Intensification of peroxone production through the paired generation of hydrogen peroxide and ozone in a continuous flow electrochemical reactor

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Abstract

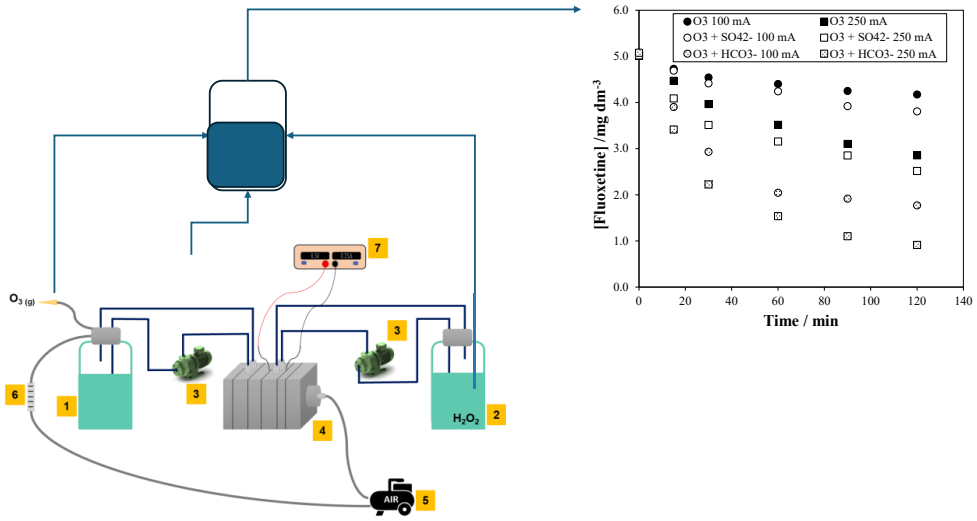
The paired electrochemical production of ozone and hydrogen peroxide is evaluated in a novel 3-D printed electrochemical cell in which the oxidants produced are tested in the removal of fluoxetine hydrochloride (FLX). To properly pair the anodic production of ozone and the cathodic production of hydrogen peroxide in the same cell, that is, with the same intensity in anode and cathode, an innovative composite 3-D gas diffusion cathode was used to decrease the current density (by increasing the effective cathode surface area) in the cathodic compartment, attaining soft operation conditions in this compartment. Meanwhile, a grid DIACHEM® lattice BDD was used in the anode to increase the harsh oxidative conditions in the anodic compartment. The results confirm the viability of pairing both processes. Current intensity positively affects the production of ozone and, less importantly, the production of hydrogen peroxide (because the current efficiency decreases with the intensity), with the contribution of electrolytes containing sulfate and bicarbonates being evaluated in the search of greener processes. The oxidants produced

were dosed to solutions containing FLX confirming that the addition of both products (electro-peroxone process) attains a significant improvement in the removal of FLX, which was explained in terms of promoting radical mechanisms for ozone oxidation (peroxone reagent).

Highlights

- Novel 3-D electrochemical cell pairs hydrogen peroxide and ozone production
- Ozone production improved at higher current densities and bicarbonate electrolyte
- Lower effect of current density on hydrogen peroxide production
- Fluoxetine removed with ozone, hydrogen peroxide, alone or in combination
- Improved FLX removal with simultaneous addition of both oxidants

Graphical Abstract



Keywords

ozone; hydrogen peroxide; process integration; peroxone; advanced oxidation processes; electrochemical treatment

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1. Introduction

In recent years, the presence of pharmaceutical compounds in waterbodies has been a major cause for concern [1]. These substances are introduced into the environment from anthropogenic sources, including incomplete absorption after oral administration, followed by physiological elimination; irregular household disposal of expired medicines; and disposal of pharmaceutical effluents generated in drug production and/or formulation facilities [2]. Most of these compounds are not currently subject to environmental regulation and, due to their potential ecological and human health impacts, are classified as contaminants of emerging concern [3].

There is a need to propose viable treatment alternatives for removing these drugs from aqueous effluents. Advanced oxidative processes (AOP) are arising as an interesting option, considering the promising results from their extensive evaluation against several pollutants [4]. These technologies are based on the in-situ formation of strongly oxidizing species, such as hydroxyl radicals ($HO^{\bullet}$) (E° $HO^{\bullet}/H_2O$ = 2.8 V/EPH), capable of degrading and, in some cases, even completely mineralizing contaminants [5]. AOPs can be classified as chemical (i.e., ozonation, Fenton process), photochemical (i.e., H_2O_2/UV, O_3/UV, O_3/H_2O_2/UV, photo-Fenton, heterogeneous photocatalysis), sonochemical (i.e., US, O_3/US, H_2O_2/US, photocatalysis/US, sono-Fenton) and electrochemical (i.e., anodic oxidation, electro-Fenton, photoelectro-Fenton, sonoelectrochemical, sonoelectro-Fenton, electro-peroxone process) [6-8]. The existence of a wide variety of technologies is an indicator of the not clear prevalence of any of them [9].

Different types of AOPs have been used in antidepressant degradation studies [10, 11] such as electrochemical [12], photochemical [13, 14], ionizing radiation [15], and ozonation oxidation [16]. Among them, electrochemical processes are prominent [10, 12, 17].

Thus, the selection of oxidative processes is of fundamental importance to guarantee the complete elimination of recalcitrant pollutants from wastewater and the non-generation of more toxic by-products than the parent compounds [18, 19]. Therefore, the synergistic effect, resulting from the combination of different types of AOPs in the same process, is an interesting alternative in the application of these technologies [20]. The integration of techniques in the same system has resulted in more efficient degradation compared to the simple association of two different AOPs in sequence, making their performance more effective [7, 21].

In this regard, great emphasis has been placed on processes that can generate ozone by aqueous phase electrolysis [22-26]. The electrochemical production of ozone occurs through the direct oxidation of water at the anode surface via a 6-electron transfer mechanism (**Eq. 1**). Ozone can also be generated by the transformation of dissolved oxygen (**Eq. 2**), a process whose efficiency is strongly influenced by the pH of the solution [27].

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- \quad (1)$$

$$H_2O + O_2 \rightarrow O_3 + 2H^+ + 2e^- \quad (2)$$

Mechanisms that explain the formation of ozone suggest the significance of the formation of hydroxyl radical mediators [28] and, consequently, harsh oxidation conditions are needed to obtain efficient processes. Ozone produced electrochemically is mostly released as a gas flow due to the poor solubility of this oxidant in water solutions [29]. This means that if not produced directly into the wastewater, its application is by dispersing the gas flux produced into the wastewater to be treated, where it must be conveniently activated. Activation of ozone, either by light or by combination with other chemicals, promotes the stimulation of radical-based oxidative mechanisms that are more effective than molecular oxidative mechanisms. One possibility is the combination with

hydrogen peroxide which leads to the formation of hydroxyl radicals in a process sometimes referred to as peroxone production (**Eq. 3**).

$$2O_3 + 2H_2O_2 \rightarrow 2H_2O + 3O_2 + HO_2^{\cdot} + HO^{\cdot} \quad (3)$$

Although hydrogen peroxide is mostly produced by the anthraquinone process, there is currently a great interest in its electrochemical production [30], which is intensified by the outstanding efficiencies reported by the combination of efficient gas diffusion electrode technologies and innovative cells with special mechanical designs that stimulate the formation and prevent its decomposition [20, 32, 33]. In the electrolytic process, H_2O_2 is generated by the cathodic reduction of oxygen, which occurs in the three phase boundaries of gas diffusion electrode (GDE) following (**Eq. 4**) [33]. Also reported is the formation of hydrogen peroxide in anodic processes, although efficiency is much lower than that achieved in cathodic processes [34].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (4)$$

Although ozone and hydrogen peroxide can theoretically be paired in the same electrochemical cell [35], it is not as simple as placing both processes together in the same cell. In fact, there is an important drawback for this combination: efficient ozone production needs harsh oxidation conditions (because it is enhanced by hydroxyl radical mediated mechanisms) [36] while efficient hydrogen peroxide production needs soft reduction conditions (because hydrogen peroxide is in fact an intermediate product in the reduction of oxygen to water) [37]. A possible alternative to solve this problem is to integrate electrodes of different sizes into the cell, so that for the same current intensity, the current densities in the anode and cathode are different, achieving high values in the anode and low values in the cathode. This can be easily achieved by using carbonaceous cathodes with high surface area [38].

This is the approach evaluated in this work, in which a specially designed cell was used to simultaneously produce gaseous ozone in the anode compartment and hydrogen

peroxide in the cathode compartment. The viability of the process and the effect of the current density and of the supporting electrolyte is evaluated, paying special attention to the use of electrolytes. In particular, bicarbonate anions are interesting because this is the most eco-friendly anion that can be used in environmental remediation, since bicarbonates are naturally contained in most water bodies and their concentrations can be more easily modified than in electrolytes containing chlorides or sulfates (the other two are the most important anions typically studied). To check whether this approach is worth, the products of the cell are applied, directly as produced, to the degradation of the antidepressant fluoxetine hydrochloride (FLX). This pharmaceutical stands out as a highly prescribed antidepressant and is consequently frequently detected in environmental waters and industrial effluents in concentrations from ng L^{-1} to mg L^{-1}, respectively [39] and conventional wastewater treatment systems have very limited capacity for removing this class of drugs [2, 39].

2. Materials & methods

Experimental setup. The electrochemical reactor used in the study was designed and 3-D printed and consists of a two-compartmented reactor in which the anode (DIACHEM® lattice BDD, manufactured with p-Si support and a double sided polycrystalline BDD coating of about 5 μm, previously use for O_3 production with high faradaic efficiencies [40]) and cathode (composite fabric GDE-carbon cloth) compartments are separated by a NAFION 117 membrane. Details on the construction of these type 3-D printed cells are provided elsewhere including the resins used, components and fluid dynamic performance [27]. The complete assembly of the reactor pieces can be seen in **Figure 1**. The surface area of the anode was 1 cm^2. The cathode consists of a GDE synthetized by deposition of a dispersion of Printex L6 carbon and 20 % (w/w) of polytetrafluoroethylene (PTFE) over a Zoltek PX30 carbon cloth, assembly by hot-pressed at 290 ºC under 2.5 tons of pressure [41], looking for increase the area for hydrogen peroxide production and,

consequently, decreasing the cathodic effective current density. Note that the system is not a MEA (membrane-electrode assembly), although the distance between the electrodes and membrane was very short (lower than 0.1 mm in the case of the anode).

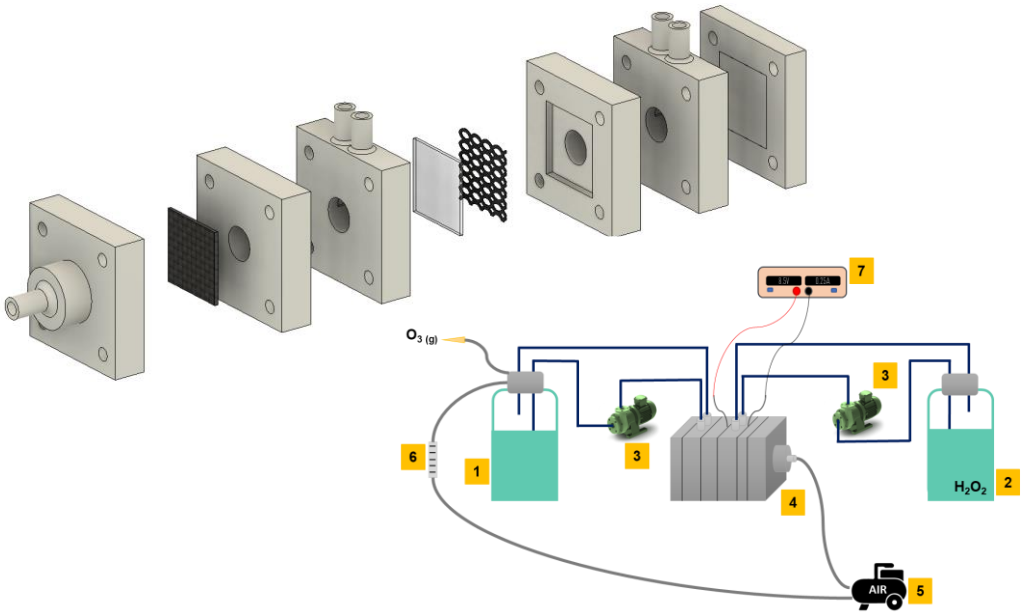

Figure 1. Components of the electrochemical cell and of the complete setup where it is installed. (1) anolyte vessel; (2) catholyte vessel; (3) peristaltic pumps; (4) electrochemical reactor; (5) air compressor; (6) air rotameter; (7) power supply.

An air compressor (Q7 Air Pump HQ-602), connected in series with a rotameter was used to supply air at a flow rate of 20 mL min^{-1} to the anolyte vase, properly sealed, to collect gaseous O_3 samples. The compressor was also connected to the cathode of the electrochemical reactor.

Two different solutions of 200 mL of sodium sulfate [Na_2SO_4] = 50 mmol L^{-1}, acidified to pH 3.0, and sodium bicarbonate [Na_2HCO_3] = 50 mmol L^{-1} were used as the electrolyte in the cathode compartment, while 200 mL of Milli-Q water was used as the electrolyte in the anode. Two peristaltic pumps (GROTHEN G328) were used to move the solutions.

The power supply (DELTA ELEKTRONIKA ES 030-10) was set in each test to provide currents corresponding to the anodic current densities evaluated: 50, 100, 250 and 400 mA cm^{-2}. The current intensities applied have the same numerical value as the anodic densities, since the electrode area is 1 cm^2. This value cannot be calculated for the cathode considering its complexity, which integrates a GDE, and a carbon felt frame, both with different areas and affected by a different non-uniform distribution of current density, in turn associated to the important differences in the electric resistance of the components.

Experimental procedure. All electrolytic oxidants production tests lasted 4 hours. Samples of 2 mL were collected from the vessel containing the catholyte at different times. The samples were analyzed by the iodometric titration method, using a thiosulfate solution ($[S_2O_3^{2-}]$ = 0.001 mol L^{-1}) after adding an excess of potassium iodide (KI) and sulfuric acid (H_2SO_4 20% v/v), to determine the concentration of total oxidants. Moreover, to determine the gaseous ozone produced in the anode compartment, the outlet gaseous stream was bubbled for 1 min in a tube containing 10 mL of Milli-Q water, and analyzed by the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method, using Spectroquant Merck test kits (Hach, Model: DR2000).

After running the oxidants characterization experiments, the catholyte solutions, where H_2O_2 was produced in SO_4^{2-} and HCO_3^- medium, were duly stored for future FLX degradation tests.

FLX degradation tests. Electrolytic production of ozone and hydrogen peroxide was operated until reaching steady state conditions. Several bottles thermostatized at 20 ºC were filled with 50 mL of a solution containing 5 mg L^{-1} FLX and sodium sulfate or bicarbonate in the same concentration of that used in the oxidant production tests. 50 mL of the catholytes produced were added to each of these bottles applying current densities of 100 and 250 mA cm^{-2} in the two electrolytes, while the electrogenerated ozone in the

outlet air was bubbled into the bottom of the solution for 120 min. Two more tests only added the solution of non-processed catholytes and ozone to test the performance of the treatment in the absence of chemical ozone activation to peroxone. Fluoxetine concentrations were measured at different reaction times using a high-performance liquid chromatography equipment (Agilent 1100 Series), using a C18 column (4.6 mm × 250 mm, 4 μm), 35% acetonitrile (ACN):65% H_2O (0.1% trifluoroacetic acid, TFA) as the mobile phase, at a flow rate of 1 mL min^{-1}. The injection volume was 50 μL, the temperature was 40 °C, the UV wavelength used for detection was 227 nm and the detention limit was 0.1 mg L^{-1}.

3. Results & Discussion

Figures 2a and 2b respectively show the production of ozone in the anode and oxidants (mainly hydrogen peroxide) in the cathode during the electrolysis carried out at different anodic current densities ranging from 50 to 400 mA cm^{-2}. As seen, within this range, an increase in the current density leads to an increase in the amount of ozone produced in the anodic compartment. However, the influence on the production of hydrogen peroxide is almost negligible, being the time course of the concentrations measured in the different tests (made at different current densities) almost overlapped, except for the initial samples in the highest current density tests.

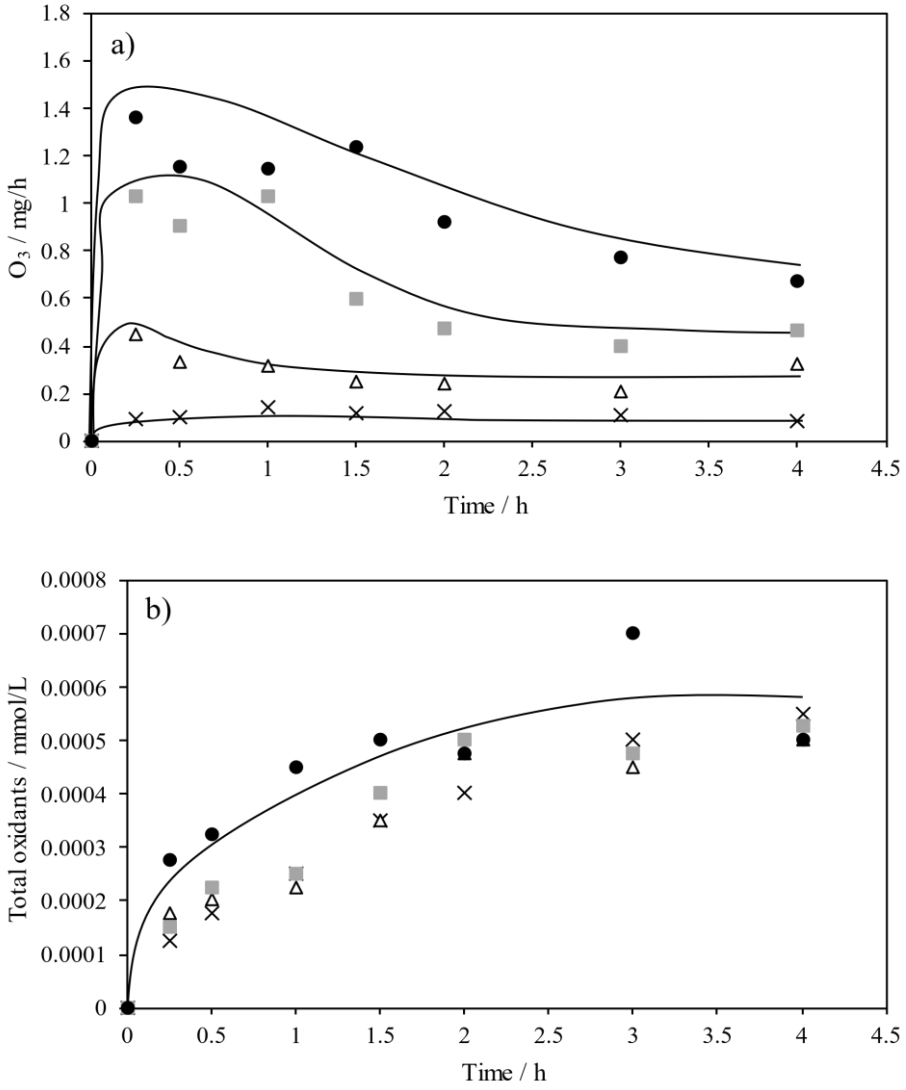

Figure 2. Production of ozone (A) and hydrogen peroxide (B) during the electrolysis of 50 mmol L^{-1} sodium sulfate solutions at 50 mA cm^{-2} (×) 100 mA cm^{-2} (△) 250 mA cm^{-2} (■) 400 mA cm^{-2} (●).

Regarding the production of ozone, this gaseous oxidant is produced and separated continuously in the anodic chamber using an air flow (20 mL min^{-1}) for O_3 entrainment. During each test, a fast increase is observed in the production rate, up to reaching a maximum from which the production settles down to a steady state value. Production of ozone is known to follow **Eqs. 1 and 2**. The trend observed indicates the interaction of ozone with other species formed on the anode surface that act as scavengers, i.e., they

react with ozone and deactivate part of the production of this oxidant. Considering the composition of the electrolyte, in which sodium sulfate is the main component, the most plausible alternative is the formation of peroxosulfates species. These species are known to react with ozone following reactions that produce strongly oxidizing radicals (sulfate and hydroxyl radicals) that, in the absence of potential species ready to be oxidized, eventually form oxygen, as shown in **Eqs. 5 and 6** for the di and mono peroxo-species, being the second species the expected as primary in strongly acid conditions.

$$S_2O_8^{2-} + O_3 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ + 2O_2 \quad (5)$$

$$H_2SO_5 + O_3 \rightarrow H_2SO_4 + 2O_2 \quad (6)$$

Regarding the cathode, the concentration of hydrogen peroxide is verified to increase up to a steady state value. This process occurs through the reaction shown in **Eq. 4**. Note that, contrarily to ozone, H_2O_2 is produced in discontinuous mode in this compartment because the catholyte is recirculated between the reservoir tank and the cell, and no inlet of fresh electrolyte or outlet of product is connected. Hence, the stabilization in the concentration is the consequence of the balance between the production and the decomposition rate of this oxidant which, in turn, is expected to follow a first order decomposition rate with a kinetic constant k_{decomp} [42]. Steady state concentration is then related to all these parameters by **Eq. 7**.

$$[H_2O_2]_{ss} = (I \cdot \eta)/(n \cdot F \cdot k_{decomp}) \quad (7)$$

Where I is the intensity applied in the system (A), η is the faradaic efficiency of the process, n is the number of electrodes involves in the H_2O_2 generation (n = 2 in this case), F is the faraday constant (96500 C mol^{-1}) and k_{decomp} is the first order decomposition rate kinetic constant.

The influence of the current density is very low, and this can only be explained in terms of an almost direct relationship of k_{decomp} with the current intensity, that is, considering that higher current densities also promote the decomposition of the hydrogen peroxide produced.

The production of a gaseous oxidant is advantageous because it can be separated or stripped (depending on the solubility) from the electrolyte easily and can then be added to any waste without any additional species. After the interaction of the oxidant with the pollutant, only the derivatives of the pollutants and the reduction products of the oxidant will remain in the treated wastes. Interestingly in the case of ozone, its reduction product is not a pollutant but oxygen, which highlights a positive point from the environmentally-friendly perspective. This is not the case of using oxidants produced and contained in liquid electrolytes matrices, in which the other species contained in the electrolyte may become secondary pollutants once added to the waste. Although the oxidant reaches its objectives, these secondary species remain in the treated waste as secondary contaminant, much less significant in terms of hazardousness, but more persistent over time. Thus, although the reduction product of hydrogen peroxide is water, the sulfates added with the oxidant solution during the treatment of a waste will remain in the treated waste. A plausible alternative is the production of oxidants in electrolytes containing greener salts, among which bicarbonates outstand. Bicarbonates are anions in equilibrium with carbonates and atmospheric carbon dioxide (**Eq. 8**) which are naturally contained in water and soils. This means that the negative impact associated to their addition is expected to be much lower.

$$CO_2(g) \leftrightarrow CO_2(aq)\ (H_2CO_3) \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + H^+ \quad (8)$$

Figure 3 shows that a change in the supporting electrolyte does not influence either ozone or hydrogen peroxide production.

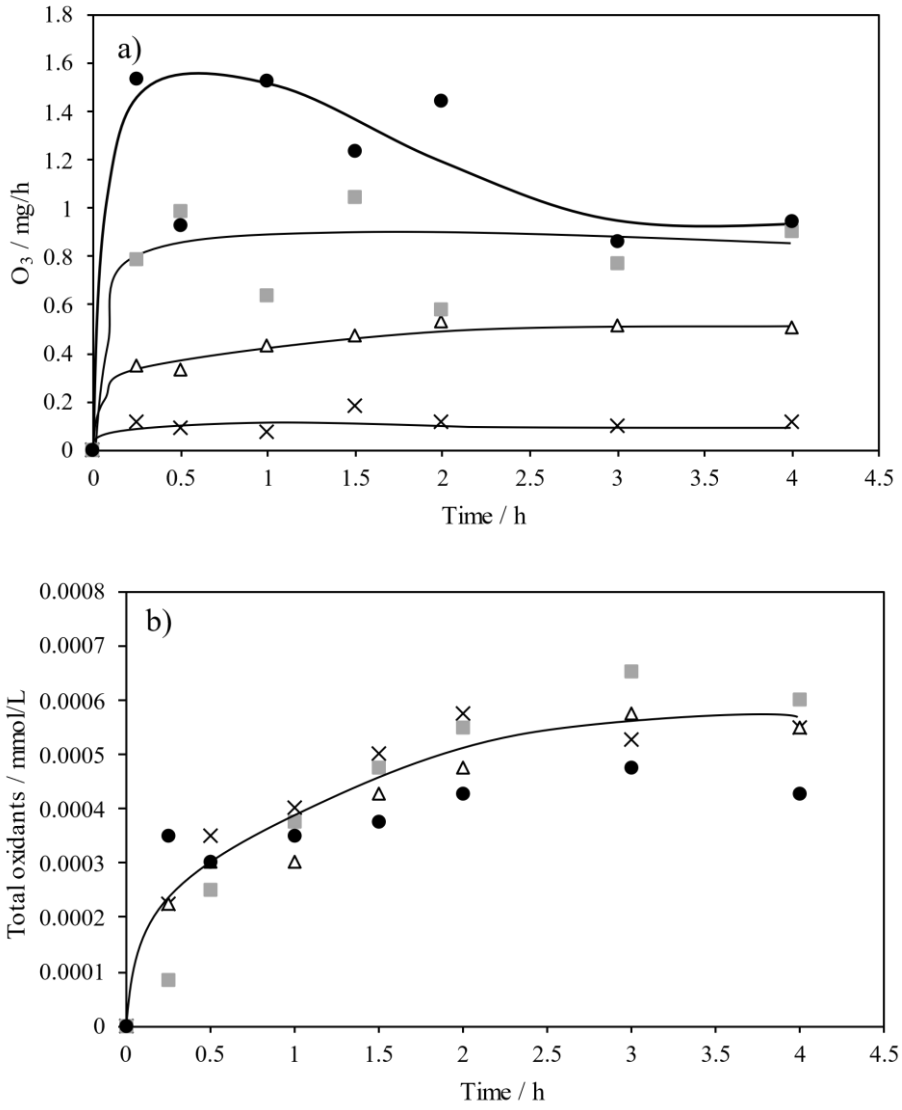

Figure 3. Production of ozone (A) and hydrogen peroxide (B) during the electrolysis of 50 mmol L^{-1} sodium bicarbonate solutions at 50 mA cm^{-2} (×) 100 mA cm^{-2} (△) 250 mA cm^{-2} (■) 400 mA cm^{-2} (●).

This means that a greener combination of both electrolytic processes can be attained with approximately the same production rates. Again, the trends observed in the continuous production of ozone suggest the interaction of the ozone with a scavenger, which in this case should be peroxocarbonates, considering the composition of the anolyte [43] following **Eqs. 9 and 10**.

$$H_2CO_4 + O_3 \rightarrow H_2CO_3 + 2O_2 \quad (9)$$

$$C_2O_6^{2-} + H_2O + O_3 \rightarrow 2CO_3^{2-} + 2H^+ + 2O_2 \quad (10)$$

The concentrations of oxidants measured in the cathodic processes are slightly higher than those obtained in the test made with sulfate and, neglecting the potential crossing of oxidants from the anodic to the cathodic chamber (crossover phenomenon), they can be explained by the stabilization that hydrogen peroxide may undergo by its equilibrium with peroxocarbonates. Thus, in mixtures hydrogen peroxide-carbonates, this equilibrium may be important and help to explain the better performance observed [44].

Batch tests are interesting because they help to evaluate the general trends of the processes studied more efficiently (every point of the curve gives independent information, opposed to continuous evaluation from each continuous test, in which only information about the steady state is valuable). However, information obtained by continuous processes is of a higher significance, because they represent the real conditions that must be applied to a real industrial process. Hence, the process was transformed from discontinuous to continuous operation by feeding the catholyte tank with 200 mL h^{-1} of a fresh catholyte solution and the withdrawal of the same flowrate of product from the tank. Although the current density does not strongly influence peroxide production, ozone production is strongly influenced by this variable. Therefore, the highest current tested (400 mA cm^{-2}) is evaluated as the best choice for the simultaneous production of the oxidants under study, H_2O_2 and O_3. Again, no differences were observed in the production of ozone between the use of sulfate or bicarbonate salts, again confirming the robustness of the ozone production technology. The results from the production of hydrogen peroxide are shown in **Figure 4** in terms of concentration at the outlet stream and total production versus time.

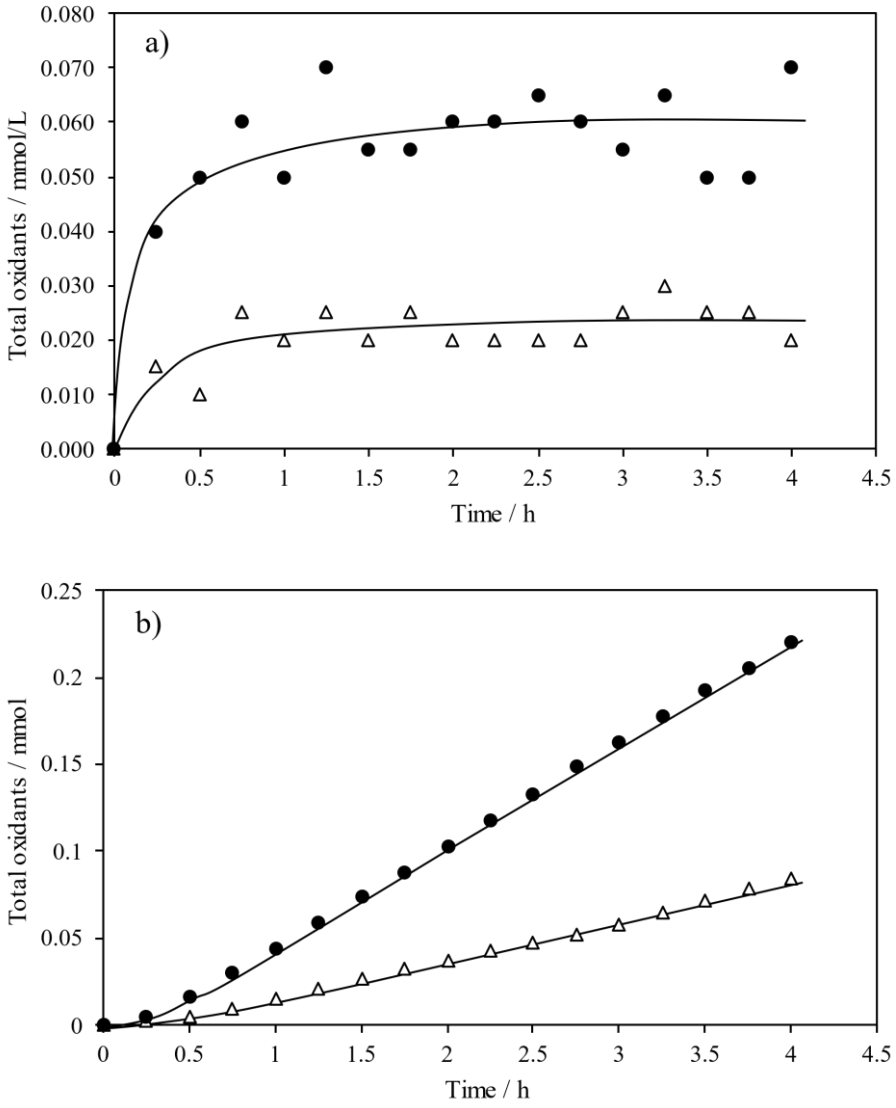

Figure 4. a) Concentration and b) total production of hydrogen peroxide electrogenerated at 400 mA cm^{-2} in sulfate (△) and bicarbonate (●) medium.

The steady state is reached in less than 1 hour, time from which the H_2O_2 concentration at the outlet only fluctuates around the steady state value. In this case, the differences between the use of sulfate and bicarbonate are larger, and clear advantages of using bicarbonates can be seen, which may be explained in terms of the higher ratio of carbonates. Hence, in terms of the higher possibilities of stabilization of the hydrogen peroxide.

One of the applications of oxidants electrogenerated can be the degradation of pollutants. In this work, the oxidants were applied for degrading fluoxetine hydrochloride (FLX), which was selected as a model contaminant of emerging concern. **Figure 5** shows FLX degradation over the time when the oxidants electrogenerated are dosed to a solution containing this pharmaceutical compound. From these, a comparative study can be made between degradation using only gaseous O_3 and simultaneously using O_3 and H_2O_2 generated in sulfate and bicarbonate media.

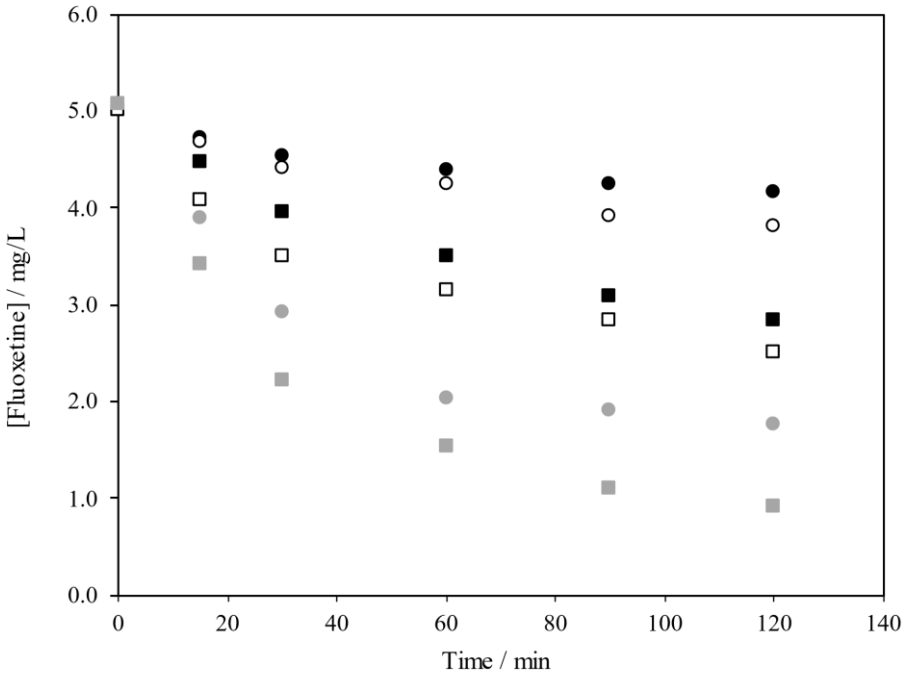

Figure 5. FLX concentration over time for different catholyte media and current densities: (●) O_3 100 mA cm^{-2}; (○) O_3 in H_2O_2/SO_4^{2-}, 100 mA cm^{-2}; (●) O_3 in H_2O_2/HCO_3^-, 100 mA cm^{-2}; (■) O_3 250 mA cm^{-2}; (□) O_3 in H_2O_2/SO_4^{2-}, 250 mA cm^{-2}; (■) O_3 in H_2O_2/HCO_3^-, 250 mA cm^{-2}.

The comparison between the tests performed shows significant differences. The lowest final concentration of FLX, i.e, the best degradation, occurs when using gaseous O_3 and H_2O_2 produced in HCO_3^- medium, applying 250 mA cm^{-2} (electro-peroxone

generation). The result is consistent with those of the previous tests, in which the production of oxidants was found to be favored both by the application of large current densities and the use of bicarbonate solutions as the catholyte. Hence, what it is actually observed is the direct result of adding higher concentrations of oxidants. However, in each test, the electric current passed, and the energy applied depended on the specific conditions of the tests (current density and electrolyte). Once the oxidants in the anodic and cathodic compartments are produced, the decision to apply one or both is arbitrary. It is thus interesting to compare these results not in terms of removal, but rather in terms of current efficiency (expressed as mg of FLX degraded per Ah) and energy efficiency (in which the cell voltage is considered in the calculation). Equations 11 and 12 were used to calculate both parameters, where $[FLX]_0$ is the concentration of FLX in the synthetic waste before starting electrolysis, $[FLX]_t$ is the concentration of the pollutant after the application of galvanostatic electrolysis, both in mg/L, with an intensity I (in A) for t (h) units of time, E is the cell voltage (in V) and F is the Faraday constant. Both parameters are shown in **Figure 6**.

$$(\text{current efficiency})_t = \frac{([\text{FLX}]_0 - [\text{FLX}]_t) \cdot V}{\frac{I.t}{F}} \quad (11)$$

$$(\text{energy efficiency})_t = \frac{([\text{FLX}]_0 - [\text{FLX}]_t) \cdot V}{\frac{I.E \cdot t}{F}} \quad (12)$$

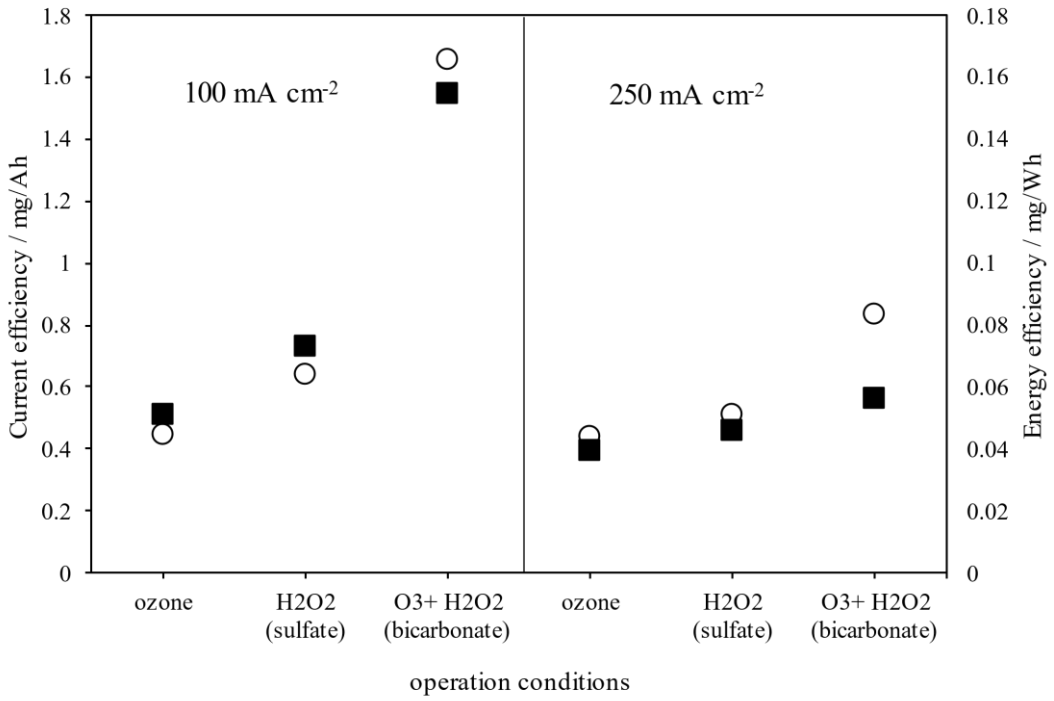

Figure 6. Effect of the electrolyte composition and anodic current density on the current (■) and energy (○) efficiencies for the degradation of FLX.

According to the values obtained from the efficiency viewpoint, the operation at lower current densities is more convenient, although the total reduction obtained for the same operation time is lower. This is the typical behavior observed in most electrochemical processes and indicates that under hasher conditions, there is a promotion not only of side reactions, but also of the effect of scavengers and, in both cases, oxygen is the promoted species. Likewise, even though the cell voltages are higher because of the lower ionic conductivity of the electrolyte, the efficiencies reached in electrolytes with bicarbonates are higher, reaching values over 0.15 mg Wh^{-1}. This is a good outcome because this electrolyte is also greener and, hence, the treatment leads to a treated wastewater that does not contain persistent species, such as sulfates. In addition, the combined use of both oxidants, produced simultaneously, can achieve a four-fold improvement regarding only ozone dosing, highlighting the approach proposed herein.

Conclusions

The following conclusions can be drawn:

- Although the production of ozone and hydrogen peroxide are known to require very different current density conditions (harsh for ozone and mild for hydrogen peroxide), the production of both oxidants can be carried out simultaneously in a specifically designed 3-D printed electrochemical cell. To obtain different operation current densities for the same current intensity, a 3-D cathode is used by attaching a GDE and a carbon felt, which allows increasing the surface area and maintaining a lower cathodic current density in the same cell.
- Although current density does not strongly influence hydrogen peroxide production, ozone production is strongly influenced by this variable. Therefore, the highest current is considered the best for the simultaneous production of the oxidants under study, H_2O_2 and O_3. Furthermore, the bicarbonate medium achieved greater production of both oxidants.
- Fluoxetine can be successfully degraded by gaseous O_3, which is improved when electrochemically generated H_2O_2 solutions are added at the same time. In addition, the catholyte formed by the bicarbonate solution is more efficient in degrading the pollutant, as is the application of a higher current density. Although the removal rate increases with current density, efficiencies are negatively affected by an increase in the current, and advise operating at low current densities in these systems.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could influence the work reported in this paper.

Author statement

Isabela Matos Gaudio de Souza: Investigation, Data curation, Formal analysis, Writing – original draft. Ismael. F. Mena: Investigation, Writing – original draft. Angela Moratalla Tolosa: Investigation, Writing – original draft. Larissa Pinheiro de Souza: Validation, Writing – review & editing. Cristina Sáez Jiménez: Validation, Supervision, Writing – review & editing. Antonio Carlos Silva Costa Teixeira: Project administration, Validation, Funding acquisition, Supervision, Writing – review & editing; Manuel Andrés Rodrigo: Conceptualization, Funding acquisition, Project administration, Supervision, Validation, Writing – review & editing.

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