# Scale-up in PEM electro-ozonizers for the degradation of organics

M. Rodríguez-Peña[1,2], J.A. Barrios Pérez[2], J. Lobato[1], C. Saez[1], C.E. Barrera-Díaz[2], M.A. Rodrigo[1,*]

[1] Department of Chemical Engineering. Faculty of Chemical Sciences and Technologies. University of Castilla La Mancha. Campus Universitario s/n. 13071 Ciudad Real. Spain.

[2] Facultad de Química. Universidad Autónoma del Estado de México, Paseo Colón intersección Paseo Tollocan S/N, C.P. 50120, Toluca, Estado de México, México

**Abstract**

This work focuses on the scale-up of electro-ozonizers by evaluating the production of ozone and the degradation of clopyralid synthetic wastes using three commercial PEM electrolyzers. The mechanical concept of the three cells is similar: a single compartment cell equipped with a MEA (consisting of a polymer exchange membrane and two pressed diamond coatings electrodes), powered with monopolar electric connection and where water flows on the surface of the electrodes, although the main electrolyte is the Nafion proton exchange membrane. However, their size and recommended operating conditions are not as similar, and their comparison becomes a good scaleup case study. The CabECO® cell consists of 2 MEAs with a total surface area of 24 cm$^2$, a maximum operating current density of 2. 0A. The Mikrozom® cell consists of only one MEA with a net surface electrodic area of 112 mm$^2$ and a maximum operation current density of 1.0 A. Finally, the CONDIAPURE® cell consists of a single MEA with a total surface area of 146 cm$^2$ and a

maximum operation current density of 10.0 A. The performance under mild and extreme operating conditions was compared and the results show that, although the cell concept is similar, the results obtained differ very significantly. The three PEM electrolyzers tested can produce ozone efficiently and mineralize completely clopyralid. The only intermediates measured come from the cathodic hydrodechlorination of clopyralid and oxidative intermediates were only detected at trace concentrations. CabECO® cell demonstrates an outstanding performance with very high current efficiencies in the production of ozone. However, the highest mineralization efficiencies are obtained with the Microzon®, which, although it is the PEM electrolyzer with the smallest active area, is the most efficient because can reach high ozone concentrations and achieve the best clopyralid mineralization. Efficiencies as high as 0.47 mg $O_3$ $Wh^{-1}$ can be obtained with this cell. Slightly lower values are reached by the CabECO® cell (0.38 mg $O_3$ $Wh^{-1}$). Enlarging electrode surface area does not seem to be a good strategy from the viewpoint of efficiency and it seems to promote side reactions that compete with ozone production and with the degradation of organics. This means that stacking rather than electrode enlarging should be the strategy more advisable for scaling up the electro-ozonation technology.

**Keywords**

Commercial electrolysers; electro-ozonators; EAOP; ozone; PEM cell; mineralization

**Highlights**

- PEM electrolyzers produces important concentrations of ozone
- Comparison of three commercial electrochemical cells with different sizes

- Significant differences in performance even <mark>though</mark> they are based on the same mechanical concept.

- Large removals of organics.

*author to whom all correspondence should be addressed: manuel.rodrigo@uclm.es

**Introduction**

After three decades of massive study of the applicability of advanced electrochemical oxidation technologies for the removal of organics contained in wastewater, it is worth to try to increase the technology readiness level by evaluating what real commercial cells can really do [1]. Regarding electrochemical wastewater treatment, most of the work carried out in the recent years is focused on the evaluation of the reaction conditions by improving the operation conditions or the electrode electrocatalytic properties, neglecting the important effect of the mechanical design of the electrochemical cells [2–7]. Recent studies have pointed out that the influence of the cell design on the treatment performance can be even more important than these widely studied topics [8–11]. In this field, it is more common that information is obtained in the form of patents rather than in scientific papers. In fact, many of the details that made a cell better than other are very complex and difficult to be understood, because of the required combination of many different inputs (local turbulence in each point [12] , better exchange of temperature[13], better current distribution [14–16], etc.) to reach success and it is not common to find this type of scientific discussion in conventional scientific paper except for those based on CFD modelling [15,17–20]. In addition, because of the extreme complexity, it is worth to use reproducible systems, that is, commercial cells whose performance can be contrasted by other researchers in the same or in different applications. Thus, the real application needs for the use of commercial prototypes and the understanding of their performance is a must in the search of a real applicability of the technology.

Recently, it has been pointed out the important impact of ozone produced during electrolysis on the removal of organics during electrochemical oxidation processes [21–24]. The use of PEM electrolyzers has been found to be a good choice to promote these oxidation mechanisms, because this type of cells does not only promote the formation of ozone, but they also can operate more efficiently in wastewater with low ionic conductivity [25–27]. These results have also been evaluated in disinfection studies [28–32].

In PEM electrolyzers, the electrode is connected to their counter-electrode throughout a polymer exchange membrane, where protons and/or other ions can circulate compensating the charge of the electrons flowing throughout the electric circuit of the electrochemical device [33–35]. Because of that, this type of devices is less sensitive to water conductivity and, even, they can be applied in the treatment of extremely low conductivity water or wastewater. Even in the treatment of biphasic flows and also in the direct treatment of gases. Recently, a commercial cell, the CabECO® cell, was tested for the disinfection of strongly faecally polluted water showing outstanding results. The supplier (the German company CONDIAS GmBH) manufactures three different cells based on the same principle but with different sizing: the previously mentioned CabECO®, the MIKROZON® and the CONDIAPURE® cells. Concept is similar: a single compartment cell in which a single or divided MEA consisting of a polymer exchange membrane and two pressed electrodes are powered monopolarly and water flows on the surface of the electrodes. However, their size and recommended operating conditions are not as similar, and their comparison becomes a good scaleup exercise. The CabECO® cell consists of 2 MEAs diamond-Nafion-diamond connected in parallel and with a total surface area of 24 cm$^2$ a maximum operating current density of 2.0 A. The MIKROZON® cell consists of only MEA diamond-Nafion-diamond

with a net surface electrodic area of 112 mm$^2$ and a maximum operation current density of 1.0 A. Finally, the CONDIAPURE® cell consists of a single MEA diamond-Nafion-diamond with a total surface area of 146 cm$^2$ and a maximum operation current density of 10.0 A. Recently a comparison of their performance in disinfection was carried out but no information about ozone production and use was looked for in that work [31]. Additionally, ozone generation by PEM electrolyzer has been previously studied and a phenomenological model has been proposed to understand the processes inside the cell and to characterize it. Relevant data were obtained but there is still a gap that this manuscript aims to fill.

This work is focused on the comparison of the performance of the three cells in their maximum and recommended operation conditions paying attention to the production of ozone and other oxidants and to the degradation of clopyralid (selected as model of organic) in synthetic wastewater. This will help to understand the strong and weak points of the technology and contribute to its proper scale-up.

**Materials & Methods**

**Chemicals.** Double de-ionized water (Millipore Milli-Q system, resistivity:18.2μΩ cm-1 at 25 C) was used to prepare solutions of sulfuric acid (H$_2$SO$_4$) and perchloric acid (HClO$_4$) which were used as electrolyte. Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid) was used as model of organic (herbicide). Methanol and formic acid (HPLC grade) were used to prepare the mobile phase in HPCL analysis (Sigma-Aldrich, Spain).

**Electrochemical cells.** Electrochemical ozone generation was performed in three different PEM electrolyzers equipped with BDD electrodes and Nafion® proton exchange membranes: CONDIAPURE® is equipped with two diamond electrodes and a Nafion®

proton exchange membrane. The surface area of the diamond electrodes is 146 cm$^2$. The CAbECO® cell is equipped with 4 diamond electrodes mounted in two stacks with a Nafion® cation exchange membrane separating the anode and cathode (24 cm$^2$ of active area= and the MIKROZON® cell is equipped with two electrodes (112 mm$^2$) in a membrane electrode array with Nafion® cation exchange membrane. Further data are shown in other papers [25,29–31,36]. The three cells were installed in the same setup but operated separately (Figure 1). The solution is continuously fed to the electrochemical cell from the reservoir tank by a micropump (GB-P25 J F5 S A head coupled to a DB 380 A 24 V engine) (with speed control 0-5V DC) supplied by TechmaGPM s.l.r. (Milan,tItaly). The PEM electrolyzers were powered by a Delta Elektronika ES030-10 power supply, with a range of voltage of 0–30 V and intensities of 0-10A (Delta Elektronika, Netherlands). The temperature was controlled at 18ºC by a plate heat exchanger. The recirculated volume in all cases was 2 L of H$_2$SO$_4$ (initial conductivity: 330 $\mu$s cm$^{-1}$) and HClO$_4$ (initial conductivity: 265 $\mu$s cm$^{-1}$) solution and the flow rate was 150 L h$^{-1}$.

**Figure 1.** Experimental setup in discontinuous mode: 1) tank, 2) heat exchanger, 3) micropump, 4) power supply, 5) CONDIAPURE® cell,  6) CabECO® cell, 7) power supply, 8) MIKROZON® cell, 9) power supply. CONDIAPURE® setup (blue line), CabECO® (red line) and MIKROZON® (yellow line).

**Analytical procedures** Dissolved ozone concentration was measured throughout the experiment with a colorimetric method with N,N-diethyl-p-phenylenediamine (DPD), using Spectroquant Merck test kits (Hach, Model: DR2000). The degradation of 100 mg $L^{-1}$ of Clopyralid was followed by High Performance Liquid Chromatography (HPLC) and Total Organic Carbon (TOC). The technical analytical techniques can be found in previous work [25,37–39].

**Results & discussion**

**Production of ozone.** To compare the performance of the three commercial PEM electro-ozonizers evaluated in this work, four tests were carried out at two current densities: the manufacturer's recommended current density and the maximum allowable current density for safe operation of the cell. This later current density can be reached during a limited period of time, but it is not convenient for prolonged use.

Because the application looked for is the removal of organics, ozone scaping by stripping is not considered in these tests. This is important because the real production of ozone for the three cells is much higher. However, the surplus ozone transferred to the gas phase is not available for the oxidation of organics contained in wastewater and should not be accounted for a real wastewater treatment. In addition, another important information can be drawn from the tests, because two different supporting electrolytes were evaluated considering the

very important role of the potential scavengers formed in the electrolyte: perchlorate and sulfate. Another important point considered was the mode of operation (continuous or single pass operation and discontinuous or batch with recirculation ), which is expected to also have an important role, because of the very different fluid-dynamic condition and the accumulation of scavengers in the discontinuous mode.

Regarding the operation in continuous mode, that is, when the electrolyte is continuously fed to the cell and it is not recirculated, Figure 2 shows the production of ozone attained. As seen, the highest concentration of ozone is obtained when working with supporting electrolytes with $HClO_4$ and at high current intensity (Figure 2), although these intensity conditions are not recommended because a prolonged use can lead to shorten the lifetime of the cell. When comparing the three PEM electrolyzers, the lower concentration and stability of ozone is found when working with the CONDIAPURE® cell, in spite of being the cell with the higher electrode surface area. The recommended value by manufacturer is 416.7, 41.6 and 60.3 mA $cm^{-2}$ for the MIKROZON®, CabECO® and CONDIAPURE® cells and the maximum allowable values is 833.3, 83.3 and 86.2 mA $cm^{-2}$, respectively. This means that a higher current density has a positive impact on the production of ozone with all technologies tested.
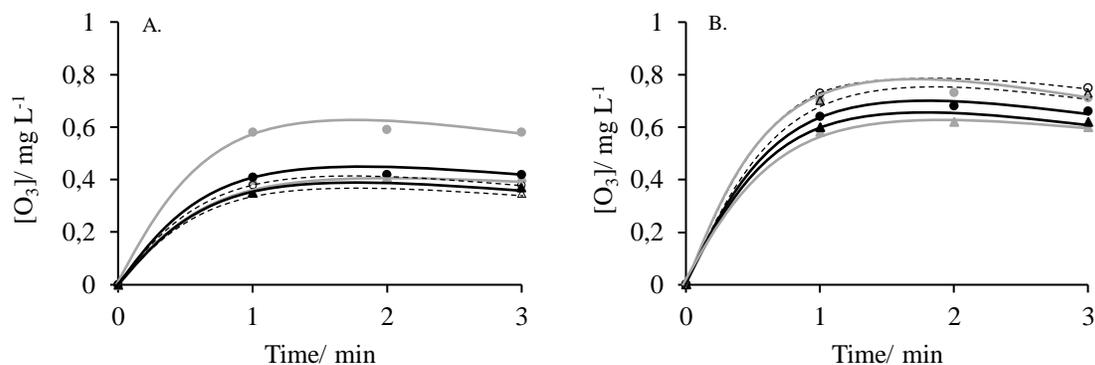
**Figure 2.** Influence of PEM electrolyzer in the electrogeneration of ozone in continuous mode. Part A. MIKROZON® cell (0.5A, dashed line), CabECO® cell (1A, grey line) and CONDIAPURE® cell (7A, black line). Part B. MIKROZON® cell (1A, dashed line), CabECO® cell (2A, grey line) and CONDIAPURE® cell (10 A, black line). Electrolyte: (●) $HClO_4$, (▲) $H_2SO_4$.

To highlight this point, several figures of merit are presented here. In the case of ozone generation, the calculation of the efficiency is based only on the concentration of ozone remaining in the water in the steady state ($[O_3]_{ss}$) and it does not consider ozone that it is released to the gas phase, because we are considering in this work that it does not lead to the oxidation of organics. From Figure 2, the energy efficiency for the generation of ozone can be estimated considering the flowrate of produced ozone ($m_{O_3}$) in continuous mode and the power consumption (W). This flowrate of ozone ($m_{O_3}$) at the steady state can be calculated using Eq. 1, where q is flowrate (L h$^{-1}$), whereas power consumption can be calculated using Eq. 2, where I is the applied intensity (A) and V is the cell voltage (V). It can be assumed that this cell voltage remains practically constant throughout the experiment. Ratio between both parameters gives the energy required to produce ozone (Eq. 3). Additionally, the area

loading can be estimated by dividing the ozone electrogenerated ($m_{O_3}$) by the electrode area ($A_{electrode}$) according to equation (4).

$$m_{O_3}(g\,h^{-1}) = Q * [O_3]_{ss} \quad (1)$$

$$W\,(W) = V * I \quad (2)$$

$$\text{Energy efficiency }(g\,kWh^{-1}) = \frac{m_{O_3}}{W} \quad (3)$$

$$\text{Area loading }(g\,m^{-2}h^{-1}) = \frac{m_{O_3}}{A_{electrode}} \quad (4)$$

Table 1 shows the energy efficiency for the generation of ozone in optimum condition using the three PEM cells in $H_2O_4$ and $HClO_4$ media. As can be observed, values obtained range between 1.38 and 9.38 g $(kWh)^{-1}$ and the best performance is obtained with MIKROZON® cell and in electrolytes consisting of perchloric acid. These values are within the same range of those reported in the literature. Thus, Arihara and coworkers have reported 5.71 g $(kWh)^{-1}$ in ozone generation using a similar cell equipped with BDD as anode, Pt mesh as cathode and a Nafion membrane [40,41]. Values obtained are rather good as it is supported by the high faradaic efficiencies reported in Table 2.

**Table 1.** Energy efficiency for the generation of ozone in optimum condition using the three PEM cells.

| Electrolyte | Ozone generation / g $(kWh)^{-1}$ | | |
|---|---|---|---|
| | MIKROZON® | CabECO® | CONDIAPURE® |
| $H_2SO_4$ | 8.42 | 6.25 | 1.27 |
| $HClO_4$ | 9.38 | 7.20 | 1.34 |

**Table 2.** Faradaic efficiency in continuous mode.

| Electrolyte | Faradaic efficiency (%) | | | | | |
|---|---|---|---|---|---|---|
| | MIKROZON® | | CabECO® | | CONDIAPURE® | |
| $H_2SO_4$ | 35.18 | 36.69 | 20.61 | 15.08 | 2.66 | 3.12 |
| $HClO_4$ | 38.20 | 37.70 | 29.65 | 17.59 | 3.02 | 3.32 |

The resulting area loading of the three cells was very different and it ranges from the 1004.5 g h$^{-1}$m$^{-2}$ obtained by the Mikrozon® to the 6.8 g h$^{-1}$m$^{-2}$ attained by the CONDIAPURE® with an intermediate value of 44.4 g h$^{-1}$m$^{-2}$ in the CabECO® (all data calculated in $HClO_4$). This confirms that a larger cell area favors secondary reactions that compete with ozone production or contribute to the scavenging of the ozone produced. In this point, it is important to take in mind that the optimum current density informed by the manufactured for the three cells is very different.

In the discontinuous mode (Figure 3) the changes in the concentration of ozone in the electrolyte during each test follows an increasing trend during a first stage, up to a maximum from which a continuous decrease is observed. This trend has been previously related to the formation of scavengers, among which hydrogen peroxide seems to be very important. Also, other scavengers can be formed during the electrolysis from the species contained in the electrolyte. Thus, in the electrolyte with $H_2SO_4$, the ozone concentration decreases faster that in the electrolyte with $HClO_4$, because $H_2SO_4$ lead to the formation of peroxosulfate species which then react with the ozone [42].
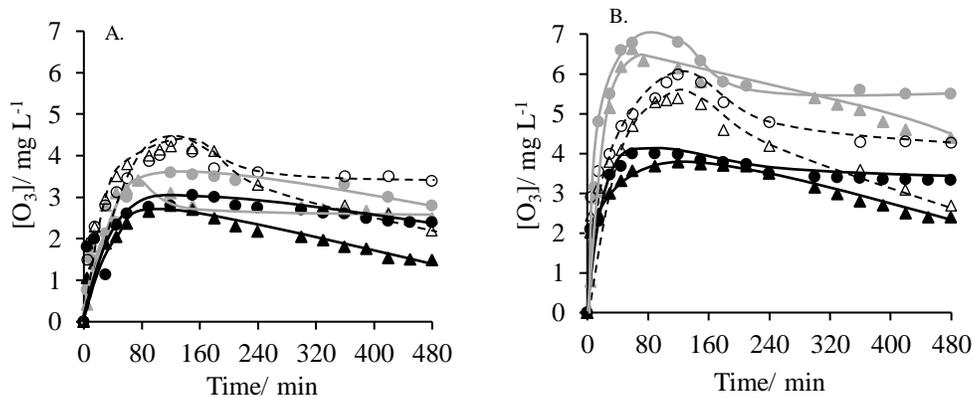
**Figure 3.** Influence of PEM electrolyzer in the electrogeneration of ozone in discontinuous mode. Part A: MIKROZON® cell (0.5A, dashed line), CabECO® cell (1A, grey line) and CONDIAPURE® cell (7A, black line). Part B: MIKROZON® cell (1A, dashed line), CabECO® cell (2A, grey line) and CONDIAPURE® cell (10 A, black line. Electrolyte: (●) $HClO_4$, (▲) $H_2SO_4$.

According to the intensity applied, the ozone concentration reached improves at higher current intensities. In discontinuous mode, the PEM electrolyzer, CabECO® shows the best performance over CONDIAPURE® and MIKROZON®, although the three cells use the same technology including the same materials for the membrane and electrodes of the membrane electrode assembly.

**Degradation of Organics.** Although ozone formation during wastewater electrolysis has been widely discussed in the literature, very few works have focused on shedding light on the actual influence of ozone production on the removal of organics. In fact, because of the very important interactions of ozone with other species formed during the electrochemical

oxidation process, which lead to many different species such as radicals hydroxyl or sulfate, or the much less effective oxygen, its real role has been neglected and very important conclusions have been skipped out, which may have a relevance in the applicability of the technology.

Figure 4 shows the time-course of the ozone concentration produced in the aqueous electrolyte when the three cells are operated at their maximum capacity in the presence and absence of an organic (clopyralid) in the electrolyte.
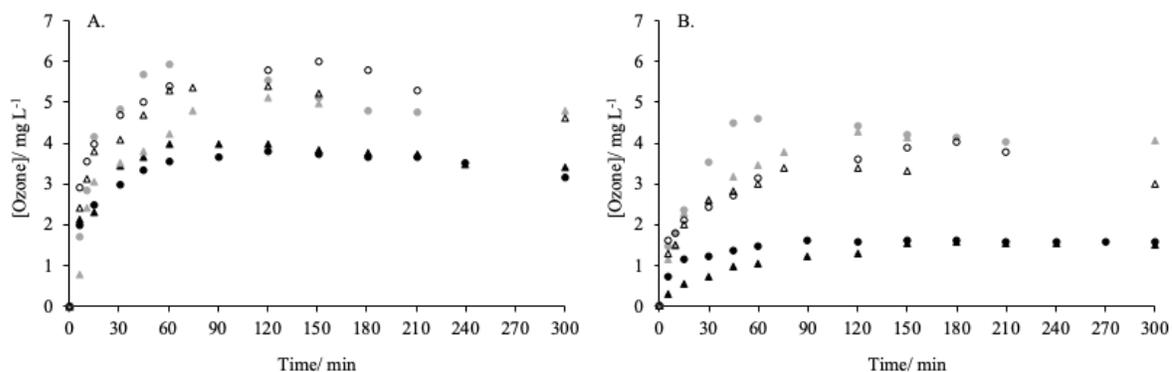


**Figure 4.** Ozone concentration in discontinuous mode in absence (Part A) and presence (Part B) of Clopyralid. CONDIAPURE® (black), CabECO® (grey), MIKROZON ® (empty symbol). Electrolyte: (●) $HClO_4$, (▲)$H_2SO_4$

For the sake of clarity all tests without clopyralid are plotted in Part a, and those with clopyralid in Part b, and it can be seen that concentration of ozone decreases very importantly in all cases with the presence of organics, which can be explained in terms of the consumption of ozone by the oxidation of organics with the ozone. Also, because of the use of current for the direct oxidation of organics, leading to less charge for the production of ozone.

To understand better the process, the changes in the concentrations of organics needs also to be evaluated. Figure 5 shows the changes in the concentration of clopyralid and those in the concentration of total organic carbon. In comparing the presence of sulfates or perchlorates in the liquid electrolyte solution, it can be seen that the degradation is more efficient with sulfate than with perchlorate anions. This is more clearly seem for the CONDIAPURE® cell but it is a general trend also observed in the MIKROZON® and in the CabECO® cells. This can be explained because of a promotion in the degradation of clopyralid and intermediates with persulfates, which seems to be more relevant in the case of the CONDIAPURE®. The PEM electrolyzer that show the best efficiency is the MIKROZON® cell, because it achieved the complete degradation of clopyralid and mineralization only after applying 2.5 Ah dm$^{-3}$ and 5.5 Ah dm$^{-3}$ respectively, while in CabECO®, it is necessary to pass 5.3 Ah dm$^{-3}$ for clopyralid degradation and 11.6 Ah dm$^{-3}$ for mineralization and in CONDIAPURE® the clopyralid degradation and mineralization is achieved after passing 10 Ah dm$^{-3}$ and 32 Ah dm$^{-3}$ respectively. Changes in the TOC and clopyralid are strongly related. This was expected because the electrochemical oxidation of wastewater containing very low concentrations of organics behaves as an almost direct electrochemical combustion process in which once the pollutant starts its oxidation, this process continues up to the complete mineralization.
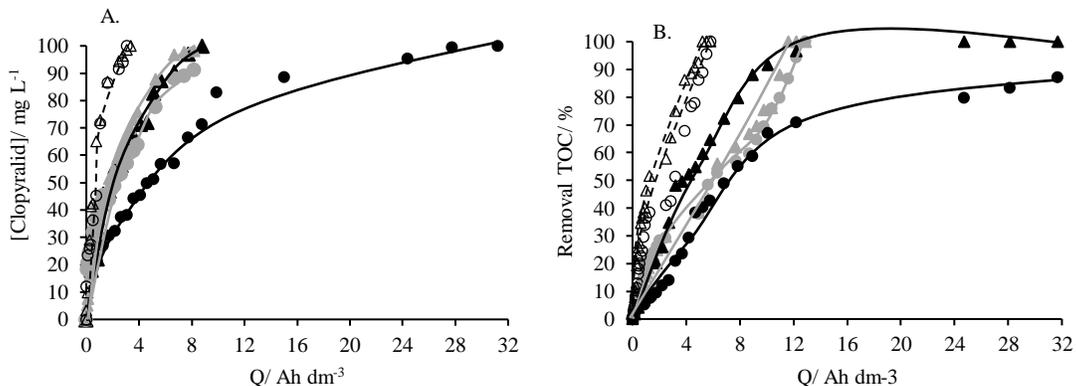
**Figure 5.** Clopyralid degradation (part A) and mineralization (part B) attained by three different PEM electrolyzers. CONDIAPURE® (black line), CabECO® (grey line), MIKROZON® (dashed line). Electrolyte: (●) $HClO_4$, (▲)$H_2SO_4$.

In fact, the only two intermediates detected, 6-chloropicolinic acid ($C_6H_4ClNO_2$) and picolinic acid ($C_6H_5NO_2$) (Figure 6) are not oxidative but reductive species of clopyralid and can be associated to electro-dehalogenation processes which may occur on the surface of the cathode. In addition, the extremely low concentrations, and the depletion after application of electric charge indicates the very low relevance of these intermediates. Other species were detected but at trace concentrations, supporting the high efficiency of the processes and the robustness of the technology.
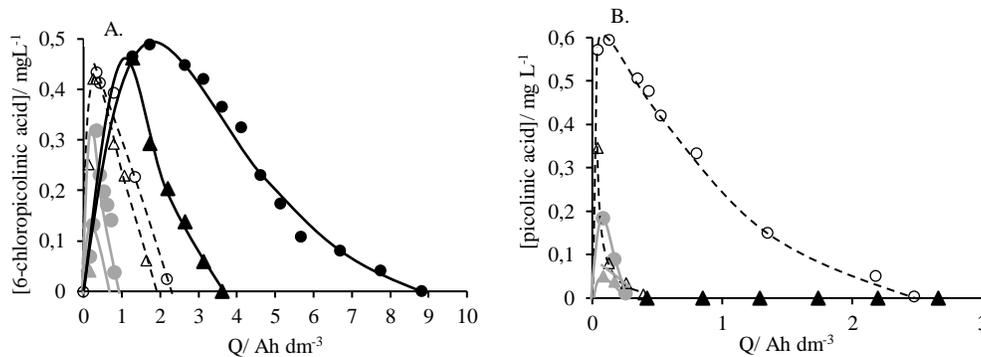
**Figure 6.** Intermediaries of Clopyralid degradation by three different PEM electrolyzers. CONDIAPURE® (black line), CabECO® (grey line), MIKROZON® (dashed line).

Electrolyte: (●) $HClO_4$, (▲) $H_2SO_4$

Degradation rates of organics are not directly related to the production of ozone. Thus, differences observed in the degradation rate of organics are much higher than the differences observed in the production of ozone. This means that ozonation is one of the mechanisms during the electrochemical treatment of organics with PEM electrolyzers but clearly is not the primary mechanisms.

Figure 7 shows the time-course of the cell voltages and Figure 8 the clopyralid removal efficiency (mg clopyralid (Wh)$^{-1}$) of the three electro-ozonizers in the different tests made.
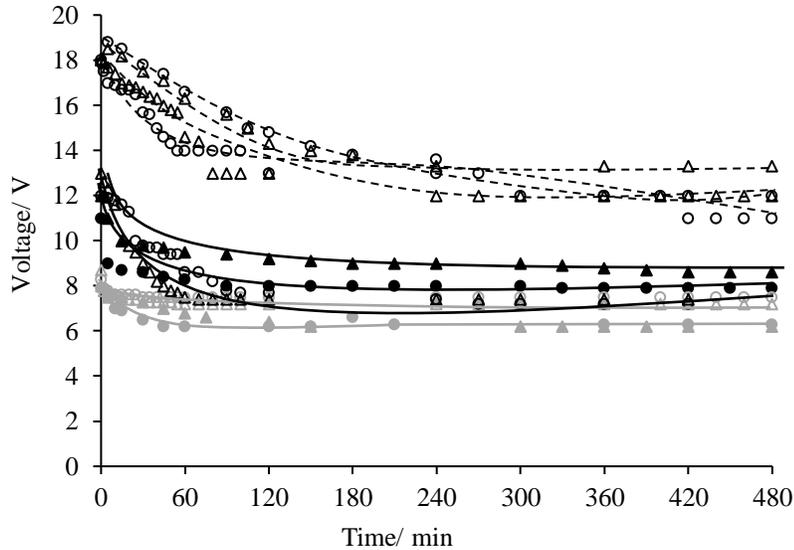
**Figure 7.** Voltage evolution during electrolysis using CONDIAPURE® (black line), CabECO® (grey line), MIKROZON® (dashed line). Electrolyte: (●) $HClO_4$, (▲) $H_2SO_4$. .

The most suitable design is that of CabECO® because the lower cell voltage is attained. However, the highest efficiencies (Figure 7) are obtained by the MIKROZON® for which the highest value obtained was 0.47 mg $(Wh)^{-1}$. Considering that the concentration of intermediates is almost negligible in comparison with clopyralid and the relationship between Theoretical Oxygen Demand and CP (g COD $g^{-1}$ CP), this efficiency corresponds to approximately 0.53 mg COD $(Wh)^{-1}$ with an area loading of 334.8 g COD $h^{-1}$ $m^{-2}$ for the Mikrozom® which obtained the best performance. Efficiencies are higher in the case of the sulfate supporting electrolyte, pointing out the role of the mediated oxidation by other species.
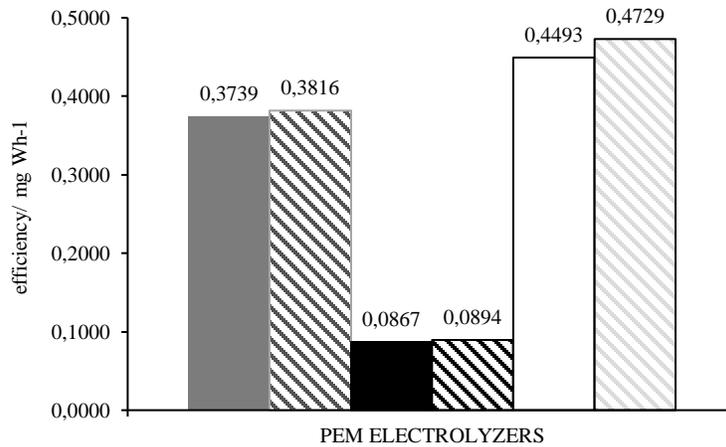
**Figure 8.** Efficiencies of PEM electrolyzers. CONDIAPURE® (black), CabECO® (grey), MIKROZON® (empty). Electrolyte: $HClO_4$ (dashed column), $H_2SO_4$ (full column).

There is a significant difference between the efficiencies obtained in CabECO® and CONDIAPURE® cells even though a very similar current density is applied in both cases and this can inform about the difficulties in scaling up this type of PEM electrolyzers and advice against the increase in the size of the electrodes for larger applications and the convenience of the stacking strategy for scaling up.

**Conclusions**

From this work, the following conclusions can be drawn:

- The applied current has an important role in the electrogeneration of ozone. Ozone concentration increases as the current increases, since higher potentials are reached that favour the production of ozone over the evolution of oxygen.

- A larger active area does not necessarily increase the concentration of electrogenerated ozone. Scale up by enlarging electrode surface area does not seem to be a good strategy from the viewpoint of efficiency and it seems to promote side reactions that compete with ozone production and with the degradation of organics. To improve the efficiency of the system it seems to be better to place in series pairs of electrodes inside the cell as is the case of the CABECO®.

- The three PEM electrolyzers tested can degrade and mineralize completely clopyralid. The only intermediates measured come from the cathodic hydrodechlorination of clopyralid and oxidative intermediates were only detected at trace concentrations.

- The highest efficiencies are obtained with the MIKROZON®, which, although it is the PEM electrolyzer with the smallest active area, is able to reach the highest ozone concentrations and achieve the best clopyralid mineralization. Efficiencies as high as $0.47$ mg $O_3$ $Wh^{-1}$ can be obtained with this cell. Slightly lower values are reached by the CabECO® cell ($0.38$ mg $O_3$ $Wh^{-1}$)

**Author statement**

M. Rodríguez-Peña: Investigation; Writing - original;draft; Methodology; Data curation;

J.A. Barrios Pérez: Supervision;  Validation; Formal analysis; Writing - review & editing.

J. Lobato: Supervision; Validation; Formal analysis; Writing - review & editing.

C. Saez: Supervision; Validation; Formal analysis; Writing - review & editing.

C.E. Barrera-Díaz: Conceptualization; Funding acquisition; Supervision; Writing - review & editing

M.A. Rodrigo: Conceptualization; Funding acquisition; Supervision; Writing - review & editing

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