



## Toward real applicability of electro-ozonizers: Paying attention to the gas phase using actual commercial PEM electrolyzers technology

M. Rodríguez-Peña<sup>a,b</sup>, J.A. Barrios Pérez<sup>b</sup>, J. Llanos<sup>a</sup>, C. Saez<sup>a</sup>, C.E. Barrera-Díaz<sup>b</sup>, M. A. Rodrigo<sup>a,\*</sup>

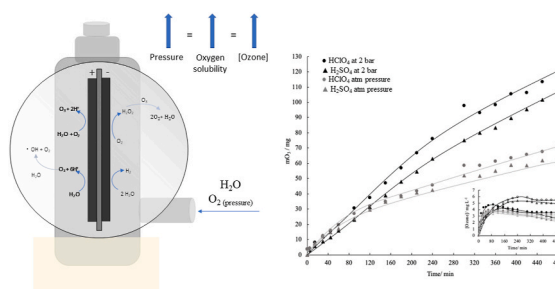
<sup>a</sup> Department of Chemical Engineering, School of Chemical Sciences and Technologies, University of Castilla La Mancha, Campus Universitario S/n, 13071, Ciudad Real, Spain

<sup>b</sup> Facultad de Química, Universidad Autónoma Del Estado de México, Paseo Colón Intersección Paseo Toluca S/N, C.P. 50120, Toluca, Estado de México, Mexico

### HIGHLIGHTS

- A commercial CONDIAPURE® cell has been evaluated for ozone production.
- Important improvements when operating at high pressures and low temperatures.
- Importance of electrolyte composition to accomplish large productions of ozone.
- Very important contribution of the gas phase: ozone is stripped from the electrolyte.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This work focuses on increasing the TRL of electro-ozonizer technology by evaluating the effect of electrolyte composition and operation conditions on the production of ozone, using an actual commercial cell, CONDIAPURE®, in conditions similar to what could be expected in a real application. Not only is attention paid to the changes in the concentration of ozone in the liquid phase, but also to those observed in the gas phase. The electrolyte and its recirculation flowrate, as well as operation temperatures and pressures are found to have significant influence on production rates. The most efficient way to produce ozone is operating at low temperatures and high pressures. In this work, 0.25 and 0.21 mg O<sub>3</sub>/min were obtained operating at 10 A in electrolytes consisting of aqueous solutions of perchloric and sulfuric acid, respectively, in tests carried out at 13 °C and 2 bars of gauge pressure. The negative effect of scavengers that appear electrochemically along the production of ozone is very important and seems to be partially compensated when organics are present in the solution due to the competition between the reaction of these scavengers with ozone or organics.

### 1. Introduction

Ozone (O<sub>3</sub>) is a powerful oxidant with an outstanding potential,

which is only outstripped by fluorine and some radical species (Jones and James, 1999). It is considered eco-friendly because no harmful by-products are formed during its use, in contrast with other highly

\* Corresponding author.

E-mail address: [manuel.rodrigo@uclm.es](mailto:manuel.rodrigo@uclm.es) (M.A. Rodrigo).

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oxidizing compounds such as chlorine (Ding et al., 2020). Thus, during oxidation processes, ozone is transformed into  $O_2$  and  $H_2O$  and when it reacts with the organic species the oxidation process proceeds through the oxygenation of pollutants up to their mineralization, typically leading to less harmful species (Broséus et al., 2009; Varga and Szigeti, 2016) than other oxidation technologies. Because of that, it is very appreciated in environmental applications, not only for the treatment of organics contained in wastewater, but also for disinfection (Rajab et al., 2015; Gomes et al., 2017; Pérez-Calvo, 2019). However, its application is somewhat limited due to the high cost associated to its generation by means of conventional methods, e.g., the well-known corona discharge, since high voltages are required and there are serious mass transfer problems associated to the dissolution of ozone in water (Wang and Chen, 2013; Poznyak et al., 2019; Rekhate and Srivastava, 2020; Yan et al., 2020). As a result of this, the electrochemical generation of this oxidant is starting to capture the attention of the scientific community as an alternative for conventional methods, as it seems to be feasible to achieve a high concentration and quality of ozone, at once preventing mass transport problems, since ozone is produced directly in the water (Isidro et al., 2018, 2019, 2020; Lara-Ramos et al., 2020; Herraiz-Carboné et al., 2021).

With a view to increasing the readiness of technologies, it is convenient to obtain results using cells available in the market rather than in-house cells manufactured in the laboratory. This will help to approach to more realistic solutions and increase the possibilities of applying such technology at full-scale applications. Recently, PEM electrolyzers, i.e., those in which the anode and cathode are connected to a PEM membrane, have shown outstanding performance in the generation of ozone, while the electrolyte composition has been pointed out as a very important input to explain the production of ozone (Chen et al., 2016; Frensch et al., 2018; Yu et al., 2018; Souza et al., 2020). In fact, with a very simple phenomenological model, the dynamics of the ozone concentration in the electrolyte during electrolysis tests can be easily understood. Though, very little attention has been paid to the gas phase, where the ozone extracted from the electrolyte may be contained and, if properly managed, could be successfully applied to processes to achieve higher efficiencies of use.

In previous works (Rodríguez-Peña et al., 2021a, 2021c, 2021c) the performance of PEM cells for the electrogeneration of ozone was evaluated, monitoring the dissolved ozone in liquid phase and evaluating the role of the main parameters. In this work, we want to go further and the monitoring of liquid and gaseous phases is carried out to account for the actual production of ozone in this type of technology, considering the stripping of ozone that takes place in the electrolyte as well, and the effect of different parameters in the gas phase to know the real influence ozone production capacity in the CONDIAPURE® cell.

## 2. Materials and methods

### 2.1. Chemicals

Double deionized water (Millipore Milli-Q system, resistivity:  $18.2 \mu\Omega \text{ cm}^{-1}$  at  $25^\circ\text{C}$ ) was used to prepare water solutions. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and perchloric acid ( $\text{HClO}_4$ ) were used as media for the electrolyte; clopyralid (CP), supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim, Germany), to prepare synthetic wastewater; and, methanol and formic acid (HPLC grade), to prepare the mobile phase in HPCL analyses (Sigma-Aldrich, Spain).

### 2.2. PEM electrolyzer and setup

The experiments were carried out in a CONDIAPURE® cell (supplied by CONDIAS GmbH, Germany) described in previous works (Rodríguez-Peña et al., 2021b). This electrolyzer is equipped with two diamond electrodes and a proton exchange Nafion® membrane. The active area of the diamond electrodes is  $146 \text{ cm}^2$ . Fig. SM1

(Supplementary materials) shows the experimental setup. The polyvinyl chloride (PVC) tank is filled with the electrolyte solution and pressurized to the desired value. The solution is recirculated with a micropump (GB-P25 J F5 S A head coupled to a DB 380 A 24 V engine) (with speed control 0–5 V DC) supplied by TechmaGPM s.l.r. (Milan, Italy). The temperature was controlled by a plate heat exchanger. To avoid material corrosion due to ozone, polyamide materials were used as connections and pipes in the experimental setup. A Delta Elektronika ES030-10 power supply (Delta Elektronika, Netherlands) powered the cell. In this work, an ozone analyzer (IN USA Incorporated model H1-X) connected to the tank was used to determine the ozone concentration in the gas phase.

### 2.3. Analytical techniques

Ozone concentration in the liquid samples was measured by the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method, using Spectroquant Merck test kits (Hach, Model: DR 2000). Ozone gas concentration was measured by a gaseous phase ozone analyzer (IN USA Incorporated model H1-X), which operates according to the electromagnetic radiation absorption principle. Ozone exhibits a peak of absorption at a wavelength of 253.7 nm, in the ultraviolet range of the spectrum. Clopyralid concentration was monitored by High Performance Liquid Chromatography (HPLC), while Total Organic Carbon (TOC) using a Multi N/C 3100 Analytik Jena TOC analyzer. More details on these analytical techniques can be found elsewhere (Santos et al., 2020a, 2020b, 2020b).

### 2.4. Experimental procedure

The tests were carried out in discontinuous mode using three different solutions:  $\text{Na}_2\text{SO}_4$  (pH 6.8),  $\text{H}_2\text{SO}_4$  (pH 3.0) and  $\text{HClO}_4$  (pH 3.0). The studied flowrates were 20 and  $150 \text{ L h}^{-1}$  and the applied current was 10 A for all the cases. These values are within the ranges recommended by the cell supplier. The influence of pressure was studied at 2 bar (gauge pressure) and at atmospheric pressure. In the organic pollutant oxidation tests, the solution was prepared with the same concentrations of sulfate or perchlorate as the other tests, plus  $100 \text{ mg L}^{-1}$  of clopyralid.

### 2.5. Ozone generation

The total concentration of ozone was calculated by measuring the dissolved ozone concentration and ozone gas concentration according to Eq. (1); where:  $V_l$  is the volume of the liquid phase;  $[\text{O}_3]_l$ , dissolved ozone concentration;  $V_g$ , volume of the gas phase;  $[\text{O}_3]_g$ , ozone gas concentration; and,  $q_g$  is the flow of the gas phase.

$$\text{MO}_3(t) = V_l * [\text{O}_3]_l + V_g * [\text{O}_3]_g + \int q_g [\text{O}_3]_g dt \quad (1)$$

## 3. Results and discussion

**Influence of the electrolyte recirculation flowrate on the production of ozone.** Fig. 1 shows the amount of ozone produced in a CONDIAPURE® cell operated at 10 A in discontinuous mode, when the electrolyte is recirculated at low ( $20 \text{ L h}^{-1}$ ) and high ( $150 \text{ L h}^{-1}$ ) flowrates, according to the electrolyte flowrate recommendations of the manufacturer (in the technical specifications datasheet). This amount comprises ozone in liquid and gas phases and as observed, it increases continuously over time. The inset in Fig. 1 shows changes in the concentration measured in the electrolyte (liquid phase) and in the gas phase during electrolytic tests. Regarding the concentration in the liquid phase, as expected due to previous works (Rodríguez-Peña et al., 2021a, 2021b, 2021c, 2021b), it increases in a first stage up to a maximum,

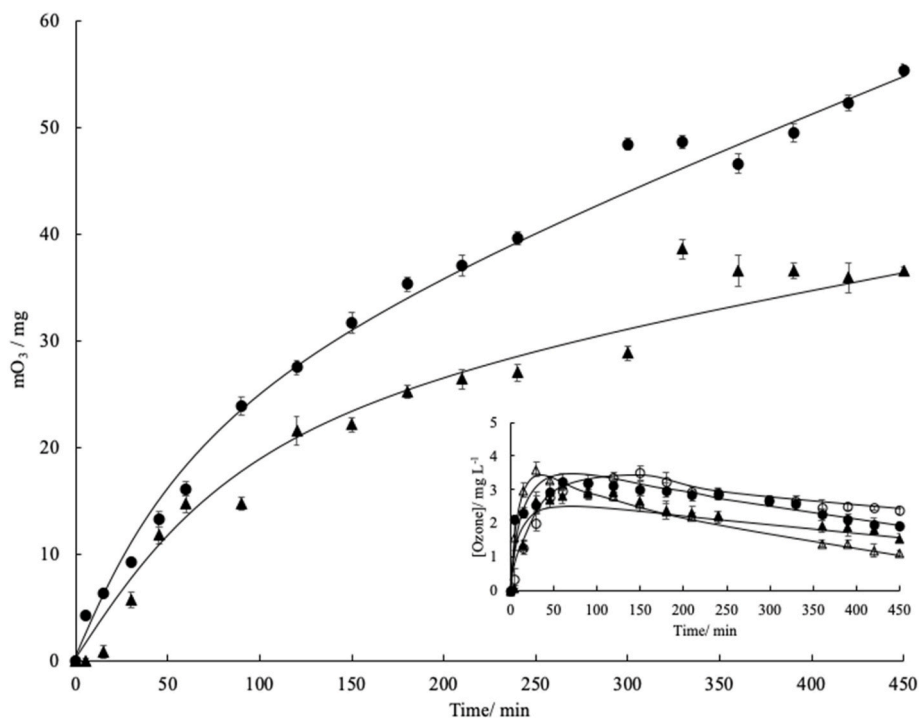


Fig. 1. Influence of the flowrate on the total production of ozone in discontinuous mode: ● 150 L h<sup>-1</sup>, ▲ 20 L h<sup>-1</sup>. Inset: Ozone concentration in discontinuous mode in liquid and gas phase ● ozone dissolved at 150 L h<sup>-1</sup>, ○ ozone gas at 150 L h<sup>-1</sup>, ▲ ozone dissolved at 20 L h<sup>-1</sup>, △ ozone gas at 20 L h<sup>-1</sup> (20 °C, 10 A, H<sub>2</sub>SO<sub>4</sub> pH 3.60).

from which a constant decay is noticed. In relation to the gas phase, a very similar trend is observed; this indicates the stripping of ozone contained in the electrolyte, which flows out of the system and should be accounted and managed for a more efficient application of electro-ozonizer technology. By comparing such figures, it is noticed that the first stage in the plot of concentrations also corresponds to a higher slope in the total production of ozone (0.2 mg O<sub>3</sub>/min); whereas during the second stage (when the ozone concentration contained in the liquid phase is lower), there is an important production of ozone, but the slope of the plot (which corresponds to the rate of production) decreases down to 0.06 mg O<sub>3</sub>/min when using a high electrolyte flowrate, and to 0.03 mg O<sub>3</sub>/min when using a low flowrate. This means that faradaic efficiencies are very low, ranging from 0.02 to 0.4%, depending on the electro-transfer considered: six electrons in the production of ozone from water (Eq. (2)) or two electrons in the production of ozone from oxygen (Eq. (3)) (Wang and Chen, 2013).



Thus, in the comparison of the two recirculation flowrates tested, a positive effect of the electrolyte flowrate is observed in the total production of ozone, which also reflects a higher concentration of ozone in the liquid phase. However, no influence is observed on the decay rate, as the concentration of ozone in the liquid phase decreases with the same rate, regardless of the electrolyte flowrate used. Results can be easily understood by considering that the ozone in gas phase increases when the flowrate increases, because of the promotion in the stripping of the ozone from the liquid phase. As stated in previous works (Rodríguez-Peña et al., 2021b, 2021c, 2021c), the decay in the liquid phase is associated to the interaction of ozone with scavengers such as hydrogen peroxide, produced anodically and cathodically, and many others depending on the electrolyte composition; i.e., peroxosulfates, which can be formed in this system from the anodic oxidation of sulfuric acid contained in the electrolyte formulation (Rodríguez-Peña et al.,

2021a; Rodríguez-Peña et al., 2021b). The stripping promoted by a higher flowrate allows an easier removal of the ozone produced in the liquid phase, avoiding this interaction, and yielding higher net amounts of ozone. In addition, the slightly higher concentration of ozone observed in the liquid phase must be explained in terms of a promotion in the mass transfer processes associated to higher turbulence, which are associated with an improvement in efficiency by promoting the availability of oxygen in the vicinity of the electrode surface and preventing the accumulation of bubbles near the electrodes. Fig. SM2 (supplementary materials) shows the relation between ozone concentration in liquid and gas phases. Such concentrations are strongly related, and it may be suggested that the system operates at a near pseudo-equilibrium state between liquid and gas concentrations. Nonetheless, the high dispersion observed in this plot stands for the transient response in the absorption process, as no sufficient time has passed to reach the steady state.

**Influence of the electrolyte on the production of O<sub>3</sub>.** As stated in the previous section, and in previous papers as well (Rodríguez-Peña et al., 2021a; Rodríguez-Peña et al., 2021b), the decay in concentration of ozone measured in the liquid phase is associated to the presence of scavengers, that is, predator species formed in the electrolyte over electrolysis. Otherwise, if these species were not formed, the concentration of ozone in the liquid should reach a constant value, in which production and degradation rates balance, and hence, a decrease in the concentration would go unnoticed. Fig. 2 compares the total production of ozone in the CONDIAPURE® cell operated at 10 A, with three different electrolyte formulations: HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>. Regardless of the supporting electrolyte, a very important production of ozone is noticed with a continuous increase, in which two zones can be clearly differentiated: one with a higher slope, and a second with a lower net production rate. Nevertheless, an important effect of the electrolyte composition on the production of ozone is observed. The inset displays the concentrations measured in the liquid phase, in which the increase in the concentration of ozone up to a maximum and a later decrease in the ozone concentration are clearly observed once again, underscoring the

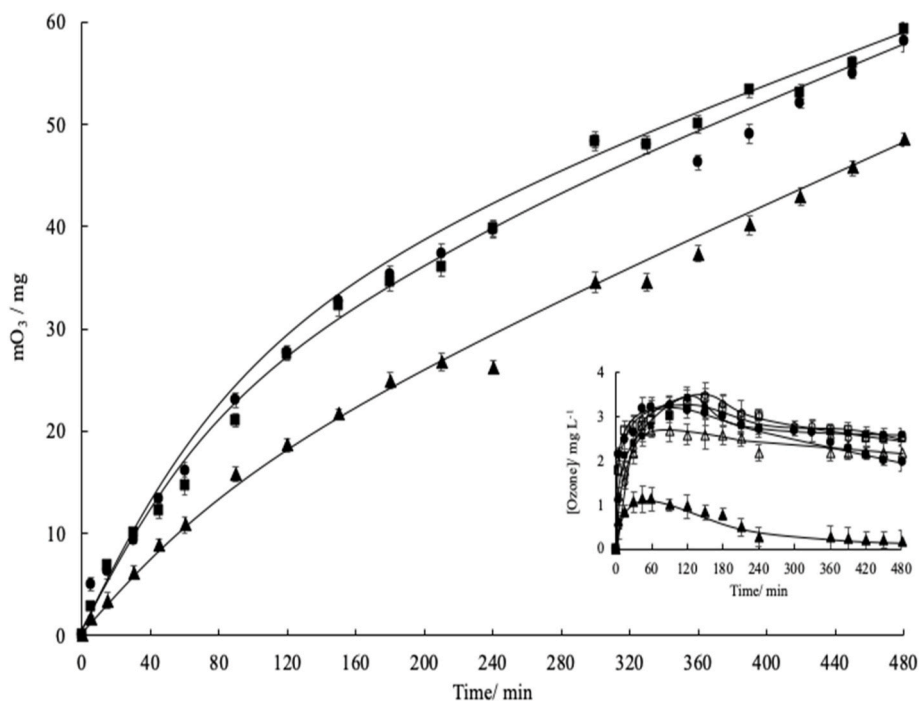


Fig. 2. Electrolyte influence in the total production of ozone in discontinuous mode: ■  $\text{HClO}_4$ , ●  $\text{H}_2\text{SO}_4$ , ○  $\text{Na}_2\text{SO}_4$ . Inset: Ozone concentration in discontinuous mode in liquid and gas phase ■ ozone dissolved  $\text{HClO}_4$ , □ ozone gas  $\text{HClO}_4$ , ● ozone dissolved  $\text{H}_2\text{SO}_4$ , ○ ozone gas  $\text{H}_2\text{SO}_4$ , ○ ozone dissolved  $\text{Na}_2\text{SO}_4$ , △ ozone gas  $\text{Na}_2\text{SO}_4$  (20 °C, 150 L  $\text{h}^{-1}$ , 10 A).

relevance of scavengers on the production of ozone, as they consume an important part of the ozone electrochemically produced. The electrolyte containing sodium sulfate achieved the worst results. Differences are lower in the case of the two strongly acidic electrolytes, even though perchlorate reaches better net productions of ozone. This gas is known to be more stable at pH conditions below 6. Thus, according to previous works, the rate of ozone decomposition to form •OH increases as pH does (Rosales et al., 2016; Mena et al., 2018; Bavasso et al., 2020; Kim et al., 2020; Rodríguez-Peña et al., 2021a, 2021b), and this can help to explain the worse results observed in non-acidic electrolytes. In a later section, this point is going to be further evaluated.

Regarding the anions contained in the electrolyte, ozone stability improves when working with  $\text{HClO}_4$ , since the production of peroxosulfate radicals, which are responsible for decomposition, does not

occur and the main scavenger for ozone is hydrogen peroxide, which not only is cathodically produced by oxygen reduction, but also anodically by water oxidation (de León, 2020; Zhao et al., 2020; Rodríguez-Peña et al., 2021a). This explains the higher ozone decay behavior in  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ , as in these cases peroxosulfate radicals are formed in addition to hydrogen peroxide, resulting in a more efficient cocktail of reagents to scavenge ozone. As regards ozone in the gas phase, it could be noted that it follows the same trend of the ozone concentration in the electrolyte, which supports the existence of a pseudo-equilibrium between ozone in both phases, apart from the case of  $\text{Na}_2\text{SO}_4$ , for which the concentration of ozone in the liquid phase is lower than expected due to the limited stability of ozone at higher values of pH (as previously explained).

**Influence of temperature.** Fig. 3 shows the influence of the

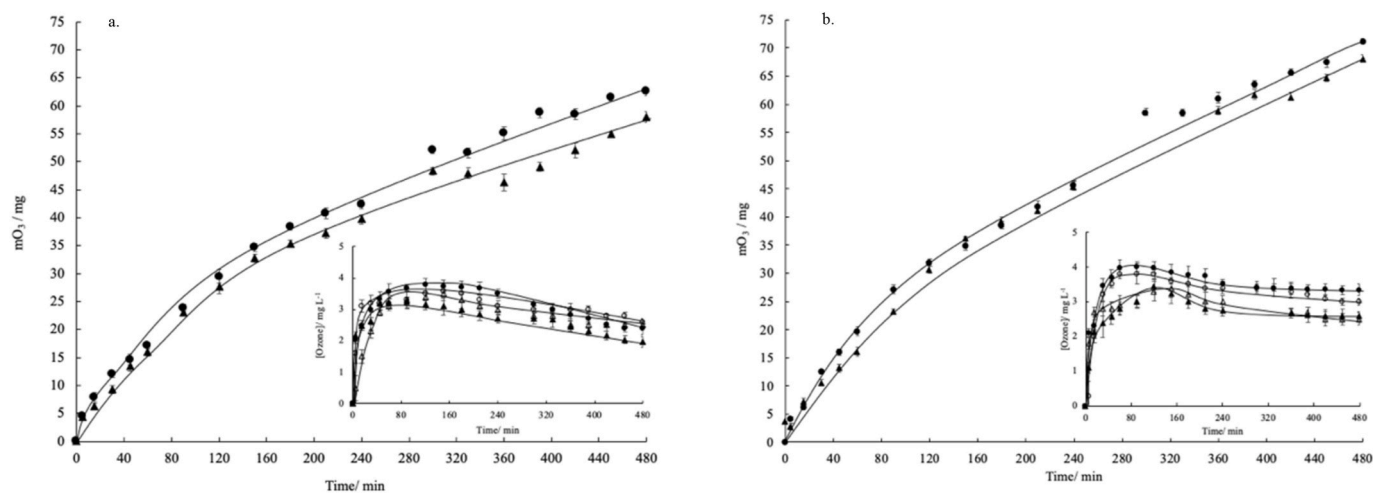


Fig. 3. a. Temperature influence in the total production of ozone in discontinuous mode in  $\text{H}_2\text{SO}_4$ : ● 13 °C, ○ 20 °C. Inset: ● ozone dissolved at 13 °C, ○ ozone gas at 13 °C, ○ ozone dissolved at 20 °C, △ ozone gas at 20 °C. b. Temperature influence in the total production of ozone in discontinuous mode in  $\text{HClO}_4$ : ● 13 °C, ○ 20 °C. Inset: ● ozone dissolved  $\text{HClO}_4$  at 13 °C, ○ ozone gas  $\text{HClO}_4$  at 13 °C, ○ ozone dissolved  $\text{HClO}_4$  at 20 °C, △ ozone gas  $\text{HClO}_4$  at 20 °C (150 L  $\text{h}^{-1}$ , 10 A).

operating temperature on the amount of ozone that is produced by the CONDIAPURE® cell in electrolytes containing perchloric and sulfuric acid by comparing the performance of ozone production tests carried out at 13 and 20 °C. In the inset, the concentrations of ozone measured in the liquid and gas phases are also shown. As noticed, a decrease in temperature has a favorable effect on the production of ozone and, again, a better performance in the supporting electrolytes containing perchloric acid is noticed. These results can be explained in terms of the balance between the concentrations of ozone in liquid and gas phases, and also because of the effect of temperature on ozone decomposition (MKS Instruments, 2004; Wei et al., 2017). In Fig. SM3 (Supplementary materials), the concentrations of ozone in gas phase are plotted versus the concentrations in liquid phase showing the gas-liquid pseudo-equilibrium, which is more favorable for the liquid phase when operating at lower temperatures owing to the expected increase in the solubility of gases at lower temperatures. Thus, by comparing Fig. SM3 and SM2 it is noticed how the dissolution of ozone is more efficient at lower temperatures as the slope of the plot is lower. In this way, temperature is not a parameter that limits the electrochemical production of ozone, but one that affects its solubility in the liquid phase (Rischbieter et al., 2000). In water treatments, it is preferred to contain the largest possible amount of ozone dissolved in the water, meaning that at low temperatures the efficiency in its application would improve. In the same way, it is verified that media have effects only on ozone solubility, not in the cell capacity to generate ozone, because the electrolyte is a Nafion membrane.

**Influence of operation pressure.** To evaluate the effect of operation pressure, electrolysis tests were carried out at atmospheric pressure and at a gauge pressure of 2.0 bar (see Fig. 4) to assess whether the performance of electro-generation of ozone improves with pressure. These experiments were carried out at low temperature considering the important improvements observed in the previous section. As noticed in Fig. 4, pressure directly affects the capacity of the system to produce ozone: an increase in pressure becomes an increase in ozone production. Again, this increase is higher in electrolytes containing perchloric acid.

As it is reported, ozone production is not only attained by the oxidation of water (as shown in Eq. (2)), but also by oxidation of oxygen (as shown in Eq. (3)), which becomes a primary mechanism in acidic

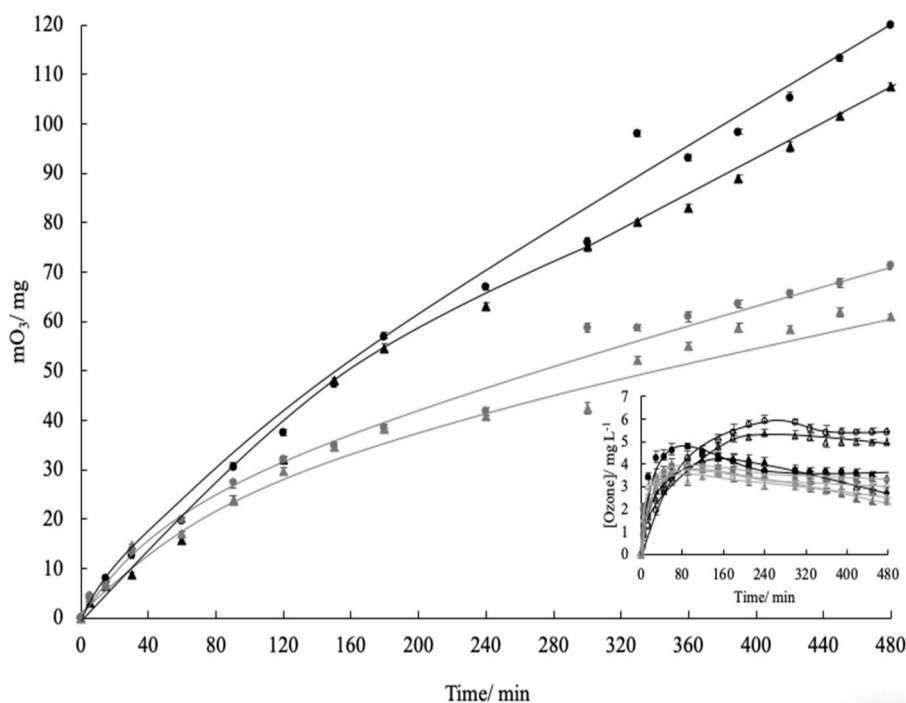
electrolytes. When operation pressure increases in the system, the oxygen solubility is higher and the production of ozone by oxygen increases, as it was demonstrated in a previous work (Rodríguez-Peña et al., 2021a), when the efficiency of ozone production by oxygen was found to increase with pressure. In the inset in Fig. 4, the pressure increases ozone generation, though it does not improve the stability of ozone in water. For that reason, the ozone concentration in the gas phase is higher at 2.0 bar (gauge pressure) than at atmospheric pressure and the concentration of ozone dissolved is only slightly higher.

The highest rates of ozone production are 0.25 and 0.21 mg O<sub>3</sub>/min, respectively, in electrolytes containing perchloric and sulfuric acid which corresponds to efficiencies of 0.17–0.50% (perchloric) and 0.14–0.42% (sulfuric), if the raw matter is considered oxygen or water as previously shown in Eqs. (1) and (2).

**Influence of the presence of organics in the electrolyte.** Fig. 5 shows the changes in the concentration of ozone during the electrolysis of electrolytes containing 100 mg L<sup>-1</sup> of Clopyralid (CP) or without CP. As noticed, the concentration reaches a maximum and remains almost constant in the case of electrolytes with organics (ozone depletion rate is much lower in the presence of clopyralid), which indicates that the predator species present in the use of H<sub>2</sub>SO<sub>4</sub> (peroxosulfate radicals) are helping to degrade the organic compound and are not available for ozone decomposition. Once again, it is noticed that concentrations of ozone in gas and liquid phases are in pseudo-equilibrium. As well, the total ozone production measured in presence of clopyralid is lower because the ozone produced should be also used for the degradation of the organic pollutant (Fig. 5 b).

(13 °C, 150 L h<sup>-1</sup>, 10 A).

Another important observation is that the degradation of clopyralid shows a faster rate when the electrolyte contains H<sub>2</sub>SO<sub>4</sub> as compared with electrolytes containing HClO<sub>4</sub> (Fig. 6). Ozone is more selective than hydroxyl and peroxosulfate radicals. In this context, when the concentration and stability of ozone in the solution is higher, the degradation of clopyralid seems to be slower. Thus, the synergy between the production of sulfate radicals and •OH by the reaction of ozone with peroxymonosulfate has been studied elsewhere (Yang et al., 2015), which shows that when degradation occurs by O<sub>3</sub>/PMS, it increases 54% in half



**Fig. 4.** Pressure influence on the total production of ozone in discontinuous mode (● HClO<sub>4</sub>, ⊗ H<sub>2</sub>SO<sub>4</sub>) at 2 bar (black) and without pressure (grey). Inset: ● ozone dissolved HClO<sub>4</sub>, ⊗ ozone dissolved H<sub>2</sub>SO<sub>4</sub>, ○ Ozone gas HClO<sub>4</sub>, △ ozone gas H<sub>2</sub>SO<sub>4</sub>, at 2 bar (black) and without pressure (grey) (13 °C, 150 L h<sup>-1</sup>, 10 A).

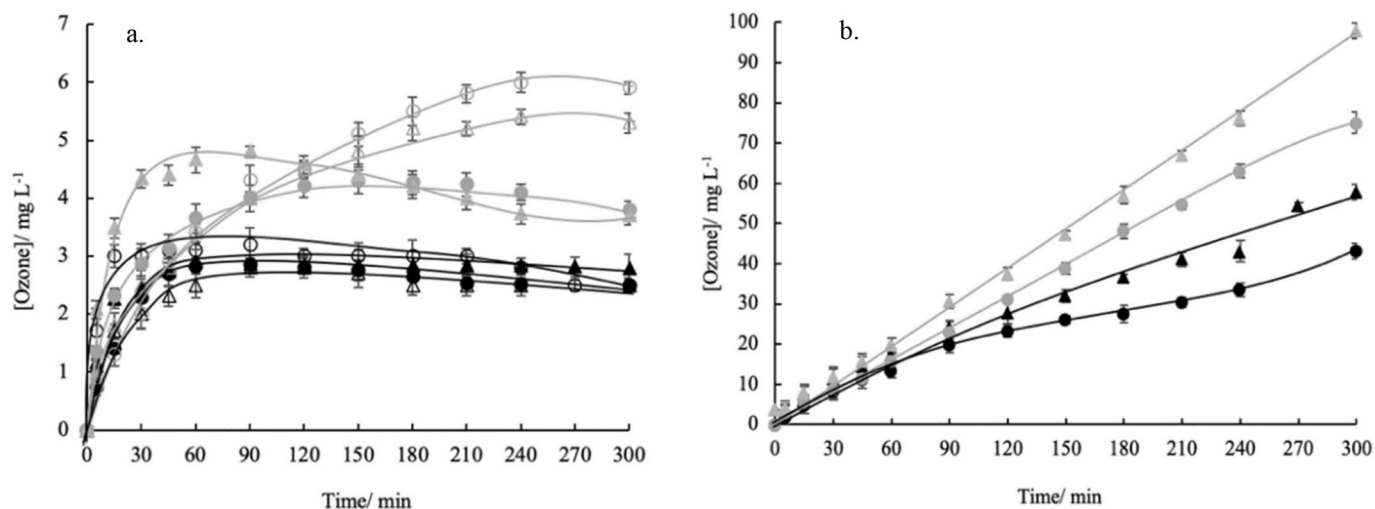


Fig. 5. Production of ozone in discontinuous mode at a gauge pressure of 2.0 bar in presence of 100 mg L<sup>-1</sup> Clopyralid and absence of Clopyralid. a. Ozone concentration: ● ozone dissolved HClO<sub>4</sub>, ○ ozone dissolved H<sub>2</sub>SO<sub>4</sub>, ○ ozone gas HClO<sub>4</sub>, △ ozone gas H<sub>2</sub>SO<sub>4</sub>, with clopyralid (black), without clopyralid (grey). b. Ozone total concentration: ● HClO<sub>4</sub>, ○ H<sub>2</sub>SO<sub>4</sub> with clopyralid (black), without clopyralid (grey).

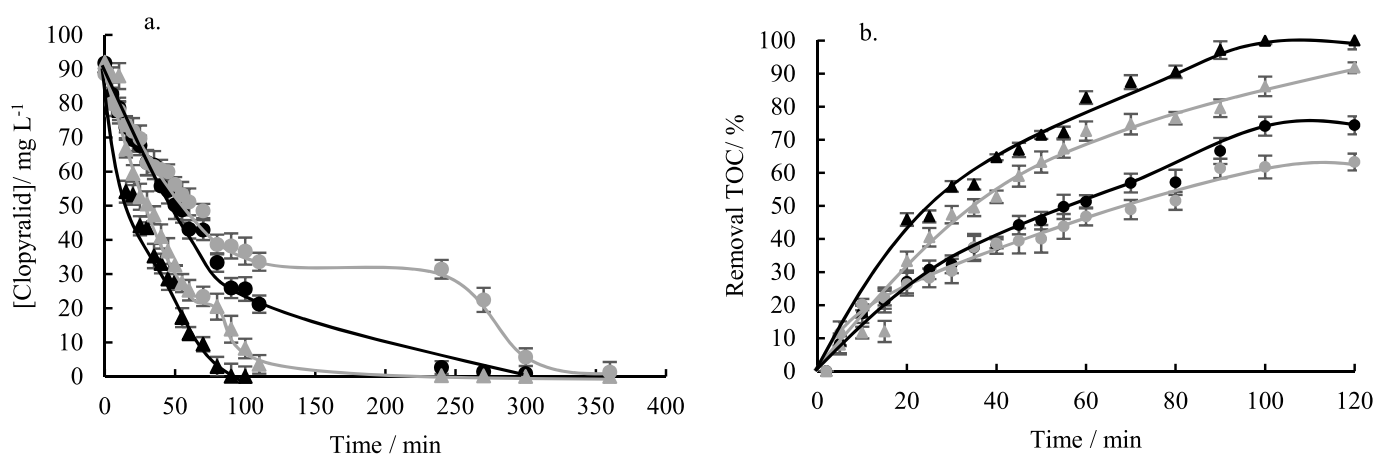


Fig. 6. Degradation of an organic compound a. Clopyralid degradation ●HClO<sub>4</sub>, ○ H<sub>2</sub>SO<sub>4</sub> at 2 bar (black symbol), without pressure (grey symbol). b. Mineralization ●HClO<sub>4</sub>, ○ H<sub>2</sub>SO<sub>4</sub> at 2 bar (black symbol), without pressure (grey symbol) (13 °C, 150 L h<sup>-1</sup>, 10 A).

the time as compared with O<sub>3</sub>. In high-pressure experiments, ozone stability improves and the generation of peroxosulfate radicals is prevented. When using electrolytes with HClO<sub>4</sub>, no peroxosulfate radicals are generated, so the degradation of clopyralid only occurs by ozone and directly on the anode. In H<sub>2</sub>SO<sub>4</sub> and without pressure, the generation of peroxosulfate radicals and hydroxyl radicals increases and for that reason, the degradation of clopyralid is faster because degradation occurs by ozone, hydroxyl radicals and peroxosulfate radicals directly on the anode. Furthermore, the comparison of PEM electrolyzers and a conventional ozonator was studied by Lara-Ramos et al. (2020), showing that the electrical efficiency in mineralization shows better performance with PEM electrolyzers than with ozonators in similar operating conditions, which allowed them to observe that a conventional ozonator is not able to entirely mineralize clopyralid, only achieving a 5-percent mineralization in 180 min. However, in the present work the ozonation of clopyralid by a CONDIAPURE® cell can reach total mineralization in 120 min only.

#### 4. Conclusions

The CONDIAPURE® cell is a good alternative for the electro-generation of ozone, while operating conditions such as temperature and electrolyte formulation do not have any extremely important effect

on the capacity of the cell to generate ozone. This allows working in mild conditions, making the process more viable and easier to operate. However, both the temperature and the supporting electrolyte are key to improve the solubility and stability of dissolved ozone. On the other hand, pressure shows a relevant effect on total production because it increases the solubility of oxygen and approximately doubles the concentration of ozone. However, the pressure does not improve the stability of the dissolved ozone or help to obtain a higher rate of degradation of the organics. In the experiments at higher pressure, 90% mineralization was obtained, while complete mineralization was obtained when working at atmospheric pressure, which is an advantage because it reduces operating costs. The synergistic effect between the oxidants promoted by the electrolyte contributes to improve the mineralization of clopyralid, showing an increase in the rate of degradation in the electrolyte containing sulfate as compared to those containing perchlorate.

#### Author statement

M. Rodríguez-Peña: investigation; writing – original draft; methodology; data curation. J.A. Barrios Pérez: supervision; validation; formal analysis; writing – review and edition. J. Llanos: supervision; validation; formal analysis; writing – review and edition. C. Saez: supervision;

validation; formal analysis; writing – review and edition. C.E. Barrera-Díaz: conceptualization; funding acquisition; supervision; writing – review and edition. M.A. Rodrigo: conceptualization; funding acquisition; supervision; writing - review and edition.

### Declaration of competing interest

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

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2021.133141>.

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