

# ON THE PRODUCTION OF OZONE, HYDROGEN PEROXIDE AND PEROXONE IN PRESSURIZED UNDIVIDED ELECTROCHEMICAL CELLS

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## Abstract

This work is focused on the characterization of the production of ozone, hydrogen peroxide and hydroxyl radicals (peroxone) in pressurized undivided electrochemical cells. BDD and MMO electrodes were compared as anodes and RVC, graphite and stainless steel as cathodes. Gauge pressures in the range 2-4 bar were applied. Results demonstrate the complexity in the production of oxidants in an undivided cell, allowing to propose a model of the set of reactions (both electrochemical and in the bulk) occurring in the system. A higher pressure decreases the accumulation of ozone meanwhile hydrogen peroxide production is maximized at intermediate values of pressure. Combining BDD and graphite is the best combination for enhancing the production of hydroxyl radicals for which a negligible influence of pressure was observed. These results would allow to select the proper design to maximize the efficiency in the production of each of the oxidants studied.

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**Keywords:**

Ozone; hydrogen peroxide; perozone; pressurized electrochemical cell; mechanisms

**Highlights**

- An undivided cell is a versatile device to produce oxygen-based oxidants.
- Higher pressure lowers ozone accumulation in the electrochemical cell.
- Pressure has a negligible influence on the production of hydroxyl radicals.
- Perozone and peroxy-salts productions are crucial to understand the process.
- BDD/graphite offers the best performance for hydroxyl radicals production.

## 1. Introduction

The use of ozone ( $O_3$ ) and hydrogen peroxide ( $H_2O_2$ ) as safe alternatives to other oxidants, such as chlorine, in industrial applications (which include water and waste treatment, wood pulp bleaching and chemical syntheses) has been in focus in the last years, due to their outstanding oxidizing properties and their decomposition into non-toxic  $O_2$  as reduction product [1].

The production of ozone for being used in water and wastewater treatment is performed by electric discharge (corona process) of a purified oxygen gaseous stream and its subsequent dissolution into the waste. This is a process characterized by the poor efficiency of the ozone production (with specific consumption around  $5 \text{ kWh kg}^{-1}$ ) and by the low efficiency in the mass transfer of ozone from the gas to the aqueous environment [2]. In turn, the production of hydrogen peroxide is carried out by the well-known anthraquinone process, which is known to have a high environmental impact associated to the high power consumption needed and the formation of organic wastes [3].

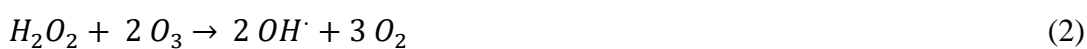
Because of the high impact and low efficiency of the conventional ways for the formation of hydrogen peroxide and ozone, the electrochemical production is becoming a real alternative for achieving an efficient and environmentally friendly production [4-6]. The electrochemical production of ozone offers many advantages, which include low voltage operation and the possibility of generating high concentrations of ozone in the gas and liquid phases with a high current efficiency [7]. Moreover, the generation of ozone directly inside the water or wastewater overcomes some of the most relevant drawbacks of the conventional ozone generation systems regarding the limited mass transfer [8, 9]. Many studies have evaluated the influence of the role of the electrode material [10] and supporting electrolyte [11] on the electrochemical production of ozone, showing that the presence of anions with high electronegativity and/or the use of anodes with high overpotential for the oxygen evolution reaction resulted in an enhanced production of ozone.

On the other hand, the electrochemical production of  $H_2O_2$  by the reduction reaction of dissolved oxygen (Equation 1) has also attracted increasing attention, because of its high efficiency and low energy consumption [12-14]. An increasing number of studies have

evaluated the role of several key variables in the production of hydrogen peroxide. Among them, oxygen pressure outstands as a key variable to assure high production yields of hydrogen peroxide, due to the increase in oxygen concentration according to the Henry's law [15, 16]. Additionally, several electrode materials have been tested trying to reach higher production rates, being the modified carbonaceous materials with high surface area the preferred cathode materials to promote the reduction of oxygen to hydrogen peroxide [17-19].



The peroxone process is the reaction of  $O_3$  with  $H_2O_2$ , giving rise to  $OH\cdot$  radicals according to Equation 2, that allows the pollutant abatement at relatively low cost as compared to other Advanced Oxidation Processes AOPs [20]. This process has been proposed as a promising technology to deal with water pollutants as it is proposed as the most practical way of upgrading the ozonation process to an AOP system [21, 22].



Due to the key importance of the production of both chemicals and their strong interaction in the peroxone process, the present work aims to look for the best conditions for the electrochemical production of ozone, hydrogen peroxide and/or hydroxyl radicals in undivided electrochemical cells. The role of pressure and electrode material are evaluated in the search for the conditions that lead to an optimized electrochemical production depending on the target of the process (enhancing the accumulation of hydrogen peroxide, the accumulation of ozone or the production of hydroxyl radicals).

## 2. Materials & Methods

### 2.1. Materials.

Deionized water (Millipore Milli-Q system, 18.2 M $\Omega$  cm, 25 °C) was used to prepare all solutions and all chemicals were analytical grade (ACS). Salicylic acid ( $\geq 99\%$ ), 2,3-

dihydroxybenzoic acid (2,3-dHBA, 99%), 2,5-dihydroxybenzoic acid (2,5-dHBA, 98%) and catechol (1,2-Dihydroxybenzene,  $\geq 99\%$ ) were all purchased from Sigma-Aldrich, Spain) and they were used to characterize hydroxyl radicals. Oxygen (99.999 %) was supplied by Air Liquide (Madrid, Spain).

## 2.2. Electrochemical treatment.

Boron-doped diamond (BDD) plate electrodes (3D-mesh Diachem® diamond electrode supported on niobium) were acquired from Condias GmbH (Germany) ( $sp^3/sp^2$  ratio 176; thickness 0.2 cm) and used as anodes. A Ti | IrO<sub>2</sub>-RuO<sub>2</sub> electrode was used as model of mixed metal oxide (MMO) anode, and it was provided by PCCell (Germany) with a square grid-shaped geometry of 7.5 x 7.5 and a thickness of 0.2 cm. The main material used as cathode was Reticulated vitreous carbon (RVC) coated with Carbon Black (CB) and Polytetrafluoroethylene (PTFE). The RCV was provided from Duocel®, with 45 pores per inch (approximate surface area of 2700 m<sup>2</sup> m<sup>-3</sup>[23]) with dimensions of 9.5 x 8 x 0.5 mm<sup>3</sup>. To prepare it, it was used an ink with 1 mg mL<sup>-1</sup> of CB and 5 mg mL<sup>-1</sup> of PTFE into isopropanol. The RVC electrodes were placed over a home-made plate, which reached a temperature of 130 °C and 200 mL of the ink was sprayed (100 mL on each side of the electrode) slowly to allow the isopropanol to evaporate and leave the CB/PTFE mixture on the electrode surface. After this, the RVC-CB/PTFE electrodes were annealed at 360 °C for 1 h starting at room temperature at a heating rate of 12 °C min<sup>-1</sup> [14]. For comparison purposes in this work stainless steel (square shaped 100 mm side with a geometric area of 100 cm<sup>2</sup>; AISI 304; Mervilab, Spain) and Porous Graphite (square shaped 100 mm side and 10 mm width, with a geometric area of 100 cm<sup>2</sup>; from Pocofoam® SARL-Lyon, France, surface area of 4735 m<sup>2</sup> m<sup>-3</sup>[24]), were also tested as cathodes. The total wet geometrical area was 5 cm<sup>2</sup>.

A picture of the undivided high-pressure reactor used in this work is shown in Figure 1. It was made of rigid polyvinyl chloride and it is directly connected with a O<sub>2</sub> vessel and to a glass collector to receive the electrolyte samples. All experiments were performed at galvanostatic operation mode using a Amel 2053 potentiostat / galvanostat. In each electrolytic test, the reactor was filled with a solution containing 1 liter of electrolyte solution containing deionized water with a pH of 4, which was adjusted using sulphuric acid. This parameter was monitored throughout the experiments and once it dropped to a

value of  $3.0 \pm 0.1$ , it remained stable. Each test lasted 180 minutes with an applied current of 0.25 A, which was settled because of previous optimization tests.

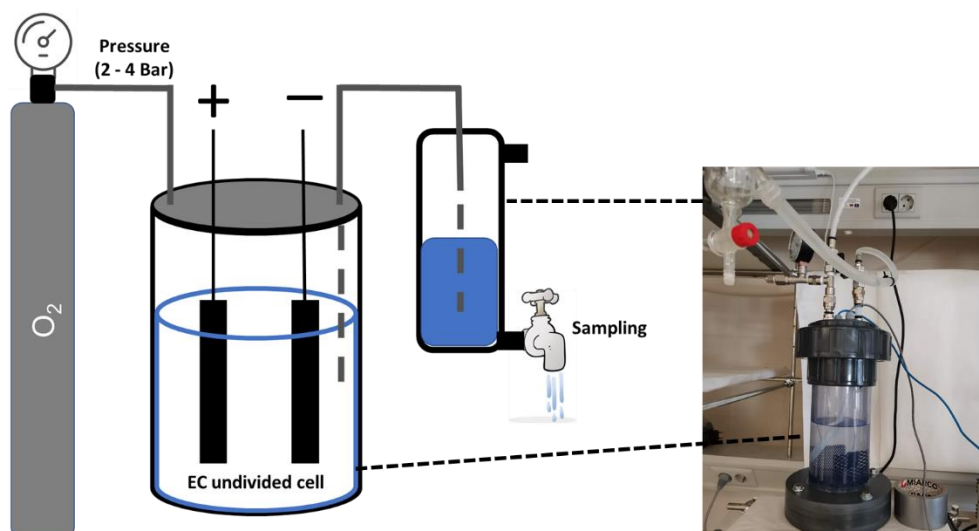


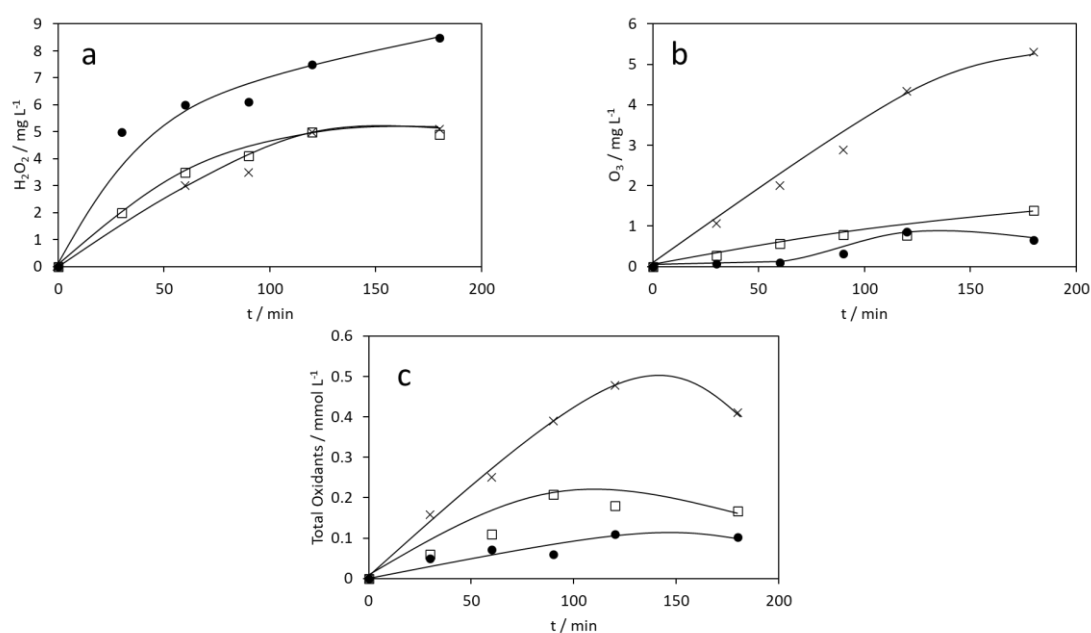
Figure 1. Schematic representation and picture of the electrochemical undivided cell used in this work.

### 2.3. Analytical.

Conductivity and pH were monitored using a Crison Cm 35 conductivity meter and a GLP22 Crison pH meter, respectively. Hydrogen peroxide concentration was measured by the potassium titanium (IV) oxalate method (detection limit:  $0.0385 \mu\text{g/l H}_2\text{O}_2$ ), according to standard DIN 38 409, part 15, DEV-18. The titanium solution was supplied by Merck, and the absorbance was determined at  $\lambda = 407 \text{ nm}$  using an Agilent 300 Cary series UV-visible spectrophotometer [15]. Ozone concentration was measured using a Spectroquant® 100607 test (detection limit:  $0.010 \text{ mg/l O}_3$ ) from Merck (Darmstadt, Germany), and the absorbance was determined using a Pharo 100 Merck spectrophotometer. Total oxidants were determined by iodometric titration. The evolution of salicylic acid and its intermediates has been determined to measure hydroxyl radicals *in vivo*, by calculating the hydroxylated derivatives of salicylic acid using high performance liquid chromatography (HPLC) with a UV detector (Jasco, Japan) according to a method described elsewhere [25]. The mobile phase consisted of 10% (v/v) HPLC-grade acetonitrile, 10% methanol, 0.03 M citric acid (Baker), 0.3 M acetic acid (flow rate of  $1 \text{ cm}^3 \text{ min}^{-1}$ ). The injection volume was  $20 \mu\text{L}$  and the UV detection wavelength was 296 nm.

### 3. Results and discussion

As previously explained in the introduction section, pressurization has been found as a key parameter in the production of ozone and hydrogen peroxide. Because of that, the first stage of the work consisted of evaluating the influence of the applied oxygen pressure on the accumulation of hydrogen peroxide and ozone. Figure 1 shows the evolution of the concentration of both species and total oxidants with time, under working pressures of 2, 3 and 4 bar.



**Figure 2.** Evolution of hydrogen peroxide (a), ozone (b) and total oxidants (c) concentration. I=0.25 A. Volume: 1 L. x: 2 bar; ●3 bar; □ 4 bar. Cathode: graphite; anode: BDD.

The accumulation of hydrogen peroxide follows the expected trend when increasing the pressure from 2 to 3 bar, that is, an increase in the production and accumulation of hydrogen peroxide for a higher value of pressure. This behaviour can be explained by the higher oxygen concentration at greater pressure, enhancing the production of hydrogen peroxide by Equation 1 as it has been widely reported in the literature [15, 16, 26].

Nevertheless, the system does not follow the expected trend when increasing the pressure from 3 to 4 bar. The production rate of hydrogen peroxide should be greater for increasing pressure according to the existing literature and Henry's law, which states that the concentration of oxygen increases for increasing values of pressure. Thus, if the

accumulation of hydrogen peroxide decreases for higher production rates, the unique plausible explanation should be found in the role of other reactions that consume hydrogen peroxide. These reactions could be electrochemical as hydrogen peroxide can be either oxidized (Equation 3) or reduced (Equation 4) on the electrodes surface [27, 28]. Moreover, it is worth noting the role of species that reacts with hydrogen peroxide in the bulk and acts as scavenger species. Ozone is the most important, although not the unique, scavenger of hydrogen peroxide in the system due to the well-known peroxone reaction, expressed by Equation 2 [20].



The rate of the electrochemical degradation of hydrogen peroxide is expected to increase for higher concentration due to the enhanced mass transfer rate of this species to the electrode surface [29] but it should not be affected by a pressure variation. Conversely, a greater value of pressure also raises the solubility of ozone, further increasing the rate of Equation 2 and lowering the accumulated mass of hydrogen peroxide. This may explain the existence of an optimal value of pressure for the production of hydrogen peroxide when the process is performed in an undivided reactor, as it is the case of the present study.

Regarding the accumulation of ozone and total oxidants, an increasing value of pressure decreases the concentration of ozone accumulated in the system. When using BDD electrodes, ozone is expected to be produced mainly by the oxidation of water according to Equation 5, although it can also proceed involving oxygen as reagent (Equation 6). In this point, it is important to bear in mind that ozone from water can only occur in materials such as BDD electrodes [30, 31].



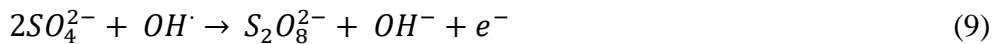
The clear decrease observed in the concentration of ozone for increasing pressure may be attributed to various overlapped effects. First, it confirms the increase of the rate of



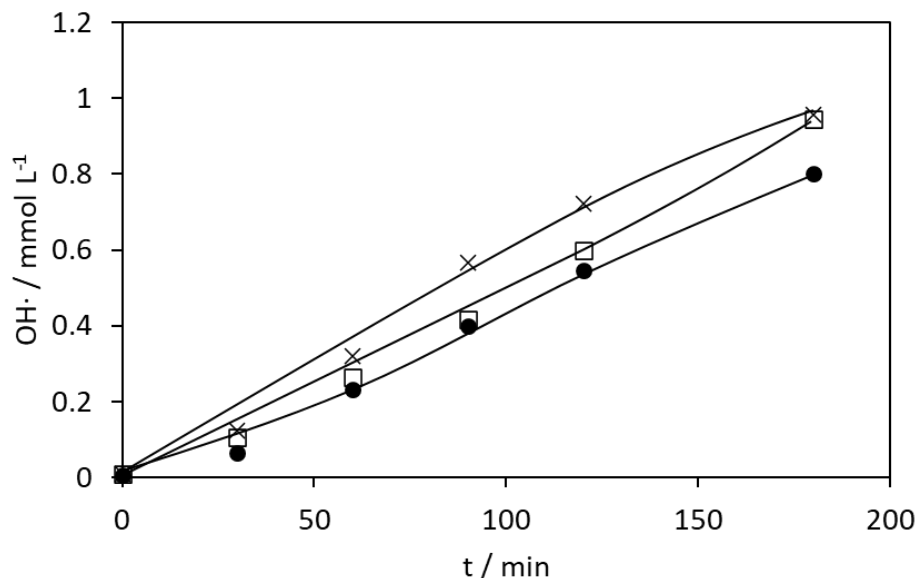
peroxone reaction (Equation 2), that affects the accumulation of both hydrogen peroxide and ozone. Secondly, it implies that the main mechanism for ozone production under the conditions tested here is that shown by Equation 5, which does not depend on the concentration of oxygen and whose equilibrium is unfavored by the accumulation of ozone, according to the Le Chatelier principle. Moreover, the chemical decomposition of ozone following Equation 7 may also be favored by an increasing availability of ozone in water due to the increase in pressure. This is in line with previous works devoted to the production of ozone [1, 30].



Regarding the concentration of total oxidants, it follows a trend like that of ozone. To explain this behaviour, it is important to bear in mind the complex pool of reactions that are taking place in the system, both electrochemical on the electrodes surface or in the bulk. First, hydroxyl radicals are produced anodically by the BDD anode (Equation 8) and are available to react with the chemical species in the nearness of the electrodes due to the non-active behaviour of the BDD anode [32-34]. Moreover, hydroxyl radicals can be formed in the bulk by the peroxone reaction (Equation 2), be used in the formation of peroxodisulfate from sulfate ions (Equation 9) or recombine to form hydrogen peroxide according to Equation 10. Finally, ozone and persoxodisulfate or hydrogen peroxide may recombine and react according to equations 11 and 12.



Due to the key role of hydroxyl radicals in this sequence of reactions, three tests with salicylic acid were also performed, following the experimental procedure described in Section 2, to study the influence of pressure on the formation of this radical. The evolution of its concentration is gathered in Figure 3.

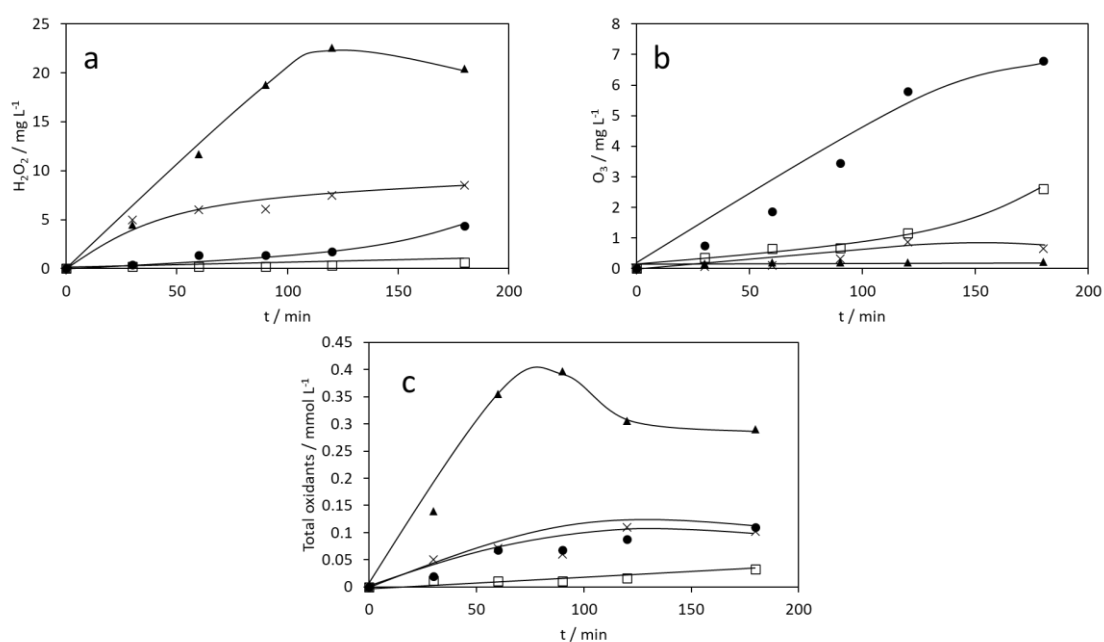


**Figure 3.** Evolution of hydroxyl radicals (concentration) for tests with salicylic acid.  $I=0.25$  A. Volume: 1 L. x: 2 bar; ● 3 bar; □ 4 bar. Cathode: graphite; anode: BDD.

As it can be observed in Figure 3, the concentration of hydroxyl radicals is almost constant regardless the value of pressure applied to the system. The set of reactions described by equations 1 to 12 gives the complex scenario described by figures 2 and 3. The oxidants measured in Figure 2.c should be the sum of peroxodisulfate, hydrogen peroxide and ozone (because of the extremely short lifetime of hydroxyl radicals). As it has been previously explained, the increasing pressure should enhance the formation of hydrogen peroxide and, consequently, the formation of hydroxyl radicals via peroxone reaction. Conversely, a higher concentration of hydroxyl radicals would enhance the production of peroxodisulfate, which would act as ozone scavenger according to Equation 11, causing a decrease in both the concentration of ozone and total oxidants. Taking all this information into consideration, the result is that the applied pressure has not a plausible influence in the amount of hydroxyl radicals detected in the system as the positive and negative effects that the pressure causes in its production may overlap each other.

In order to further evaluate the role of any of these reactions, the next stage of the work consisted of the assessment of the influence of the electrode material. To do this, tests

were carried out at constant pressure of 3 bar. Three materials were compared as cathodes. First, two carbonaceous materials with different specific surface area: 1) graphite (with the highest surface area) and 2) reticulated vitreous carbon (with the lowest surface area). Moreover, stainless steel was also compared as a model of cathode material that would not promote the generation of hydrogen peroxide. Finally, an additional test was performed with graphite (cathode) and a mixed metal oxide (MMO) anode, in order to limit the generation of available hydroxyl radicals. Figure 4 shows the concentration of hydrogen peroxide, ozone and total oxidants measured in these tests.



**Figure 4.** Influence of electrode material on the evolution of hydrogen peroxide (a), ozone (b) and total oxidants (c) concentration.  $I=0.25$  A. Volume: 1 L. x: Graphite (cathode)-BDD (anode); ● SS (cathode)-BDD (anode); □ RVC (cathode)-BDD (anode); ▲ Graphite (cathode)-MMO (Anode). All experiments were performed at a 3-bar pressure.

The first remarkable conclusion that can be obtained from Figure 4 is that the use of a MMO anode leads to a negligible production of ozone (concentration measured in the order of the detection limit of the method) but the highest accumulation of both total oxidants and hydrogen peroxide. This inverse relation between the accumulation of hydrogen peroxide and ozone confirms the key role of the peroxone reaction (Equation 2), being ozone the main scavenger species of hydrogen peroxide. The formation of available hydroxyl and oxygen radicals has been described in literature to be essential in the electrochemical generation of ozone [4]. The mechanism for the production of ozone

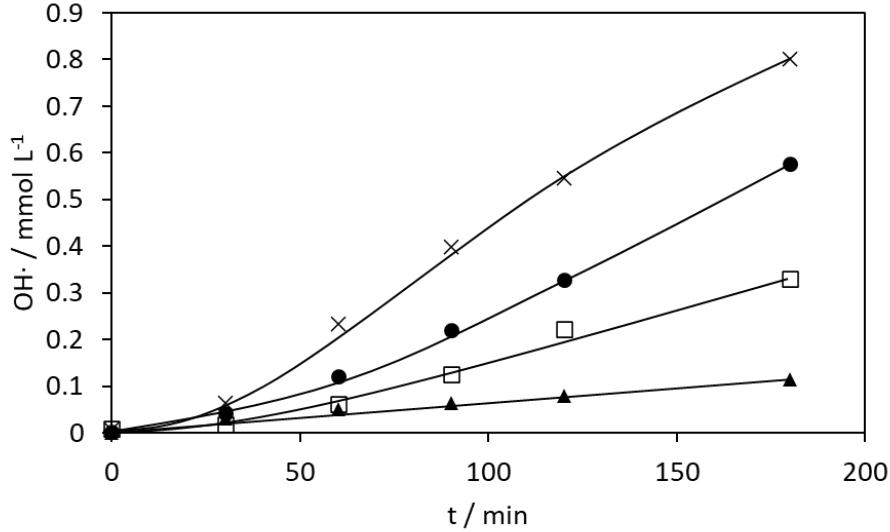
by oxidation with BDD anodes was firstly proposed by Michaud and coworkers [37], who proposed that ozone is produced from the hydroxyl radicals formed by water oxidation (Equation 8). The formation of ozone implies the oxidation of hydroxyl radicals to atomic oxygen (equation 13), that may produce ozone by reaction with oxygen (equation 14).



Additionally, it is well-known that the availability of hydroxyl radicals in the electrode surface is dramatically reduced when using an active anode as MMO, as compared to BDD [32], explaining the marked reduction of ozone concentration and the consequential maximum concentration of hydrogen peroxide. This maximum concentration of hydrogen peroxide is directly linked to the higher concentration of oxidants that is shown in Figure 4.c.

This marked inverse relation between the production of hydrogen peroxide and ozone is also confirmed when comparing the results obtained with graphite and RVC. The accumulation of hydrogen peroxide should be directly linked to the available surface area of the electrodes [19], so its production is expected to be higher for the graphite electrode, as it is represented in Figure 4.a. As for the rest of the tests, the lower accumulation of hydrogen peroxide originates a greater concentration of ozone for RVC electrode (Figure 4.b).

As it was the case for the study of the applied pressure, three further tests were planned with salicylic acid for evaluating the production of hydroxyl radicals. Figure 5 shows the results obtained in these tests.



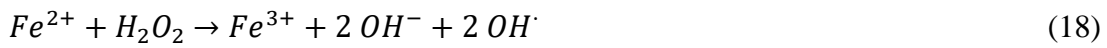
**Figure 5.** Evolution of hydroxyl radicals concentration for tests with salicylic acid.  $I=0.25$  A. Volume: 1 L. x: graphite (cathode)-BDD (anode); ● SS (cathode)-BDD (anode); □ RVC (cathode)-BDD (anode); ▲ graphite (cathode)-MMO (Anode). Pressure: 3 bar.

As it can be observed in Figure 5, the maximum concentration of hydroxyl radicals is generated by the combination of an anode that promotes the formation of ozone (BDD) and a cathode that enhances the production of hydrogen peroxide (graphite), confirming that the peroxone reaction is a relevant source of hydroxyl radicals in this system. Apart from the production of hydroxyl radicals by the BDD anode (Equation 8) and from that produced by the peroxone reaction (Equation 2), it is also possible to produce this species by the so-called superoxide anion ( $O_2^-$ ), obtained as an intermediate in the reaction of oxygen reduction to produce hydrogen peroxide [28, 35]. This superoxide anion could reduce ozone and promote its decomposition to hydroxyl radicals according to equations 15 and 16. Altogether, these results confirm that the combination of these two electrodes is optimal if the target of the work is maximizing the production of hydroxyl radicals.

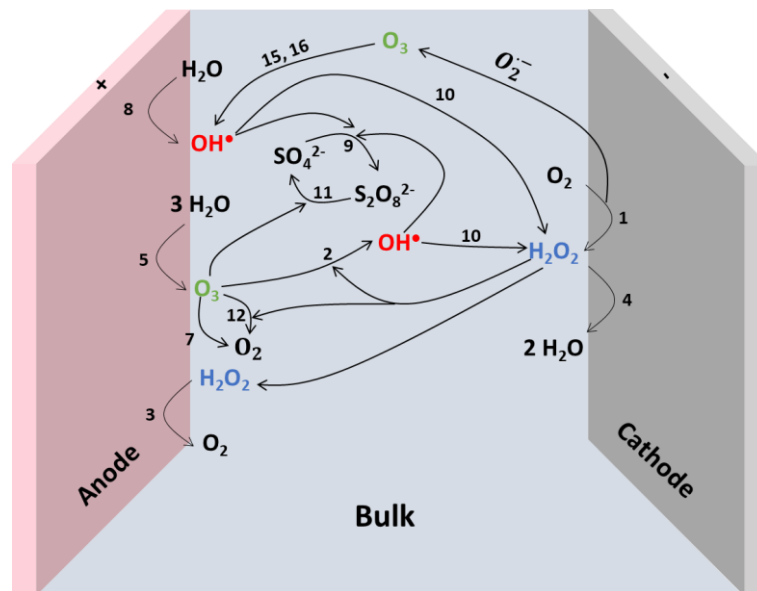


It is worth noting the high concentration of hydroxyl radicals measured with stainless steel as cathode. As the production of hydrogen peroxide (and consequently the contribution of peroxone reaction) is expected to be negligible with this cathode, this result highlights the important impact of the direct generation of hydroxyl radicals by BDD anode. Moreover, the fact that this system (SS-BDD) produces the second largest

concentration of hydroxyl radicals is in line with previous works that affirms that when BDD is used as anode, the main source of this species is the oxidation of water by the anode (Equation 8) [31, 32]. In this case, a potential contribution of the generation of hydroxyl radicals from an heterogeneous Fenton reaction [36, 37], as indicated by equations 17 (oxidation of iron) and 18 (Fenton reaction), could theoretically be produced. Nevertheless, this contribution is expected to be negligible as the cathodic protection of the stainless-steel electrode may prevent or dramatically limit the oxidation of iron by Equation 17.



Taking account these observations, Figure 6 represents a schematical representation of the reactions that are taking place in this complex system, including the interactions between them. The numbers included in the Figure refers to the number of the equations in the text.



**Figure 6.** Schematic representation of the set of reactions taking place in the electrodes and the bulk.

From the general scenario described by Figure 6 it is clear the strong interaction between all species that can be formed in the bulk, being the hydroxyl radical the key species of

the system. It can also be clearly observed the important roles of both reactions 2 (peroxone reaction) and 9 (sulfate/peroxodisulfate) in the production/consumption of ozone, hydrogen peroxide and hydroxyl radicals. Altogether, it can be stated that an undivided electrochemical cell is a versatile instrument that can be designed as a function of the main aim of the process by selecting the proper electrode materials and operation conditions. For an enhanced production of hydroxyl radicals, it is necessary to promote all lines depicted in Figure 6, what implies the use of a BDD anode (promoting the generation of both ozone and hydroxyl radicals) and graphite (enhancing the generation of hydrogen peroxide). In this case, increasing the pressure has not a positive influence in the concentration of hydroxyl radicals (as previously explained in the discussion of Figure 3). On the contrary, if the accumulation of hydrogen peroxide or ozone is aimed, it is necessary to deactivate the interaction between both species by using an appropriate combination of cathode/anode materials: graphite/MMO anodes and intermediate pressures for the accumulation of hydrogen peroxide and SS/BDD for the accumulation of ozone.

#### **4. Conclusions**

The present work describes the complex set of reactions that occurs when ozone and hydrogen peroxide are produced in an undivided electrochemical cell, highlighting the strengths and weaknesses of this electrochemical device to produce those oxidants. The main conclusion obtained is that the choice of electrode material and operation conditions can help to optimize the production of ozone, hydrogen peroxide or hydroxyl radical, depending on the target of the process. Specifically, the following conclusions are obtained:

- The pressure has a dissimilar influence in the accumulation of the different key species of the system. First, a higher value of pressure decreases the accumulation of ozone in the undivided reactor. Conversely, the accumulation of hydrogen peroxide is maximum at the intermediate value of pressure tested in the present work (3 bar).
- The pressure has a negligible influence on the production of hydroxyl radicals due to the complex set of reactions occurring in the electrodes and in the bulk.
- Both the peroxone reaction and the formation of peroxo-salts from sulphate ions play a key role in both the formation of hydroxyl radicals and the accumulation of hydrogen peroxide and ozone.

- The combination of a BDD anode and a high surface area carbonaceous material is the best combination for maximizing the production of hydroxyl radicals in an undivided electrochemical reactor in sulphate media.

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