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Removal of herbicide 2,4-D using conductive-diamond sono-electrochemical oxidation

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ABSTRACT

In this work, the depletion of herbicide 2,4-D using electrolysis and sono-electrolysis was studied in a DIACELL® 401 electrochemical cell equipped with bipolar p-Si BDD electrodes. Results show that 2,4-D can be efficiently depleted from synthetic wastewater. In both technologies, 4-chlororesorcinol, 2-chlorophenol, 2,4-dichlorophenol, hydroquinone and benzoquinone are the main intermediates. Their concentrations are much lower under Ultrasound (US) irradiation, and complete mineralization is attained in silent and ultrasound tests. When more bipolar electrodes are connected, the removal is faster and more efficient, and the differences between the silent and the US irradiated processes are clearer. US irradiation also influences the formation of oxidants in the reaction media. Under US irradiation, production of chlorates is promoted compared with the formation of perchlorates, suggesting that perchlorates are formed on the anodic surface because this result can only be explained by enhanced chlorate transport to the bulk solution under US irradiation due to enhanced mass transport.

1. Introduction

Electro-oxidation has been extensively studied in recent years for the remediation of wastewater [1,2]. Its main advantages compared to other advanced oxidation processes are robustness and high efficiency [3–6]. The optimum performance of this technology depends on many factors, including electrode material, cell arrangement, waste composition parameters (pH, supporting electrolytes) and operating conditions (temperature and current densities) [7]. Most papers found in the literature focus on the influence of waste composition and operating conditions on treatment results; the presence of chloride in the waste and the significance of current density as the main operating parameter are largely unexamined [8,9]. Likewise, in comparing materials, the most promising electrode material is conductive-diamond coating on a p-Si support [10]. These electrodes have demonstrated very good properties, which lead to high production of hydroxyl radicals and many other oxidants [11–13].

In comparing cell arrangement, most studies have been performed at bench scale with simple cells with anodic area varying from 3 to 140 cm^2. However, there is a lack of assessment of cell design and scaling up reactors using commercial cells [14]. In particular, the use of bipolar electrodes is a promising for scaling up the remediation of wastewater [15,16]. Likewise, the combination of ultrasound irradiation and electrochemical oxidation is a promising alternative worth studying [17–20]. Ultrasonic irradiation effectiveness is based on cavitation and improvements in mass transfer. The hydrodynamic cavitation process involves the formation, growth, and sudden collapse of micro-bubbles. These gas bubbles in aqueous solution lead to the thermal dissociation of water molecules into $^{\cdot}H$ and $^{\cdot}OH$. This powerful oxidant is responsible for harsh oxidation conditions [21–25]. Ultrasound irradiation combined with electro-oxidation can be very effective for the removal of different organic pollutants such as dyes [26–28], phenolic compounds [29–31], organo-chlorinated species [32], pharmaceutical products [23,33,34], phthalates [25,35] and pesticides [24,36]. Regarding pesticides, Bringas et al. [24] evaluated the degradation kinetics of diuron using low-frequency ultrasound irradiation coupled to electrochemical oxidation with a boron-doped diamond anode. Synergistic behavior was observed when both processes were combined, improving the mineralization kinetics by 43%. Esclapez et al. [32] reported higher degradation efficiency of trichloroacetic acid using a sono-electrochemical process with platinized titanium (Pt/Ti) mesh as the anode material. Garbellini et al. [30] demonstrated that the highest levels of decay of pentachlorophenol were attained using sono-electrolysis rather than silent electrolysis

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using a diamond anode. These results can be explained by increased mass transport, minimization of inactivation electrode effects and the simultaneous generation of hydroxyl radicals by both ultrasound irradiation and the polarized BDD surface.

Pesticide remediation is a major problem, and various technologies are currently being developed to solve it [3,37,38]. This work aims to assess the performance of a combined US irradiation – electrolytic treatment for the removal of soluble organic pesticides from water. A commercial electrochemical cell Diacell type 401, equipped with bipolar boron-doped diamond electrodes and a US horn, was used to demonstrate the scalability of the system and the role of US irradiation in this promising technology. Synthetic wastewater consisted of solutions of 2,4-D herbicide with sodium chloride. Two reactions are expected to develop simultaneously in the reactor: the depletion of an organic herbicide and the oxidation of chlorides to perchlorates. This later reaction prevents the application of this technology, and thus, the aim is not to optimize the environmental remediation process (obviously, in such an application, production of perchlorate should be prevented) but simply to increase knowledge about the scalability of this type of process, taking advantage of the simultaneous occurrence of both reactions during the electrolysis of synthetic wastewater. The well-known oxidation of chloride with diamond anodes will help to obtain relevant conclusions about the influence of electro-generated oxidants.

2. Materials and methods

2.1. Chemicals

All chemicals, including sodium sulfate and sodium chloride (Fluka, Spain), 2,4-D (dichlorophenoxyacetic acid), hydroquinone, 1,4-benzoquinone, 4-chlororesorcinol, 2-chlorophenol, 2,4-dichlorophenol (Sigma–Aldrich, Spain), were analytical grade and used as received. Acetonitrile HPLC grade (Sigma–Aldrich, Spain) was used as the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 MΩ cm at 25 °C) was used to prepare all solutions.

2.2. Experimental setup

All electrolysis was conducted in a DiaCell® type 401 supplied by Adamant Technologies (Switzerland). The DiaCell® module can be assembled with one, two, three or four compartments, each of them fed with wastewater by internal parallel inlets. The boundary electrodes are monopolar Si/BDD, and when multiple compartments are in use, the separating electrodes are floating bipolar Si/BDD electrodes. All electrodes were circular (100 mm diameter) with a geometric area of 70 cm^2. The inter-electrode gap was approximately 9 mm. The BDD coating had a film thickness of 2 mm and a resistivity 100 mΩ cm. The boron concentration was 500 ppm, and the ratio $sp^3/sp^2 > 150$. The BDD electrode was cleaned for 10 min in a 1 M Na_2SO_4 solution at 15 mA cm^{-2} prior to electrolysis assays. Sono-electrochemical experiments were performed in the electrolysis set up using the same fluid-dynamic conditions. For US, the electrolysis cell was equipped with an ultrasound generator UP200S (Hielscher Ultrasonics GmbH) equipped with a titanium glass horn measuring 40 mm in diameter and 100 mm in length. The output used was continuous wave mode with percentage of cycle of 100% emitting 24 kHz, and 200 W ultrasonic power was put into to a 1000 mL cylindrical cell. More experimental details of the flow cell reactor and a schematic representation of the ultrasound-assisted system can be found elsewhere [16].

2.3. Analysis procedures and methods

Electrolysis was performed using 1.2 dm^3 of a solution containing 100 mg dm^{-3} 2.4-D at natural pH (3.5) and 3 g L^{-1} NaCl as the supporting electrolyte. Tests were performed galvanostatically (the external current intensity applied was 10 A) and in discontinuous mode. Water was recirculated between the cell and an auxiliary tank at a constant flow rate (26.4 dm^3 h^{-1}) to favor mixing conditions, gas stripping and temperature regulation. A heat exchanger coupled with a controlled thermostatic bath was used to maintain the temperature at 25 °C.

All samples taken from electrolyzed solutions were filtered with 0.45 μm nylon filters from Whatman before analysis. Measurements of pH were performed with an InoLab WTW pH-meter. The decay of herbicide and the evolution of aromatic products were followed using reversed-phase chromatography, Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD). The chromatography system was an Agilent 1100 series coupled to a UV detector. A Phenomenex Gemini 5 μm C18 analytical column was used. The mobile phase consisted of 60% acetonitrile/40% water with 2% acetic acid (flow rate = 0.4 cm^3 min^{-1}). The UV detection wavelength was 280 nm, the temperature was kept at 25 °C, and the volume injection was 20 μL. A calibration graph was constructed in the range of 0.1–150 mg dm^{-3}, and regression analysis showed a linear relationship with a correlation coefficient $r = 0.998$. The detection limit was 0.018 mg dm^{-3}.

The Total Organic Carbon concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. TOC reproducibility showed a standard error below 2%. Chemical Oxygen Demand (COD) was monitored using standard kits from Merck. Solutions were oxidized by digestion for 2 h at 150 °C in a block ECO 25 Thermoreactor (Velp Scientifica). Then, after the ambient temperature was reached, the absorbance of the samples was read at 600 nm in a spectrophotometer (Hach DR 2000). Samples containing chloride concentrations above 2 g dm^{-3} were diluted as recommended.

Chloride anions (Cl^-, ClO_3^-, ClO_4^-) were determined using ion chromatography with a Shimadzu LC-20A equipped with a Shodex IC I-524A column: mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1×10^{-3} dm^3 min^{-1}. Hypochlorite ($HClO^-$) was determined by titration with 0.001 M As_2O_3 in 2.0 M NaOH. Pretreatment of the samples was performed by adding 2×10^{-3} dm^3 of 2.0 M NaOH to increase the pH. Peroxosulfate was determinate iodometrically according to Kolthoff and Carr [39].

3. Results and discussion

Fig. 1 shows the changes in the cell potential during electrolysis and sono-electrolysis of synthetic wastewater containing the herbicide 2,4-D as the organic pollutant and sodium chloride as the salt.

In all tests, the cell voltage decreased slightly during the electrolytic and sono-electrolytic treatments down to a constant value. This behavior is typical of most electrochemical remediation tests and can be related to the change in the conductivity of the electrolyte (and hence with the resulting ohmic drop), as seen in Fig. 1b. These changes can be related to the electrolysis of water (which occurs on the surface of both electrodes) and to a lesser extent the formation of intermediates and final products from the electrolysis of 2,4-D and chloride. Changes are highly significant and within the 5.6–19.9% range, with higher observed in the case of the coupled US irradiation technology. The lower cell voltage value in the sono-electrolytic cell, which is 2.9–9.6%, is lower than in the corresponding silent electrolytic test (using only the electrochemical process). Cell voltage is directly related to the

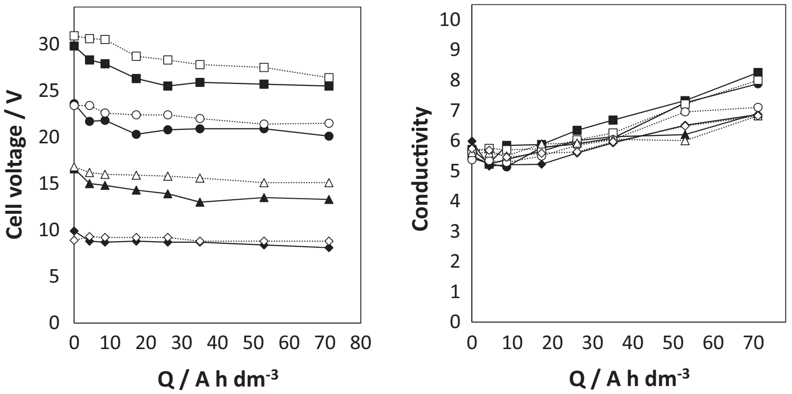

Fig. 1. Changes in the cell voltage and conductivity during the sono-electrochemical (solid symbols) and silent electrochemical (open symbols) oxidation of synthetic wastewater using a DIACELL 401 equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (♦, ◇) 1 compartment; and (▲, Δ) no compartments.

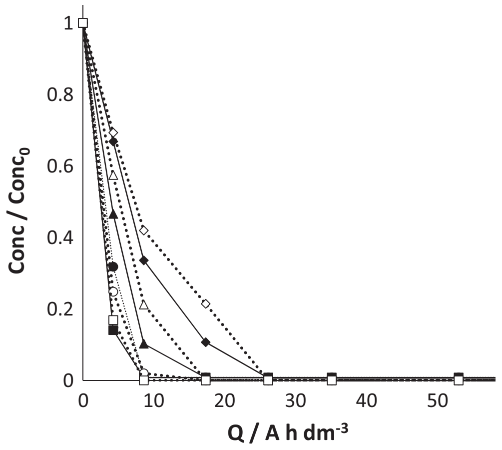

Fig. 2. Relative 2,4-D decay as a function of the applied charge per unit volume of electrolyzed solution (Q_{ap}) during the sono-electrochemical (solid symbols) and silent electrochemical (open symbols) oxidation using a DIACELL 401 equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (♦, ◇) 1 compartment; and (▲, Δ) no compartments.

energy cost in a cell in galvanostatic operation mode, and this decrease reflects a decrease in the energy cost associated with electricity. In addition, the changes in the cell potential are higher in the sono-electrolytic cell, although there is no direct correspondence with the increase in electrolyte conductivity. Lower cell voltages in the application of US irradiation could partially reduce the energy demand of this irradiation technology.

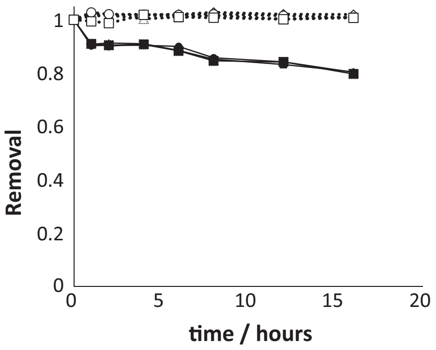

Fig. 4. Relative concentration (solid symbols) and TOC decay (open symbols) as a function of the reaction time during the sono-chemical process using a DIACELL equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (♦, ◇) 1 compartment; and (▲, Δ) no compartments.

Fig. 2 shows the changes in the concentration of 2,4-D during test treatments. US irradiation has a very positive effect on the oxidation of 2,4-D and favors faster oxidation of the herbicide.

The external current charge passed required for the complete oxidation of 2,4-D decreases with the number of bipolar electrodes; the cell with three bipolar electrodes required 2.5 times lower current charge. These observations can be easily explained by taking into account the internal electric charge supplied by the bipolar electrodes, transferring electrons from one face of the electrode to the other, without passing through an external circuit. The difference between the silent electrolysis and the

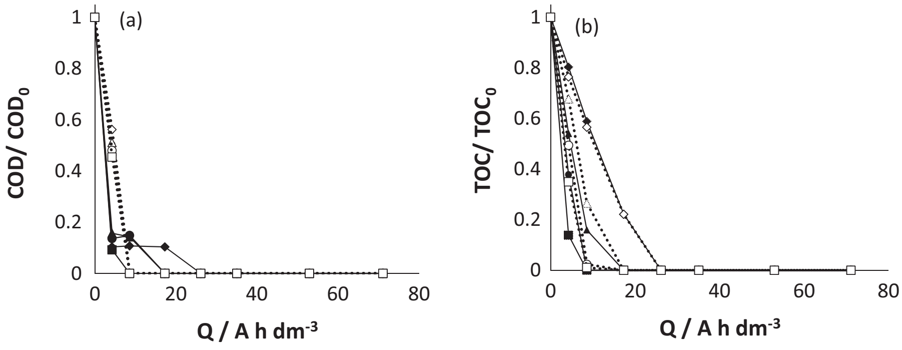

Fig. 3. Relative *COD and TOC* decay as a function of the applied charge per unit volume of electrolyzed solution (Q_{ap}) during the sono-electrochemical (solid symbols) and electrochemical silent (open symbols) oxidation using a DIACELL 401 equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (♦, ◇) 1 compartment; and (▲, Δ) no compartments.

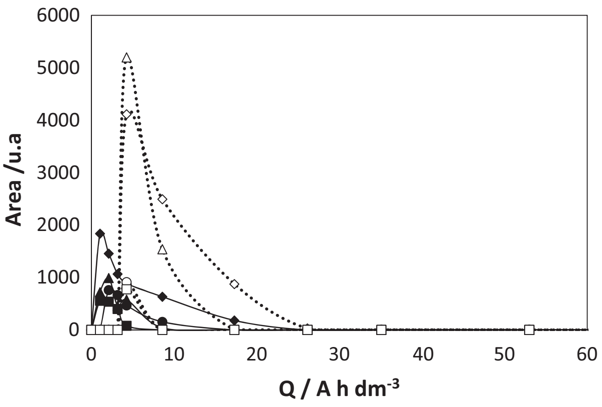

Fig. 5. Changes in the aromatic intermediates as a function of the applied charge per unit volume of electrolyzed solution (Q_{ap}) during the sono-electrochemical (solid symbols) and silent electrochemical (open symbols) processes using a DIACELL 401 equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (♦, ◇) 1 compartment; and (▲, △) no compartments.

sono-electrolysis decreased when the number of bipolar electrodes increased; however, this decrease only indicates that the raw herbicide is oxidized but it does not mean that the organic pollutant is depleted or that the treated water is less hazardous.

Both pollutant depletion and hazards are assessed using COD and TOC. Fig. 3 shows the changes in COD. Due to the presence of chlorides and the formation of a high concentration of chlorinated oxidants, this parameter changes very rapidly and total depletion is obtained at very low current. Likewise, the TOC is very efficiently removed, and the effect of US irradiation on depletion is highly significant and the opposite of what was observed for the removal of the raw pollutant; i.e., it is much more pronounced for systems with many bipolar electrodes. The combined process thus works better in systems with a higher area of bipolar electrodes.

Another important parameter to be considered in this system is the energy consumption. In a batch system, the energy consumption in an electrolytic treatment can be estimated from Eq. (1), where Q is the specific charge applied, I is the cell intensity, V is the electrolyte volume, t is the treatment time and E is the cell voltage. Likewise, energy consumption by a sonolytic treatment (assuming 100% efficiency) can be calculated from Eq. (2), where w is the US power irradiated (200 W).

$$W_{electrolysis}(\mathrm{kW\,h\,m^{-3}}) = Q(\mathrm{kA\,h\,m^{-3}})\cdot E(\mathrm{V}) = \frac{I(\mathrm{A})\cdot t(\mathrm{h})\cdot E(\mathrm{V})}{V(\mathrm{m^{-3}})} \quad (1)$$

$$W_{sonolysis}(\mathrm{kW\,h\,m^{-3}}) = \frac{\mathrm{w(kW)}\cdot t(\mathrm{h})}{V(\mathrm{m^{-3}})}. \quad (2)$$

In the silent electrolytic process, the power consumption increases with the number of bipolar electrodes from 227.4 kW h $\mathrm{m^{-3}}$ to 455.4 kW h $\mathrm{m^{-3}}$. In contrast, in the sono-electrochemistry process, the power consumption decreases from 325.4 kW h $\mathrm{m^{-3}}$ to 302.3 kW h $\mathrm{m^{-3}}$. US irradiation in electrochemical waste treatment therefore makes the most sense in electrochemical cells with multiple electrodes.

Fig. 4 focuses on the removal of 2,4-D using a single sono-chemical process in the same experimental setup. The results are highly reproducible, as the four experiments overlie each other, and it is clearly seen that no mineralization but just oxidation of the herbicide is obtained with the US irradiation; hence, the combination of technologies enhances oxidation because it speeds up removal in the electrolytic process and leads to the mineralization of the herbicide.

Regarding the formation of intermediates during the process, Fig. 5 shows the changes in the total chromatographic area of the peaks of intermediates detected during the silent electrolytic and sono-electrolytic tests (calculated by single addition of the areas obtained at each sampling time and used as an indicator of the presence of intermediates). Sono-electrolysis led to harsher oxidation conditions compared with electrolysis alone, yielding faster removal of intermediates and a lower maximum concentration. In addition, the maximum was present for a shorter amount of time (half of the time required in the sono-electrolysis experiment).

US irradiation significantly improves the mass transfer coefficient and thus the amount of pollutant that near the electrode surface. In addition, US irradiation leads to the formation of hydroxyl radicals from water hydrolysis, which also help explain the observed improvements. Hydroxyl radicals generated via this non-electrochemical mechanism are produced in the bulk solution, and hence, their action is not limited to the oxidation of pollutants at the diamond electrode surface but is extended to the whole electrolyte. This oxidation mechanism helps to explain the improvement in electrolysis with the addition of ultrasound [23,25,35].

The main intermediates detected were 4-chlororesorcinol, 2-chlorophenol, 2,4dichlorophenol, hydroquinone and benzoquinone. Their maximum concentrations are shown in Table 1.

US irradiation does not influence the nature of the intermediates formed but only their concentration, indicating that mechanism by which 2,4-D is removed is the same in the silent electrolytic and sono-electrolytic technologies. It can thus be assumed that the degradation of 2,4-D follows the oxidation pathway shown in Fig. 6 based on the rapid cleavage of the 2,4-D molecule to form 2,4-dichlorophenol, which is further oxidized to 4-chlororesorcinol. After that, dehalogenation and hydroxylation of the aromatic ring lead to the formation of chlorinated compounds. Once in chloride medium, due to the high production of the active chlorine atoms, organo chlorine species, such as 4-chlororesorcinol and 2-chlorophenol, form. These species are then oxidized to hydroquinone followed by benzoquinone. This mechanism is in agreement with mechanisms previously proposed for other Advanced Oxidation Processes [40–42].

Figs. 7 and 8 focus on chloride oxidation and the resulting chlorine speciation. As described in the introduction, this paper focuses not only on the removal of a herbicide but also on the influence of bipolar electrodes and ultrasound in the production of oxidants. The oxidation of chlorides may be used as an indicator of this

Table 1
Maximum concentration (mg $\mathrm{dm^{-3}}$) detected for aromatic intermediates.

Intermediate	Electrochemical process				Sono-electrochemical process			
	3 bipolar	2 bipolar	1 bipolar	No bipolar	3 bipolar	2 bipolar	1 bipolar	No bipolar
4-Chlororesorcinol	3.63	2.90	4.61	3.70	3.56	0	6.63	3.26
2-Chlorophenol	45.12	57.63	63.46	49.94	0	6.34	8.44	24.88
2,4-Dichlorophenol	8.41	18.95	30.18	26.23	0	0	0	13.84
Hydroquinone	0	0	1.97	2.23	12.44	11.33	11.31	3.75
Benzoquinone	0	0	11.55	9.28	0	13.22	11.15	0

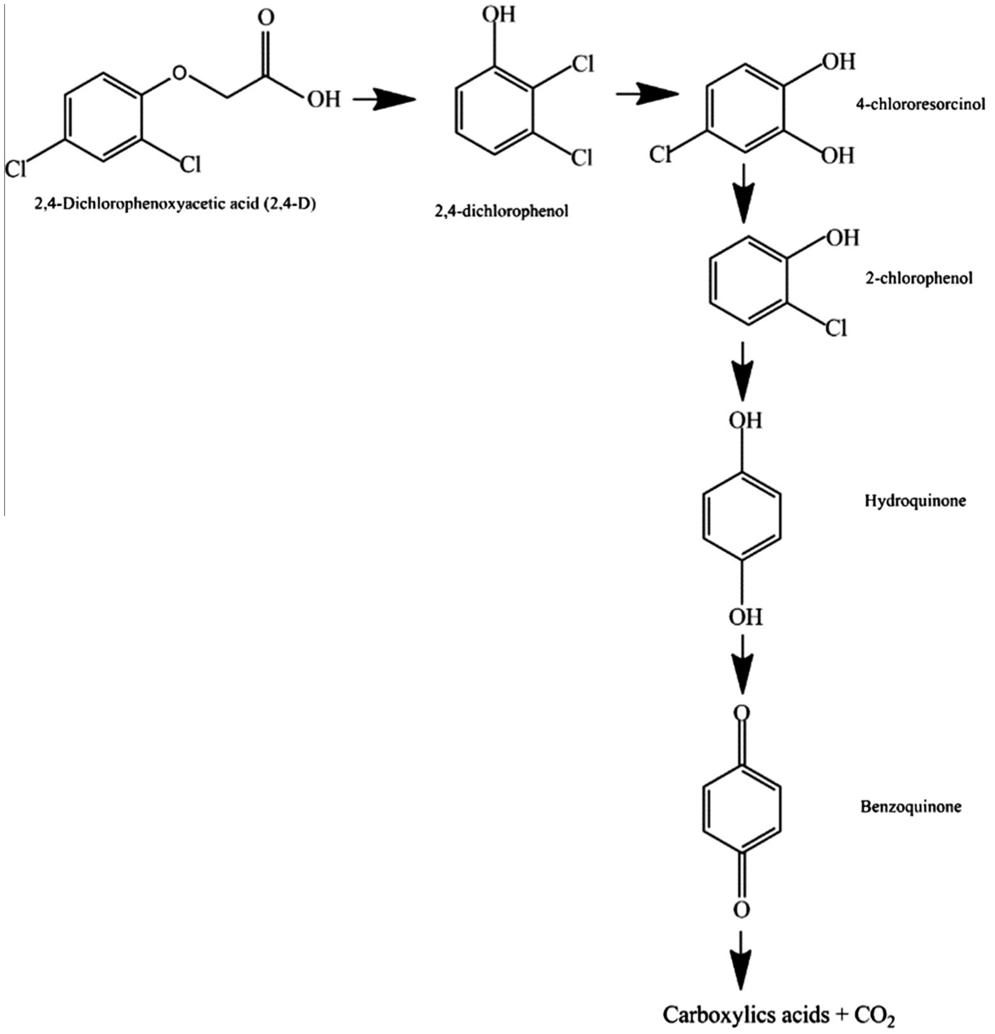

Fig. 6. Proposed mechanism for the silent electrolytic and sono-electrolytic oxidation of 2,4-D.

process because these species are oxidized to gaseous chlorine/hypochlorite and oxidation does not stop at this point but continues to chlorate and perchlorate, which despite having a high reduction potential, are very soft oxidants at room temperature and atmospheric pressure and have no influence on the oxidation process. Chloride is oxidized faster with the same current density using sono-electrolysis (Fig. 7).

This increased oxidation rate reflects the faster production of chlorate, which is produced in at much higher concentrations in the sono-electrolysis compared with single electrolysis (Fig. 8a). This species is not the final product but is further oxidized to perchlorate (Fig. 8b), which is the final product in the oxidation of chloride both in the electrolysis alone and the US-irradiated technology.

Formation of perchlorate is disfavored in sono-electrolysis compared to silent electrolysis, which is reflected by the higher concentration of chlorates and in the longer time required in the sono-electrolysis for the complete oxidation of chloride to perchlorate. There are thus significant differences in the way in which oxidants are produced and behave under the US irradiation, which may influence the results of the electrolysis of organic pollutants if the oxidants are needed for the reaction; hence, oxidant production should be taken into account. Oxidation of chlorate to perchlorate is partially prevented by US irradiation, which could be due to the lack of hydroxyl radicals to catalyze this reaction and the increase in mass transfer, which allows chlorate to escape from the hydroxyl radical cage generated around the diamond electrode surface. Obviously, perchlorate should be avoided in any remediation technology, and in this study, it was only used to increase knowledge about the production of oxidants while simultaneously depleting the herbicide.

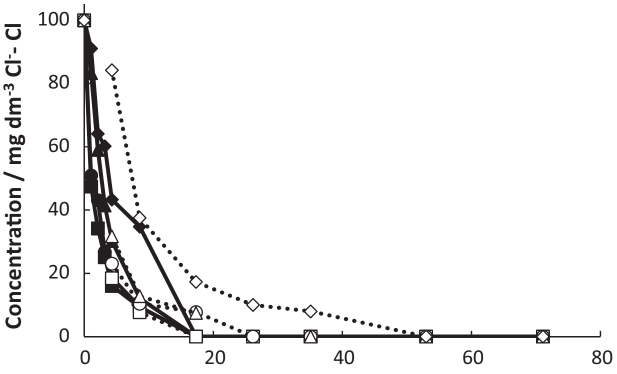

Fig. 7. Changes in the chloride concentration as a function of the applied charge per unit volume of electrolyzed solution (Q_{ap}) during the sono-electrochemical (solid symbols) and electrochemical (open symbols) processes with an external current intensity of 10 A using a DIACELL® equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (♦, ◇) 1 compartment; and (▲, △) no compartments.

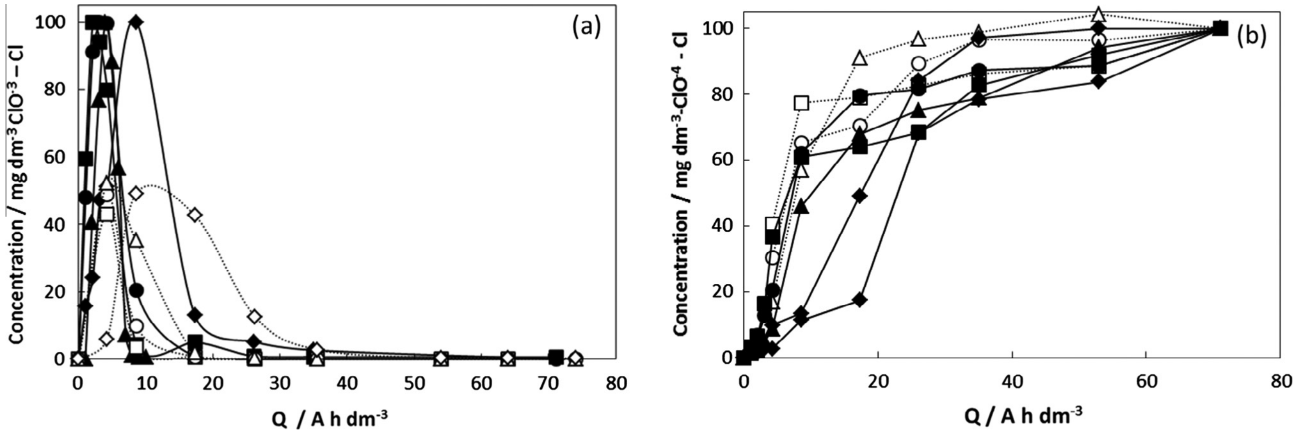

Fig. 8. Changes in the chlorate (a) and perchlorate (b) concentrations as a function of the applied charge per unit volume of electrolyzed solution (Q_{ap}) during the sono-electrochemical (solid symbols) and silent electrochemical (open symbols) processes with an external current intensity of 10 A using a DIACELL® 401 equipped with: (■, □) 3 compartments; (●, ○) 2 compartments; (♦, ◇) 1 compartment; and (▲, △) no compartments.

4. Conclusions

From this work, the following conclusions can be drawn:

- 2,4-D can be efficiently depleted from synthetic wastewater obtaining complete mineralization regardless of the number of bipolar electrodes used. Ultrasound irradiation improves results obtained using a single electrolytic processes.
- For the same external current applied, the higher the number of bipolar electrodes connected, the faster and more efficient the removal and the clearer the differences between the silent and the US irradiated processes.
- Lower cell voltages result from the application of US irradiation, which could compensate for the energy demand of this irradiation.
- 4-Chlororesorcinol, 2-chlorophenol, 2,4-dichlorophenol, hydroquinone and benzoquinone are the main intermediates found in both technologies. Their concentrations are much lower under US irradiation.
- US irradiation influences the formation of oxidants in the reaction media. Under US irradiation, production of chlorates is promoted compared with the formation of perchlorates.

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