



Does electro-peroxonation improve performance of electro-ozonation?

M. Rodríguez-Peña^{a,b}, I.F. Mena^a, J.A. Barrios Pérez^c, C.E. Barrera-Díaz^b, M.A. Rodrigo^{a,*}

^a Department of Chemical Engineering, College of Chemical Sciences and Technologies, University of Castilla La Mancha, Campus Universitario s/n, Ciudad Real 13071, Spain

^b Universidad Autónoma del Estado de México, Paseo Colón intersección Paseo Tolloca S/N, Toluca C.P. 50120, Estado de México, Mexico

^c Instituto de Ingeniería, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, Ciudad de México 04510, Mexico

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ABSTRACT

This work focuses on the comparison of the degradation and mineralization of clopyralid with electrochemically produced hydrogen peroxide (electro-H₂O₂), ozone (electro-ozonation) and their mixture (electro-peroxone) and points out important differences among the performance of the oxidation technologies. Co-existence of electrochemically produced hydrogen peroxide and ozone decreases the concentration of ozone and increases the concentration of hydrogen peroxide in the bulk, because of the formation and recombination of hydroxyl radicals. Oxidation of clopyralid and mineralization of the wastewater is less efficient with hydrogen peroxide and more efficient with ozone. Peroxone shows an intermediate performance which can be related with the oxidant's speciation produced in the wastewater. Different behavior between in situ electrochemically produced ozone and ozone dosed, indicates activation of ozone in the electrolyte during the electro-ozonation process. Results highlight the good performance of the simple electro-ozonation that overcomes other EAOPs and indicates that combination of powerful oxidants in this case does not result in the expected synergism but in antagonistic responses.

1. Introduction

In the last decades, there has been an increasing interest in the development of the so-called Advanced Oxidation Processes (AOPs), technologies specially designed to treat wastewater polluted with bio refractory anthropogenic pollutants, species whose removal is very inefficient using conventional treatment technologies [1,2]. Among them, a very promising variety are the Electrochemical Advanced Oxidation Processes (EAOP), in which electrochemical technology is used to produce the oxidants that degrade the pollutants [3–6]. These oxidants can be directly produced on the anode surface and act immediately on the pollutants. This is the case of the anodic oxidation with diamond coatings, in which hydroxyl radicals are produced by oxidation of water and they directly degrade the pollutants in the nearness of the electrode surface [7–10]. Lifetime of hydroxyl radicals is very short to allow their action in the bulk and hence their action, when they are electrogenerated, is extremely close to the anodic surface. Because of that, this type of processes is typically mass transport controlled and design of electrochemical cells looks for increased turbulence in order to improve the efficiency, especially in the case of the treatment of diluted wastewater. An alternative is the production of more stable oxidants in

situ, which can then act in the bulk of the wastewater. This is the case of the electro-Fenton technologies, in which hydrogen peroxide is produced cathodically and activated in the solution with iron II (which may also be produced or regenerated electrochemically) [11] or by other oxidants electrogenerated on the anode surface (such as persulfates, perphosphates...) [12,13]. Also, by coupling UV light irradiation or applying ultrasound waves. This is also the case of the production of oxidants such persulfates and ozone, whose advantages have been recently pointed out [14,15]. In this context, it is important to exclude oxidants produced from chloride oxidation because, except for the case of chlorine dioxide, their interaction with organic lead to the formation of hazardous chlorinated organics, species that can be even more dangerous than the parent compounds. In addition, occurrence of chlorates and perchlorates is also seen as a major inconvenience [16–18]. Thus, the treatment of wastewater by AOPs looks for the formation of powerful oxidants to achieve the mineralization of organic compounds, preferring oxidants that do not generate toxic residues, such as ozone and hydrogen peroxide that decompose to oxygen and water when oxidize organic species [19–21].

Ozone is a powerful oxidant that shows a higher selectivity than the hydroxyl radical and its electrogeneration by water and oxygen oxida-

* Corresponding author.

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

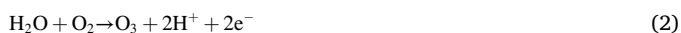
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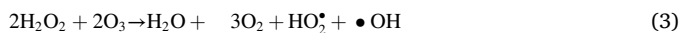
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tion (Eq. 1 y 2) shows important advantages over its conventional generation, since 1) high ozone concentrations are reached at low voltages as compared to corona technologies and 2) mass transfer problems associated to the dissolution of the ozone gas into the liquid (where pollutants are contained) are solved, because of the production of ozone in the liquid phase, increasing the efficiencies in wastewater treatment and achieving high efficiencies in the mineralization of organic compounds [22–25].



Recently, in the search of more effective AOPs, it has been proposed the use of mixtures of ozone and hydrogen peroxide, generically known as peroxone. Ozone in the presence of H_2O_2 decomposes faster to radicals and, thus, it accelerates the degradation rate of persistent compounds [4,16,26,27]. In fact, these mixtures allow the activation of both hydrogen peroxide and ozone with the formation of peroxy and hydroxyl radicals in the bulk of the solution according to Eq. 3. This reaction has a yield of 50% for the production of hydroxyl radicals (i.e. 0.5 mol of $\bullet\text{OH}$ produced per mol of O_3 consumed) and this yield is higher than those of the decomposition of O_3 with electron-rich components of dissolved organic matter in real water matrices which is usually between 13% and 27% [27–29]. As a result, many studies have shown higher removal rates (97–100%) of pharmaceuticals during the peroxone process as compared to bare ozonation [30].



As both reagents can be produced electrochemically, the peroxone can also be produced electrochemically (electro-peroxone process) [30, 31] coupling the efficient cathodic production of H_2O_2 from the electrochemical reduction of oxygen on carbon cathodes and the anodic production of ozone from the oxidation of water or oxygen on diamond electrodes [32,33]. Operation conditions for reaching high efficiencies in both processes are very different and because of that it is better to produce each oxidant in a different and dedicated electrochemical cell where conditions are optimized.

Considering this background, the main objective of this study has been to evaluate the efficiency of the electro-peroxone process for the treatment of a pesticide. The study compares the processes of electro-ozonation and electro-generation of hydrogen peroxide separately and then, the coupling between them resulting in the electro-peroxone process, where the production of oxidants, the reactions between them, the efficiency of each treatment and the viability of the coupled treatment are discussed. The effect of pressure on the electrochemical synthesis of electro-peroxone was also evaluated, considering that dissolved oxygen is the raw material for the production of ozone and hydrogen peroxide and that its solubility increases with pressure (Henry's Law).

2. Materials and methods

2.1. Chemicals

Double deionized water (Millipore Milli-Q system, resistivity: $18.2 \mu\Omega \text{ cm}^{-1}$ at 25°C) was used to prepare the solution of sulfuric acid (H_2SO_4) used as electrolyte. N,N-diethyl-p-phenylenediamine (DPD) and titanium (IV) oxysulfate (1.9–2.1%, from Sigma-Aldrich) were used as indicators of ozone and hydrogen peroxide, respectively. Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid) was used as a model of organics. Methanol and formic acid (HPLC grade) were used to prepare the mobile phase in HPLC analysis (Sigma-Aldrich, Spain).

2.2. Experimental set-up

The electro-peroxone process was carried out in discontinuous mode in the experimental setup shown in Fig. 1. The tank of polyvinyl chloride (PVC) is filled with the electrolyte solution and then, the solution is recirculated through two cells at the same time at 150 L h^{-1} with micropumps (GB-P25 J F5 S A head coupled to a DB 380 A 24 V engine, speed control 0–5 V DC, supplied by TechmaGPM s.l.r. (Milan, Italy)). The output solution from both cells is mixed in the tank from where it is recirculated again. The electrochemical generation of ozone was performed in a PEM electrolyzer CABECO® (supplied by Condias GmbH, Germany) equipped with BDD electrodes and proton exchange Nafion® membranes. It is used as received. Further details can be found elsewhere [34,35]. The hydrogen peroxide electrogeneration was carried out in a microfluidic flow-through cell (MF-FT) equipped with a BDD anode and a 3D-titanium mesh with a deposition of carbon black (CB, Vulcan® XC72 from Cabot Corporation) and PTFE (a 60% wt. Teflon® emulsion solution in H_2O , from Sigma-Aldrich) cathode. For cathode preparation, titanium mesh (from Xian Howah Technology Co., Ltd.) is immersed in boiling hydrochloric acid (HCl, 37% Scharlab) solution (20% v/v) for 15 min, then the mesh is again immersed in boiling oxalic acid (99.5% Panreac) solution (10% v/v), and finally rinsed with ultrapure water. The CB/PTFE mixture is prepared by dispersing 1 mg mL^{-1} CB and 5 mg mL^{-1} PTFE in isopropanol for 2 h at 50°C in an ultrasonic bath. Then, the titanium mesh is placed on a plate at 130°C and 200 mL of dye (100 mL on each side) is sprayed. Finally, the electrodes are heated at 360°C for 1 h using a heating rate of $12^\circ\text{C min}^{-1}$. A second layer is deposited on the electrode, repeating the procedure [36]. A Delta Elektronika ES030–10 (Delta Elektronika, Netherlands) power supplies were used for each cell power, with a range of voltage of 0–30 V and intensities of 0–10 A. The temperature was controlled at 18°C by a plate heat exchanger.

2.3. Analytical procedures

The concentration of dissolved ozone was measured throughout the experiment by a colorimetric method with N,N-diethyl-p-phenylenediamine (DPD) with a detection limit of $0.05\text{--}4.0 \text{ mg L}^{-1} \text{ O}_3$ using Spectroquant Merck assay kits (Hach, Model: DR2000). The hydrogen peroxide concentration was followed by colorimetric titration using a UV/Vis spectrophotometer (Hach, Model: DR2000) from the formation of Ti(IV)- H_2O_2 complex, which was quantified at 410 nm [37]. For this method a calibration curve was performed with samples with known concentrations of H_2O_2 with detection limit of $1\text{--}25 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$. Clopyralid degradation and intermediate were followed by Total Organic Carbon (TOC) (Analytik Jena Multi N/C 3100 TOC analyzer) and High-Performance Liquid Chromatography (HPLC) using an Agilent 1200 series coupled with a DAD detector and an analytical HPLC-DAD Eclipse Plus C18 column (Agilent 1260 Infinity). The mobile phase was a mixture of formic acid (0.1%) and methanol (70/30, v/v) at a flow rate of $1 \text{ cm}^3 \text{ min}^{-1}$. Further details of the characterization are given elsewhere [38–44].

The specific energy consumption per unit TOC mass was calculated according to Eq. 4, where I is the intensity applied (A), v is the average cell voltage (V), t is the time in hours, V is the volume (L) and TOC_i and TOC_f are the total organic carbon concentration (g L^{-1}) at times t_0 and t_f , respectively.

$$\text{Energy consumption} = \frac{I \cdot v \cdot t}{V(\text{TOC}_i - \text{TOC}_f)} \quad (4)$$

The current efficiency (CE) for clopyralid degradation was calculated according to Eq. 5, where COD_i and COD_f are the chemical oxygen demands (COD , $\text{g O}_2 \text{ L}^{-1}$) at times t_0 and t_s , respectively. F is the Faraday constant ($96,487 \text{ C mol}^{-1}$), V is the volume of the electrolyte (L), I is the current (in A), t is time, and the number 8 is a dimensional factor for consistency of units ($32 \text{ g O}_2/4 \text{ mol e}^{-1} \text{ O}_2$). COD was estimated as

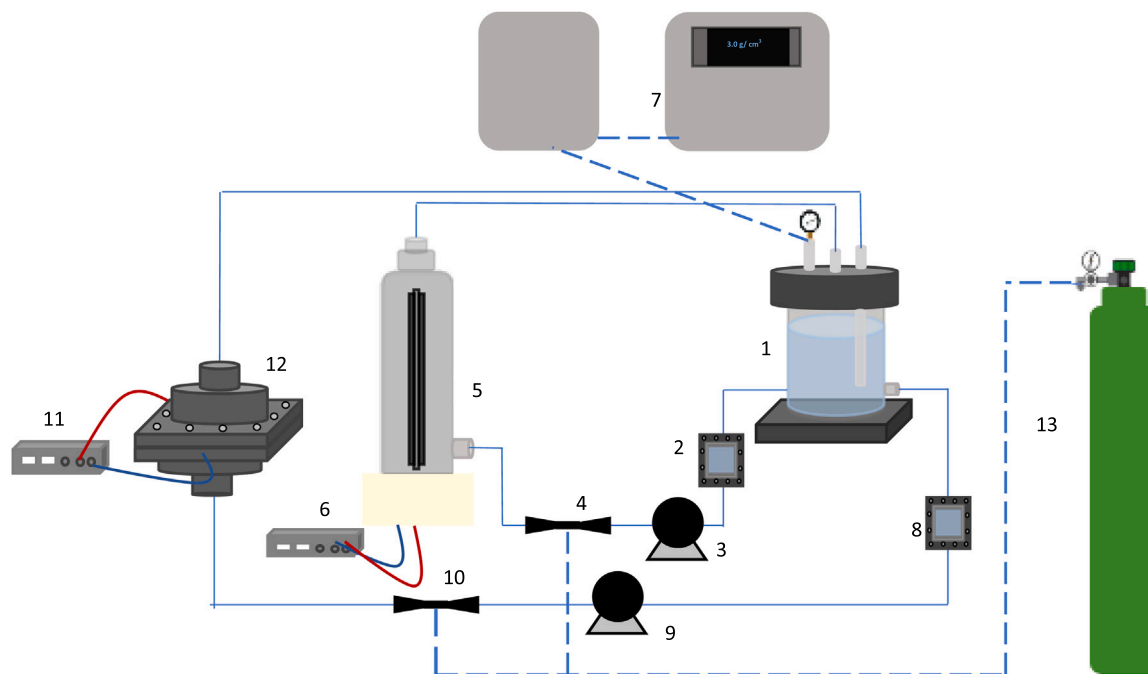


Fig. 1. Experimental setup in discontinuous mode of coupled treatment: 1) tank; 2) heat exchange 1; 3) micropump 1; 4) jet aerator 1; 5) CABECO® cell; 6) power supply 1; 7) gaseous phase ozone analyzer; 8) heat exchange 2; 9) micropump 2; 10) jet aerator 2; 11) power supply 2. 12) MF-FT cell; 13) oxygen tank.

theoretical oxygen demand (5.75 moles of O_2 are required to oxidize 1 mol of Clopyralid) assuming that the concentration of intermediates is almost nil and that clopyralid is the sole organic compound present.

$$\text{Current Efficiency (CE)} = \frac{(\text{COD}_i - \text{COD}_f) F V}{8 I t} \quad (5)$$

2.4. Experimental procedure

The tests were performed in discontinuous mode using a H_2SO_4 solution at pH3, recirculating the solution in the system through the tank and the electrochemical cells at same time and at a constant flow rate of 150 L h^{-1} . The CabECO® cell was operated at 2A and the microfluidic flow cell at 0.05 A. O_2 was introduced into the electrolyte with a Venturi mixer at 10 L h^{-1} . In the organic pollutant oxidation tests, the solution was prepared with 100 mg L^{-1} clopyralid. The single process, the ozone and hydrogen peroxide generation cells were operated separately in the same conditions. The ozonation treatment was carried out in a glass batch reactor fed with a solution of H_2SO_4 at pH 3 and 100 mg L^{-1} of clopyralid. Ozone gas obtained from the CabECO® cell was injected into the reactor (7.0 mg L^{-1}).

3. Results and discussion

Figs. 2 and 3 show the changes in the concentration of ozone and hydrogen peroxide in different electrolytic tests, where these oxidants are produced separately or together in the same electrolyte, using a double circuit setup which shares the same electrolyte reservoir tank. Current densities in each cell were selected based on results obtained in previous tests, trying to optimize the production of each oxidant. As seen, both reagents can be produced separately in an efficient way. However, the current density required is very different, as well as the type of electrochemical cell used. Ozone is produced on the surface of the anode, where the most appropriate conditions involve the use of non-active electrodes such as diamond and, simultaneously, large current densities to promote the formation of hydroxyl radicals that, in turn, favors the formation of ozone in the nearness of the anode surface by different mechanisms, involving also to other species which interact

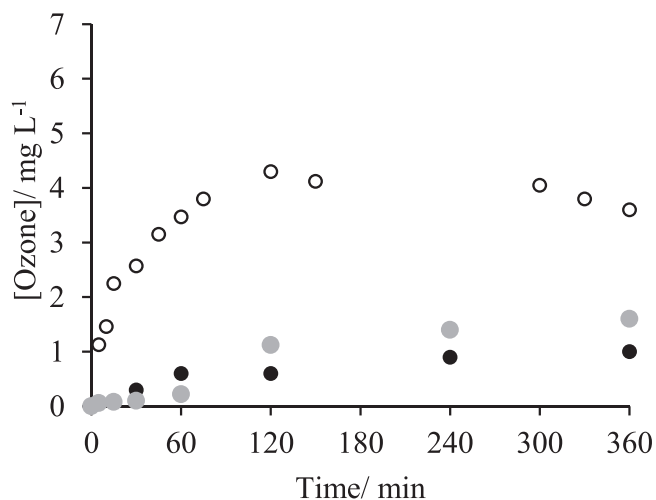


Fig. 2. Production of ozone in the absence of hydrogen peroxide (empty symbol), with hydrogen peroxide produced simultaneously at atmospheric pressure (electro-peroxone process) (full black symbol) and at gauge pressure of 2 Bar (pressurized electro-peroxone process) (gray symbol), Current intensity 2A. Electrolyte containing H_2SO_4 pH 3.

with these radicals [22]. This ozone is later transported to the bulk of the solution.

As seen in Fig. 2, concentration of ozone does not increase up to reach a steady state, but it increases up to a maximum, value from which it started to decay. This trend has been explained in previous works in terms of the production of scavengers in the electrolyte, that is, other species that can interact with ozone destroying it, and opposes a more characteristic behavior observed in the production of oxidants in which the concentration reaches a constant value [45,46]. Thus, typically, during the electrochemical production of oxidants, the formation and decomposition of the oxidant competes. The last reaction, which may be associated to cathodic reactions and, also, to chemical self-decomposition mechanisms, follows a first order kinetic with

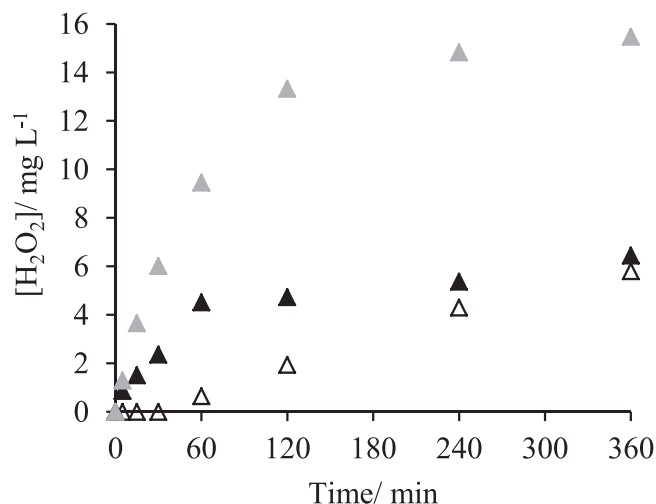


Fig. 3. Production of hydrogen peroxide in the absence of ozone (empty symbol), with ozone produced simultaneously at atmospheric pressure (electro-peroxone process) (full black symbol) and at gauge pressure of 2 Bar (pressurized electro-peroxone process) (gray symbol), Current intensity 0.05 A. Electrolyte containing H₂SO₄ pH 3.

respect to the ozone concentration and, because of that, there is a point in which the formation and decomposition rate balances and the concentration of the oxidant reaches a steady state value [14,47,48]. However, the decay observed in the concentration of ozone in Fig. 2 at longer times opposes this model, and the only way to understand this decay is by considering the formation of a second type of species with the capacity of destroying ozone. Among these species with the capability of destroying ozone, peroxy-compounds produced anodically or hydrogen peroxide produced cathodically are of interest [49]. In this work, the design of the cell used to produce ozone does not promote the direct electrochemical formation of hydrogen peroxide: cathode has a very low effective surface area with no relevant occurrence of tpb (three phase boundaries) and operation conditions are also far from those in which this species can be produced efficiently. This fact does not exclude the formation of hydrogen peroxide by other mechanisms as it is going to be described later; simply it is not promoted in the cell. Opposite, persulfates are the most important scavengers expected, because of the high concentrations of sulfate anions in the solution, which can be anodically transformed into peroxosulfates according to Eqs. 6 and 7.



Both, peroxosulfates and ozone, are produced in the nearness of the anode surface, and the high concentrations in this reaction cage near the anode surface may promote these interactions. Pathways that explain decomposition of ozone by peroxosulfates are shown in Eqs. 8 and 9.



Regarding hydrogen peroxide (Fig. 3), the operation current density required for an efficient production is much lower than that required for ozone production, and it is required a special design of reactor in which the oxygen can be reduced efficiently, allowing the interaction of oxygen with the cathode surface, following Eq. 10. Use of high cell voltages is not positive but destructive, because it is needed that reaction does not progress up to the formation of water (Eq. 11) or, even, to the reduction of water to hydrogen.



Although gas diffusion electrodes (GDE) are the most reported for this production, previous works using flow-through electrodes have demonstrated an outstanding behavior of these electrodes to produce hydrogen peroxide [50–53], which an additional advantage: they can be more easily scaled-up. Using these soft conditions and innovative electrodes, during the duration of the test, the concentrations do not reach a steady state value or a maximum, but increase almost linearly.

When both oxidants are produced simultaneously in the same electrolyte (connecting both circuits and powering both cells at the same time) important differences are observed as compared to their production separately. Concentration of ozone is much lower, which may be explained in terms of the previously described interaction of ozone and hydrogen peroxide that yields hydroxyl radicals (peroxone reagent), depleting the electrochemically formed ozone (Eq. 3). However, this is not the case regarding the formation of hydrogen peroxide, and when ozone is produced simultaneously in the same electrolyte, the concentration increases. This initially non-expected behavior can be explained in terms of the interaction between the hydroxyl radicals formed by the interaction of ozone and hydrogen peroxide, which are rearranged to regenerate hydrogen peroxide according to reaction 12, which is favored in a system in which the hydroxyl radicals are formed massively.



It is important to understand that the oxidants' reaction cocktail produced is extremely complex and all species can interact among them, suffering important transient transformations which may depend on many different inputs including temperature, mixing conditions, etc. In the reaction media, peroxomonosulfates, peroxodisulfates, ozone, hydrogen peroxide and different types of radicals are interacting continuously in a system in which, simultaneously, the electrodes are regenerating them in a nonstop way, because precursors are available at very high concentrations. Because of that, when oxygen availability is increased, by increasing operation pressure, production of hydrogen peroxide increases more importantly than that of ozone.

Complexity of the system becomes more important when organics are contained in the electrolyte, because in addition to the reactivity described, interactions between the different oxidants and the organics have to be considered to understand the complete reaction system. Thus, interactions of ozone, hydrogen peroxide and peroxone are expected to affect in a different way to depletion of organics during their electrochemical treatment. When the peroxone reagent is produced electrochemically, ozone concentration decreases importantly and hydrogen peroxide follows the opposite trend because of the recombination of hydroxyl radicals what, considering the lower oxidation capacity of hydrogen peroxide, can be negative from the viewpoint of the efficiency in the degradation of organics contained in wastewater. When the operation pressure increases, the concentration of oxygen, which is the raw matter of both processes, increases. This may help to explain the higher productions of ozone and hydrogen peroxide observed (Figs. 2 and 3). The increase in the concentration is especially important in the case of hydrogen peroxide and this reinforces the hypothesis of regeneration of this species by interaction of the hydroxyl radical formed with the mixture peroxone. Fig. 4 supports this conceptual model of the process, by showing the decay of clopyralid during its interaction with the different reagents produced and Fig. 5 shows the mineralization obtained during these tests. In these figures, it is also shown for comparison purposes, the effect of ozone dosed as chemical reagent in the system in concentrations like those produced electrochemically in the wastewater (7.0 mg dm⁻³). This ozone was also produced with an electrochemical cell but in a different electrolyte, from which it was stripped to gas phase and then, bubbled into the reaction media. This means that in this process ozone is not interacting with other electrochemically produced species, but it behaves like in a non-electrochemical ozonation process.

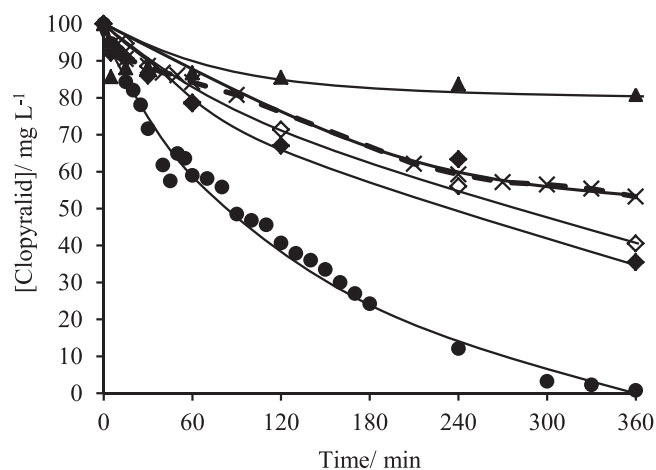


Fig. 4. Clopyralid degradation by Advanced Oxidation Processes ▲ E-H₂O₂, ● E-ozonation at atmospheric pressure, x ozonation, ◆ E-peroxonation at atmospheric pressure, ◊ E-peroxonation at 2 Bar of gauge pressure.

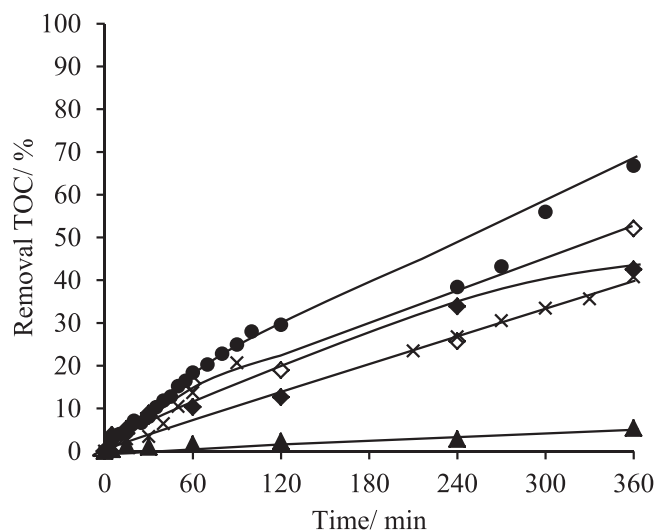


Fig. 5. TOC removal by Advanced Oxidation Processes ▲ E-H₂O₂, ● E-ozonation, x ozonation, ◆ E-peroxonation at atmospheric pressure, ◊ E-peroxonation at 2 Bar of gauge pressure.

Important differences are observed among the effect of the different oxidants on the degradation of the organic and, opposite to what it could be initially expected, it is not electro-peroxone but electro-ozonation the technology that produces the most efficient oxidant in the clopyralid degradation. Also, worth to highlight the very low oxidation capacity of the electrochemically generated hydrogen peroxide, whose effect on the oxidation of the clopyralid is very limited. Another important observation is the lower activity of the ozone added as chemical with respect to that of the ozone produced electrochemically in the system. This difference must be explained in terms of the electrochemical activation of the oxidants formed and on the role of the pH. During the chemical process (ozone added as gaseous reagent), the molecular ozone is the main species involved in the degradation at acid pH, and molecular ozone is a more selective oxidant than others. Conversely, during the electro-ozonation, a cocktail of oxidants is produced during treatment, including molecular ozone and hydroxyl radicals, because of the interaction of electrochemically formed ozone with other electrochemically formed species such as peroxosulfates. The synergistic effect of all these species, together with the direct oxidation in the electrode surface, are the responsible of the higher clopyralid degradation rate [23,46]

Furthermore, the mass transfer problems, associated to the dissolution of gaseous ozone to wastewater, are known to decrease using the electro-ozonation process, because the ozone is produced by water and into the water and the low-efficiency dissolution of ozone gas into the liquid is not required.

As well, it is important to see that ozone produced electrochemically is the most efficient oxidant, even better than peroxone. This can be explained in terms of the formation of hydrogen peroxide in the electro-peroxone processes, which is a much softer oxidant. Thus, the oxidants generated by electro-peroxone process do not show a synergistic effect: in fact, the overproduction of $\cdot\text{OH}$ can regenerate seem to be regenerating H₂O₂ (as observed in the absence of organic matter) and this is a less powerful oxidant than O₃ or $\cdot\text{OH}$. Consequently, the main degradation pathway of clopyralid occurs via H₂O₂ because it is contained in higher concentrations and this explains the slower degradation rate.

Hence, the results obtained pointed out that electro-ozonation process is the most efficient process for the pollutant degradation, because of this process skip out the inefficient dissolution of ozone gas into the wastewater and interactions of ozone with other oxidants (mainly persulfates) produce a more aggressive oxidation media with an important role of radicals. These harsher conditions are not always promoted by the interaction of ozone with other oxidants and the results obtained also show how adding hydrogen peroxide in large concentrations (formed by electrochemical production) reduces the degradation yield because of the scavenging behavior of this compound, reducing the ozone concentration in the medium.

The only intermediates detected in the different treatments were 6-chloro picolinic acid and picolinic acid. Both species are not oxidative but reductive intermediates, which are explained in terms of the sequential hydro-dehalogenation of clopyralid, which develops on the cathode surface. No other intermediates (aromatic or carboxylic acid) are detected during the tests. This means that clopyralid oxidized is mineralized almost directly, which is a typical observation in the treatment of low concentrated wastes using electrochemical oxidation technologies, well described in many previous works. Fig. 6.

Decay of clopyralid (and also mineralization results) fits well to pseudo-first kinetic order model. Fitting values, as well as regression coefficients, are shown in Table 1, where it can be observed that the degradation rate constants shows that the coupled treatment does not increase the degradation rate but takes a value in between the obtained by the electro-ozonation and the electrochemical production of hydrogen peroxide, as it may be expected according to the oxidants speciation of the resulting electrolyte. According to the current efficiency (CE), the highest efficiency is obtained with E-H₂O₂ but this process is only able to degrade less that 20% of clopyralid in 6 h versus a total elimination of clopyralid with Electro-ozonation. Apart from this, the highest CE was obtained with the single treatment over the coupled treatment. That is, electro-ozonation reaches 5.31% vs. the lower 3.39% obtained by electro-peroxone. On base of this parameter, the coupled treatment does not seem to be a good alternative to optimize treatment time and energy consumption.

Fig. 7 shows the specific energy consumption. As can be observed, the E-H₂O₂ system has the lowest energy consumption, because the cell operates at lower current intensity (0.05 A) to avoid H₂O₂ decomposition, but it attains lower mineralization percentage (Figs. 4 and 5): 5.42% removal as compared to 66.8% obtained by electro-ozonation (E-O₃). The electro-peroxone (H₂O₂-O₃) treatment shows lower energy consumption when the system is pressurized, while the higher energy consumption of coupled treatments may advice against their use.

4. Conclusions

From this work, the following conclusions can be drawn:

- The electrochemical production of ozone and hydrogen peroxide can be used for the treatment of wastewater polluted with clopyralid.

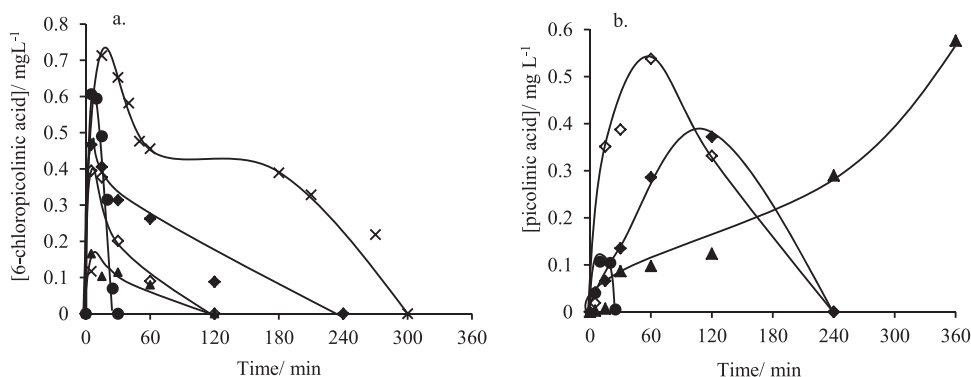


Fig. 6. Intermediaries of Clopyralid degradation by Advanced Oxidation Processes ▲ E-H₂O₂, ● E-ozonation, x ozonation, ◆ electro-peroxone at atmospheric pressure, ◊ electro-peroxone at 2 bar of gauge pressure. a. 6-chloropicolinic acid, b. picolinic acid.

Table 1

First order kinetic constants and CE for the degradation of clopyralid and mineralization using different EAOP.

Process	Clopyralid k (min ⁻¹)	r ²	TOC k (min ⁻¹)	r ²	CE %
Electro-ozonation (E-O ₃)	0.010	0.97	0.0029	0.99	5.31
Ozonación (O ₃)	0.0018	0.99	0.0013	0.99	2.50
Electro-H ₂ O ₂ (E-H ₂ O ₂)	0.0006	0.99	0.0004	0.99	41.05
Electro-peroxone (H ₂ O ₂ -O ₃)	0.0026	0.98	0.0015	0.99	3.39
Pressurized electro-peroxone (H ₂ O ₂ -O ₃)	0.0024	0.99	0.0020	0.99	3.10

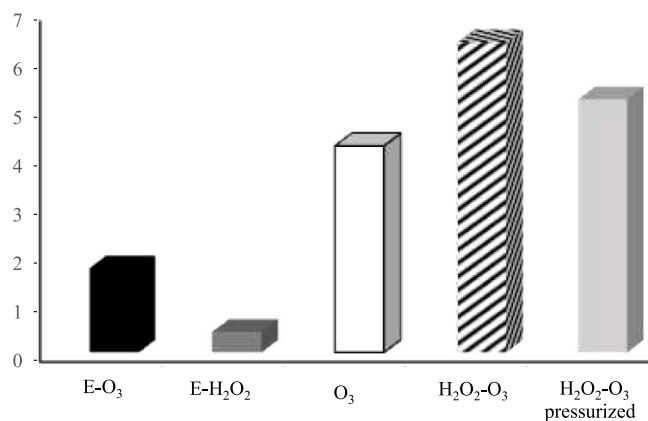


Fig. 7. Specific energy consumption Clopyralid degradation by Advanced Oxidation Processes: E-H₂O₂ (full dark gray column) E-O₃ (full black column), O₃ (empty column), H₂O₂-O₃ at atmospheric pressure (striped column) and H₂O₂-O₃ at 2 bar of gauge pressure (full light gray column).

Electro-ozonation is more efficient than the electrochemical production of hydrogen peroxide both in the oxidation of the raw molecule and in the complete mineralization of the waste.

- Electrochemical production of ozone and hydrogen peroxide can be combined into a simple electro-peroxone process. The mixture of oxidants produces a recombination with the formation of higher concentrations of hydrogen peroxide and lower concentrations of ozone which has a negative impact on the degradation and mineralization of clopyralid. Hence, no synergism but antagonistic effect is observed.
- An increase in the operation pressure shows positive effects on the electrosynthesis of ozone and hydrogen peroxide, increasing in both cases the concentration of the oxidant, because of the increased

solubility of oxygen in the electrolyte. However, the pressurized electro-peroxone process does not improve the performance of the electro-ozonation process.

- Better results obtained by the electro-ozonation process as compared to the dosing of gaseous ozone. Electro-ozonation is shown to be a fully efficient technology for the degradation of pesticides, due to the production capacity of ozone and other oxidants that generate in the medium an oxidant cocktail capable of achieving the mineralization of pesticides.
- It has been shown that coupled treatment is not a good strategy for pesticide degradation, not only because its lower current efficiency but also because its higher energy consumption as compared to single treatments.

CRediT authorship contribution statement

M. Rodríguez-Peña: Investigation, Writing – original draft, Methodology, Data curation. **I.F. Mena:** Supervision, Validation, Formal analysis, Writing – review and edition. **J.A. Barrios Pérez:** Supervision, Validation, Formal analysis, Writing – review and edition. **C.E. Barrera-Díaz:** Conceptualization, Fund acquisition, Supervision, Writing – review and edition. **M.A. Rodrigo:** Conceptualization, Fund 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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