_2\text{O}_2 \text{ h}^{-1} \text{ cm}^{-2}$ and a corresponding CE of $88 - 98 \%$ (Electrode 1 and 2, respectively) and accumulation rate (after 1 h) of $5.28 - 5.16 \text{ mg H}_2\text{O}_2 \text{ h}^{-1} \text{ cm}^{-2}$ with a CE of 55% were measured. A comparison can be performed with those studies that previously worked with CB/PTFE CF in flow-through reactors. In these cases, a maximum concentration of hydrogen peroxide around 60 [33] or $200 \text{ mg H}_2\text{O}_2 \text{ dm}^{-3}$ [32] was reported. Nevertheless, those authors focused mainly on the abatement of organics but the production of hydrogen peroxide was not comprehensively investigated.

Finally, the study of the current density also provide information about the performance of the jet aerator. Four current densities were studied under different aeration systems. At the beginning of the experiment, the jet aerator is closed and nitrogen was bubbled in the tank for 10 minutes to remove the dissolved oxygen. After this time, the power supply is switched on and the concentration of hydrogen peroxide is measured each 10 minutes. After 30 minutes, the nitrogen bubbling is substituted by air bubbling, saturating the electrolyte with dissolved oxygen but keeping the jet aerator closed yet. Therefore, for the next 30 minutes, the hydrogen peroxide is only produced from dissolved oxygen. In the last 30 minutes, the air bubbling is stopped and the jet aerator is opened. During this period, the hydrogen peroxide would be produced both from dissolved oxygen and air bubbles. The experiments were conducted with the same electrode in the order $10 - 20 - 30 - 15 \text{ mA cm}^{-2}$ and the results are shown in the Figure 8.

In every case, the production under nitrogen bubbling is close to, but not strictly, zero because the anode produces small concentrations oxygen from the anodic O_2

evolution reaction. Apart from this, different behaviors were observed at low (10 and 15 mA cm⁻²) and high (20 and 30 mA cm⁻²) current intensities. At low current densities, the dissolved oxygen is enough to sustain the production. In fact, the opening of the jet aerator, and the concomitant super-saturation of the solution, does not make any difference.

On the other hand, at high current densities (20 and 30 mA cm⁻²) the concentration of hydrogen peroxide is much lower than in the case of low current densities. As experimental data evidence, at high current densities the oxygen supplied by dissolved oxygen is not enough to react with all the current available at the cathode. Therefore, the excess of electric current must be employed in parasitic reactions, mainly in hydrogen peroxide reduction (Eq. 5), resulting in the low concentration measured in the production under dissolved oxygen. However, as soon as the jet aerator is opened, even at high current densities, the concentration of hydrogen peroxide dramatically increases.

This experimental result can be explained considering the aeration capacity of the jet aerator. Assuming a current efficiency of 100% towards hydrogen peroxide at the highest current under studied in this work (1.5 A), the consumption of oxygen is 0.90 g O₂ h⁻¹ whereas, as previously mentioned in Section 3.1, the oxygen flow supplied by the jet aerator at the working liquid flow is 4.13g O₂ h⁻¹. This way, the electrolyte is continuously saturated and the excess oxygen remain in the form of bubbles. It is interesting since oxygen is more concentrated in atmospheric, even under room conditions (≈ 8 mM), than in the aqueous electrolyte (≈ 0.25 mM) and previous studies concluded that carbon/PTFE cathodes can produce hydrogen peroxide more efficiently when are fed with oxygen in gas phase [14, 16].

351 Considering the aforementioned data, this result demonstrates that the limiting
352 current density is higher when the jet aerator is used as a consequence of the generation
353 of a super-saturated solution with dissolved oxygen and undissolved air bubbles.

354 **4. Conclusions**

355 The jet aerator super-saturates the solution in oxygen at atmospheric pressure using a
356 simple and cheap device. Also, it has been observed that the simultaneous addition of CB-
357 PTFE to CF electrodes results in a synergistic catalytic effect on the production rate of
358 hydrogen peroxide. Attention has to be paid to the distribution of the CB-PTFE along the
359 surface since it plays a key role in the performance of flow-through CF electrodes for
360 hydrogen peroxide generation. According to the experimental data, CB-PTFE modified
361 electrodes can use both dissolved oxygen and air bubbles as oxygen source to produce
362 hydrogen peroxide. The jet aerator increased the limiting current density, allowing the
363 efficient production of H_2O_2 at 15 mA cm^{-2} .

365 **Acknowledgements**

366 Authors wish to express their gratitude to Junta de Comunidades de Castilla-La Mancha
367 for the funding through the project PEII-2014-039-P and to the University of Castilla-La
368 Mancha for the pre-doctoral contract of José Fernando Pérez within the framework of the
369 Plan Propio I+D. The spanish Ministry of Economy, Industry and Competitiveness and
370 the European Union through the project CTR2016-79197-R is also gratefully
371 acknowledged.

372 **5. References**

373 [1] C.W. Jones, Applications of Hydrogen Peroxide and Derivatives, Royal Society of
374 Chemistry 1999.

375 [2] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Hydrogen Peroxide
 376 Synthesis: An Outlook beyond the Anthraquinone Process, *Angewandte Chemie*
 377 International Edition 45 (2006) 6962.

378 [3] R. Ciriminna, L. Albanese, F. Meneguzzo, M. Pagliaro, Hydrogen Peroxide: A Key
 379 Chemical for Today's Sustainable Development, *ChemSusChem* 9 (2016) 3374.

380 [4] É. Mahé, P. Bornoz, E. Briot, J. Chevalet, C. Comninellis, D. Devilliers, A selective
 381 chemiluminescence detection method for reactive oxygen species involved in oxygen
 382 reduction reaction on electrocatalytic materials, *Electrochimica Acta* 102 (2013) 259.

383 [5] D. Pletcher, F.C. Walsh, *Industrial Electrochemistry*, Springer Netherlands 1990.

384 [6] E. Petrucci, A. Da Pozzo, L. Di Palma, On the ability to electrogenerate hydrogen
 385 peroxide and to regenerate ferrous ions of three selected carbon-based cathodes for
 386 electro-Fenton processes, *Chemical Engineering Journal* 283 (2016) 750.

387 [7] Z. Qiang, J.-H. Chang, C.-P. Huang, Electrochemical generation of hydrogen
 388 peroxide from dissolved oxygen in acidic solutions, *Water Research* 36 (2002) 85.

389 [8] O. Scialdone, A. Galia, C. Gattuso, S. Sabatino, B. Schiavo, Effect of air pressure on
 390 the electro-generation of H₂O₂ and the abatement of organic pollutants in water by
 391 electro-Fenton process, *Electrochimica Acta* 182 (2015) 775.

392 [9] O. García-Rodríguez, J.A. Bañuelos, A. Rico-Zavala, L.A. Godínez, F.J. Rodríguez-
 393 Valadez, Electrocatalytic activity of three carbon materials for the in-situ production of
 394 hydrogen peroxide and its application to the electro-fenton heterogeneous process,
 395 *International Journal of Chemical Reactor Engineering* 14 (2016) 843.

396 [10] A. Özcan, Y. Şahin, A. Savaş Koparal, M.A. Oturan, Carbon sponge as a new
 397 cathode material for the electro-Fenton process: Comparison with carbon felt cathode
 398 and application to degradation of synthetic dye basic blue 3 in aqueous medium, *Journal*
 399 *of Electroanalytical Chemistry* 616 (2008) 71.

400 [11] Y.A. Bustos, J.G. Rangel-Peraza, M.N. Rojas-Valencia, E.R. Bandala, A. Álvarez-
 401 Gallegos, L. Vargas-Estrada, Treatment of industrial effluents by electrochemical
 402 generation of H₂O₂ using an RVC cathode in a parallel plate reactor, *Environmental*
 403 *Technology (United Kingdom)* 37 (2016) 815.

404 [12] M.M. Saleh, M.I. Awad, T. Okajima, K. Suga, T. Ohsaka, Characterization of
 405 oxidized reticulated vitreous carbon electrode for oxygen reduction reaction in acid
 406 solutions, *Electrochimica Acta* 52 (2007) 3095.

407 [13] F. Yu, M. Zhou, X. Yu, Cost-effective electro-Fenton using modified graphite felt
 408 that dramatically enhanced on H₂O₂ electro-generation without external aeration,
 409 *Electrochimica Acta* 163 (2015) 182.

410 [14] Y. Sheng, Y. Zhao, X. Wang, R. Wang, T. Tang, Electrogenation of H₂O₂ on a
 411 composite acetylene black–PTFE cathode consisting of a sheet active core and a
 412 dampproof coating, *Electrochimica Acta* 133 (2014) 414.

413 [15] W.R.P. Barros, T. Ereno, A.C. Tavares, M.R.V. Lanza, In Situ Electrochemical
 414 Generation of Hydrogen Peroxide in Alkaline Aqueous Solution by using an
 415 Unmodified Gas Diffusion Electrode, *ChemElectroChem* 2 (2015) 714.

416 [16] I. Yamanaka, T. Murayama, Neutral H₂O₂ synthesis by electrolysis of water and
 417 O₂, *Angewandte Chemie (International ed. in English)* 47 (2008) 1900.

418 [17] M. Geng, Z. Duan, Prediction of oxygen solubility in pure water and brines up to
 419 high temperatures and pressures, *Geochimica et Cosmochimica Acta* 74 (2010) 5631.

420 [18] W. Henry, Experiments on the Quantity of Gases Absorbed by Water, at Different
 421 Temperatures, and under Different Pressures, *Philosophical Transactions of the Royal*
 422 *Society of London* 93 (1803) 29.

423 [19] R.M. Rosenberg, W.L. Peticolas, Henry's Law: A Retrospective, *Journal of*
 424 *Chemical Education* 81 (2004) 1647.

425 [20] G.V. Kornienko, G.A. Kolyagin, V.L. Kornienko, V.A. Parfenov, Graphitized
 426 carbon materials for electrosynthesis of H₂O₂ from O₂ in gas-diffusion electrodes,
 427 Russian Journal of Electrochemistry 52 (2016) 983.

428 [21] H. Luo, C. Li, C. Wu, X. Dong, In situ electrosynthesis of hydrogen peroxide with
 429 an improved gas diffusion cathode by rolling carbon black and PTFE, RSC Advances 5
 430 (2015) 65227.

431 [22] H. Luo, C. Li, C. Wu, W. Zheng, X. Dong, Electrochemical degradation of phenol
 432 by in situ electro-generated and electro-activated hydrogen peroxide using an improved
 433 gas diffusion cathode, Electrochimica Acta 186 (2015) 486.

434 [23] M. Panizza, G. Cerisola, Electrochemical generation of H₂O₂ in low ionic strength
 435 media on gas diffusion cathode fed with air, Electrochimica Acta 54 (2008) 876.

436 [24] F. Yu, M. Zhou, L. Zhou, R. Peng, A Novel Electro-Fenton Process with H₂O₂
 437 Generation in a Rotating Disk Reactor for Organic Pollutant Degradation,
 438 Environmental Science & Technology Letters 1 (2014) 320.

439 [25] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo,
 440 Electrochemical jet-cell for the in-situ generation of hydrogen peroxide,
 441 Electrochemistry Communications 71 (2016) 65.

442 [26] E. Brillas, C.A.M. Huitle, Synthetic Diamond Films: Preparation,
 443 Electrochemistry, Characterization and Applications, Wiley 2011.

444 [27] G. Eisenberg, Colorimetric Determination of Hydrogen Peroxide, Industrial &
 445 Engineering Chemistry Analytical Edition 15 (1943) 327.

446 [28] T.R. Cumby, A review of slurry aeration 3. Performance of aerators, Journal of
 447 Agricultural Engineering Research 36 (1987) 175.

- [29] F. Dorado, M.A. Rodrigo, I. Asencio, Assembly of a Multiphase Bioreactor for Laboratory Demonstrations: Study of the Oxygen-Transfer Efficiency in Activated Sludge, *The Chemical Educator* 7 (2002) 90.
- [30] G. Coria, T. Pérez, I. Sirés, J.L. Nava, Mass transport studies during dissolved oxygen reduction to hydrogen peroxide in a filter-press electrolyzer using graphite felt, reticulated vitreous carbon and boron-doped diamond as cathodes, *Journal of Electroanalytical Chemistry* 757 (2015) 225.
- [31] E. Heitz, G. Kreysa, *Principles of Electrochemical Engineering: Extended Version of a DECHEMA Experimental Course*, VCH 1986.
- [32] G. Ren, M. Zhou, M. Liu, L. Ma, H. Yang, A novel vertical-flow electro-Fenton reactor for organic wastewater treatment, *Chemical Engineering Journal* 298 (2016) 55.
- [33] L. Ma, M. Zhou, G. Ren, W. Yang, L. Liang, A highly energy-efficient flow-through electro-Fenton process for organic pollutants degradation, *Electrochimica Acta* 200 (2016) 222.
- [34] J. Tian, J. Zhao, A.M. Olajuyin, M.M. Sharshar, T. Mu, M. Yang, J. Xing, Effective degradation of rhodamine B by electro-Fenton process, using ferromagnetic nanoparticles loaded on modified graphite felt electrode as reusable catalyst: in neutral pH condition and without external aeration, *Environmental Science and Pollution Research* 23 (2016) 15471.
- [35] J.K. Edwards, B. Solsona, E.N. N, A.F. Carley, A.A. Herzing, C.J. Kiely, G.J. Hutchings, Switching Off Hydrogen Peroxide Hydrogenation in the Direct Synthesis Process, *Science* 323 (2009) 1037.
- [36] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, *Chemical Reviews* 109 (2009) 6541.

Figure captions

Figure 1. Experimental set-up. 1. Funnel-like piece 2. Support plate 3. Rubber gasket 4. CF electrode 5. Titanium current feeder 6. Plastic supporting mesh 7. Metacrylate spacer 8. IrO₂-based anode

Figure 2. Oxygenation capacity of the jet aerator. Electrolyte: 1 dm³ 0.05 M Na₂SO₄. ● Experimental points; – Prediction of the fitted model.

Figure 3. Concentration – time curves for the electrogeneration of hydrogen peroxide on carbon felt. $j = 20 \text{ mA cm}^{-2}$. Electrolyte: 0.05 M Na₂SO₄. ● CF ■ PTFE/CF ▲ CB/CF ○ CB/PTFE/CF.

Figure 4. Effect of the CB-PTFE mass loading on the production of hydrogen peroxide. Conditions: $j = 20 \text{ mA cm}^{-2}$. Electrolyte: 0.05 M Na₂SO₄. Ratio CB/PTFE 1:5 ● 0.1 ■ 0.5 ▲ 0.7 ○ 1 □ 1.3

Figure 5. Destruction of externally-added hydrogen peroxide in the jet reactor. Conditions: $j = 20 \text{ mA cm}^{-2}$. Electrolyte: 0.05 M Na₂SO₄. Cathode: bare CF

Figure 6. SEM photographs and EDAX analysis of the upper (A and B) and transversal (C and D) areas of the modified CF electrode 1.

Figure 7. Effect of the current density on the production of hydrogen peroxide versus time (a and b) and versus specific charge (c and d) for Electrode 1 and 2. Ratio CB/PTFE 1:5; CB-PTFE load: 1 g / g CF. ● 10 mA cm⁻² ■ 15 mA cm⁻² ▲ 20 mA cm⁻² ○ 25 mA cm⁻² □ 30 mA cm⁻².

Figure 8. Hydrogen peroxide generation under different aeration conditions at different current densities. a) low current density (■ 10 mA cm⁻² ● 15 mA cm⁻²), b) high current density (○ 20 mA cm⁻² □ 30 mA cm⁻²). Electrolytic medium: 1 dm³ 0.05 M Na₂SO₄. Carbon felt modified with ratio CB/PTFE 1:5; CB-PTFE load: 1 g / g CF.

499
500
501

502
503
504

Figure 1.

505

506

507

508 **Figure 2.**

509

510

511

512 **Figure 3.**

513

514

515

516 **Figure 4.**

517

518

519

520

Figure 5.

521

522

523

524

525

526 **Figure 6.**

527

528

529

530

531 **Figure 7.**

532

533

534

535 **Figure 8.**

536