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# Degradation of 2,4-D herbicide in a recirculation flow plant with a Pt/air-diffusion and a BDD/BDD cell by electrochemical oxidation and electro-Fenton process



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## ABSTRACT

Here, 2.5 L of solutions of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide of pH 3.0 have been degraded by electrochemical oxidation (EO) and electro-Fenton (EF) using a recirculation flow plant equipped with a single Pt/air-diffusion or BDD/BDD cell containing electrodes of 20 cm<sup>2</sup> area. In EO, organics were mainly oxidized by ·OH formed at the anode surface from water oxidation, whereas in EF they were also destroyed in the bulk by ·OH generated from Fenton's reaction between added Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> produced at the cathode. In both treatments, the use of a single BDD/BDD cell always allowed larger decontamination due to the higher ability of ·OH at the BDD surface to mineralize organic intermediates. The most potent EF process with this cell gave 59% mineralization with 23% efficiency and 0.42 kW h g<sup>-1</sup> TOC specific energy after 300 min at 0.5 A. The coupling of Pt/air-diffusion and BDD/BDD cells with equal individual current in EF led to similar mineralization degree to that found for the Pt/air-diffusion one at the same total current, but in much shorter time. The effect of current on the mineralization rate, mineralization current efficiency and specific energy of each method was examined. The influence of herbicide concentration on the EF performance of the coupled cell at 2.0 A/2.0 A was also studied and 83% mineralization was obtained as maximal for 276 mg L<sup>-1</sup> 2,4-D. The herbicide decay always obeyed a pseudo-first-order reaction. A mixture of short-linear carboxylic acids was detected in all final electrolyzed solutions, which were the major organic by-products generated using the single BDD/BDD cell but formed in minor proportion in the EF processes with the Pt/air-diffusion and coupled ones.

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## 1. Introduction

The very high consumption of pesticides in agriculture and the inadequate storage or disposal of obsolete herbicides cause the contamination of these compounds in soils, groundwater, rivers, lakes, rainwater and air. It has been found that some agricultural wastewaters can reach pesticide concentration levels as high as 500 mg L<sup>-1</sup> [1,2], which need to be treated before their release into the aquatic environment. In this context, 2,4-dichlorophenoxyacetic acid (2,4-D) is an herbicide extensively used around the world. Commercial formulations of 2,4-D include esters, acids and several

salts, which vary in their properties, environmental behavior and toxicity. In the United States, for example, 2,4-D has been employed extensively, approximately in amounts of 46 million pounds per year, based on data collected from 1992 to 2000 [3]. As a selective herbicide, 2,4-D is used to control broadleaf weeds in a variety of settings from crops, rights-of-way, lawns and forests. In aerobic conditions, it degrades slowly with a mean lifetime of 13 days [4,5]. Powerful oxidation methods are required to remove this pollutant and its products from wastewaters to avoid their possible toxic effects on living beings.

Recently, the destruction of 2,4-D in waters has been performed by several chemical, photochemical and photocatalytic advanced oxidation processes (AOPs) such as O<sub>3</sub> [6–9], O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> [6,7], O<sub>3</sub>/Fe<sup>2+</sup>/UV [6], O<sub>3</sub>/TiO<sub>2</sub>/UV [9,10], TiO<sub>2</sub>/UV [9,11], UV/H<sub>2</sub>O<sub>2</sub> [7], Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> (Fenton's reagent) [12] and Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV [12,13] systems. AOPs

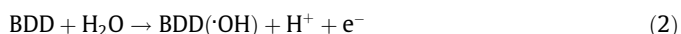
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have the common feature that can generate in situ hydroxyl radical ( $\cdot\text{OH}$ ) as oxidizing agent. This radical has a high standard redox potential ( $E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/SHE}$ ) and as a result, it can react non-selectively with most organics up to their mineralization.

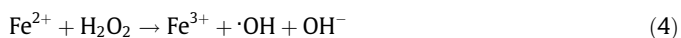
Electrochemical AOPs (EAOPs) constitute environmentally friendly emergent techniques for water remediation because they do not use toxic reagents since the electron is the principal reagent. The degradation process involves the direct reaction of organics at the anode surface by charge transfer, whereas at high current the destruction of pollutants is preferentially due to the action of the oxidizing agents produced at the anode [14–16]. The simplest and more common EAOP is anodic oxidation or electrochemical oxidation (EO), where organics are destroyed by physisorbed  $\text{M}(\cdot\text{OH})$  radical formed from water oxidation [14,17]. Although several anode materials such as Pt [18–22],  $\text{SnO}_2$  [23] and  $\text{PbO}_2$  [24–27] have been used for EO, boron doped diamond (BDD) thin-film electrodes [18–26] have shown greater oxidation ability. The BDD anode possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability, a wide potential window in aqueous medium and an extremely high  $\text{O}_2$ -evolution overvoltage, which confers a larger reactivity of  $\text{BDD}(\cdot\text{OH})$  towards organics [17,28,29]. According to the generally accepted mechanism for EO over the Pt and BDD anodes, the physisorbed  $\text{Pt}(\cdot\text{OH})$  and  $\text{BDD}(\cdot\text{OH})$  radicals are produced as follows [30,31]:



Recently, EAOPs based on Fenton's reaction chemistry have received increasing attention for water remediation [14,15]. The most popular of these methods is electro-Fenton (EF) in which  $\text{H}_2\text{O}_2$  is continuously supplied to the acidic contaminated solution contained in an electrolytic cell by the two-electron reduction of injected  $\text{O}_2$  gas at a cathode from reaction (3):



$\text{H}_2\text{O}_2$  is efficiently produced at carbonaceous cathodes like carbon felt [32–35], activated carbon fiber [36], carbon–polytetrafluoroethylene (PTFE)  $\text{O}_2$  or air diffusion [37–40] and BDD [16,41–44]. In EF, the oxidizing power of  $\text{H}_2\text{O}_2$  is enhanced by adding small amounts of  $\text{Fe}^{2+}$  to form  $\text{Fe}^{3+}$  and  $\cdot\text{OH}$  in the solution bulk from Fenton's reaction (4) [14,45]:



The principal advantage of the EF process compared with the classical Fenton reaction is the quick regeneration of  $\text{Fe}^{2+}$  ion from the reduction of  $\text{Fe}^{3+}$  ion at the cathode, enhancing the generation of  $\cdot\text{OH}$  from Fenton's reaction (4) [46]. Note that in an undivided cell, EF is expected to be more potent than EO since both kinds of  $\cdot\text{OH}$  radicals, formed at the anode surface from reactions (1) or (2) and in the solution bulk from reaction (4) respectively, act.

Our interest in the development of EO and EF methods is to demonstrate that recirculation flow plants can be used to degrade organic solutions as a first step for the further scale-up of both EAOPs at industrial level. In this way, we have recently tested the treatment of a commercial formulation of 2,4-D in a 3 L plant containing a BDD/BDD filter-press cell with  $64 \text{ cm}^2$  electrode area, obtaining excellent mineralization degrees of 63% and 81–83% at 120 min of EO and EF, respectively, operating at 2.0 A [43]. However, no more information is known about the degradation of this herbicide with other kinds of reactors in flow plants. Several authors have published the treatment of 2,4-D by EO with Pt [18], bare graphite felt [47] and BDD [18,48] anodes, as well as by EF with a BDD/ $\text{O}_2$ -diffusion [48,49] or carbon-felt [50] cathode,

but using small stirred tank reactors without considering their viability for industrial application. For this reason, we have extended the study to plants operating with Pt/air-diffusion and BDD/BDD filter-press cells, separated and coupled, under comparable conditions. These cells have been chosen because they present different performances in EF as a result of the different oxidizing species formed. In the first one, large amounts of  $\cdot\text{OH}$  are produced by Fenton's reaction (4) owing to the high  $\text{H}_2\text{O}_2$  generation from reaction (3) at the air-diffusion cathode, whereas a small participation of  $\text{Pt}(\cdot\text{OH})$  produced from reaction (1) in the mineralization process is expected [14]. In contrast, in the latter one, much lower  $\text{H}_2\text{O}_2$  is generated at the BDD cathode, yielding smaller quantities of  $\cdot\text{OH}$ , but organics can also be mineralized by the more reactive  $\text{BDD}(\cdot\text{OH})$  formed from reaction (2) [41–44].

This paper reports a comparative study on the degradation of pure 2,4-D in acidic medium under EO and EF conditions using Pt/air-diffusion or BDD/BDD cells in a 2.5 L recirculation flow plant to assess the best system that can be useful at industrial level. The influence of current on the mineralization rate, mineralization current efficiency (MCE) and specific energy for each single cell was examined. The effect of current and 2,4-D content on the EF performance was also assessed for the coupled Pt/air-diffusion-BDD/BDD cell. The 2,4-D decay and the evolution of generated carboxylic acids were followed by different chromatographic techniques.

## 2. Material and methods

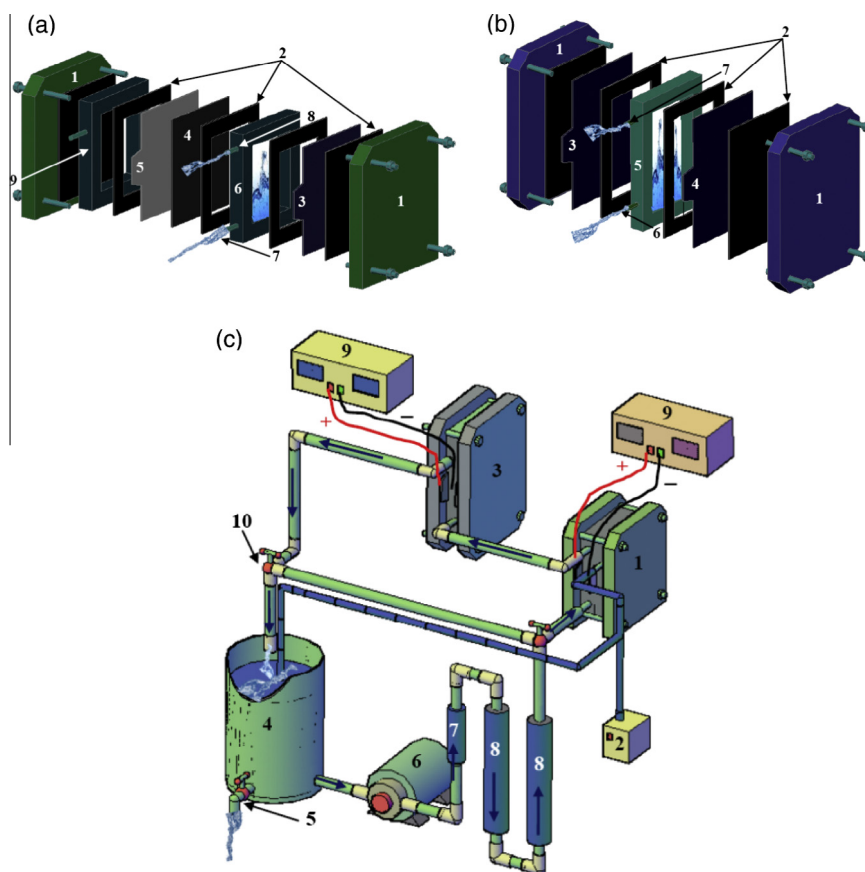
### 2.1. Chemicals

Reagent grade 2,4-D (98% purity) purchased from Merck was used as received. Carboxylic acids like oxalic, maleic, succinic, formic, acetic, glyoxylic, glycolic, malic and fumaric were of analytical grade supplied by Acros Organics, Aldrich and Fluka. Anhydrous sodium sulfate used as background electrolyte and heptahydrated ferrous sulfate used as catalyst were of analytical grade from Fluka. Analytical grade sulfuric acid purchased from Merck was used to adjust the initial solution pH to 3.0. All the solutions were prepared with ultrapure water from a Millipore Milli-Q system (resistivity  $\geq 18 \text{ M}\Omega \text{ cm}$ ). All the other chemicals were either of HPLC grade or analytical grade supplied by Fluka, Lancaster and Merck.

### 2.2. Electrochemical systems

The electrochemical assays were carried out with two different undivided filter-press reactors equipped with: (i) a Pt sheet anode of 99.99% purity supplied by SEMPISA and a carbon–PTFE air-diffusion cathode purchased from E-TEK and (ii) a BDD anode and cathode with 2–7  $\mu\text{m}$  thickness supported on niobium provided by Mekatem<sup>TM</sup>. A sketch of these cells is presented in Fig. 1a and b, respectively. All the electrodes had a geometric area of  $20 \text{ cm}^2$  in contact with the solution and were separated a distance of about 1 cm through the liquid compartment. In the Pt/air-diffusion cell, atmospheric air at an overpressure of 8.6 kPa was supplied to the air chamber in contact with the inner face of the air-diffusion cathode for the continuous  $\text{H}_2\text{O}_2$  generation from reaction (3). When the BDD/BDD cell was used under EF conditions, an air flow of  $10 \text{ L min}^{-1}$  was bubbled through the reservoir from 30 min prior to the beginning of the trial to keep the solution always saturated of  $\text{O}_2$  for  $\text{H}_2\text{O}_2$  generation at the BDD cathode.

Fig. 1c shows a scheme of the experimental set-up used for the 2,4-D treatment by EO and EF in a 2.5 L recirculation flow plant containing the coupled cells. The same electrolytic system was employed for the trials made for each separated cell. The herbicide solution was introduced in the reservoir and recirculated through the plant with a centrifugal pump at a flow rate of  $200 \text{ L h}^{-1}$



**Fig. 1.** (a) Scheme of the Pt/air-diffusion filter-press reactor. (1) End plate, (2) gasket, (3) Pt anode, (4) air-diffusion cathode, (5) Ni mesh collector, (6) liquid compartment, (7) liquid inlet in the cell, (8) liquid outlet of the cell and (9) air chamber. (b) Scheme of the BDD/BDD filter-press reactor. (1) End plate, (2) gasket, (3) BDD anode, (4) BDD cathode, (5) liquid compartment, (6) liquid inlet in the cell and (7) liquid outlet of the cell. (c) Sketch of the recirculation flow plant with the two coupled cells for 2,4-D mineralization. (1) Pt/air-diffusion cell, (2) air pump, (3) BDD/BDD cell, (4) reservoir, (5) sampling, (6) centrifugal pump, (7) flowmeter, (8) heat exchangers, (9) power supplies and (10) valve.

regulated by a flowmeter, maintaining its temperature at 35 °C with two heat exchangers. A constant current ( $I$ ) of 0.5, 1.0 and 2.0 A was provided to the cells by Agilent 6552 A DC power supplies, which directly measured their potential differences, with average values of 5.5, 7.8 and 14.8 V for the Pt/air-diffusion cell and 10.0, 13.9 and 25.4 V for the BDD/BDD one, respectively. Before the degradation experiments, the impurities of the BDD electrodes were removed and the air-diffusion cathode was activated by electrolyzing a 0.05 M  $\text{Na}_2\text{SO}_4$  solution of pH 3.0 in each cell at 2.0 A for 120 min.

### 2.3. Instruments and analytical procedures

The solution pH was measured with a Crison GLP 22 pH meter. Aliquots of 5 mL were withdrawn from treated solutions and before their analysis, they were alkalized to quench the degradation process and further filtered with 0.45  $\mu\text{m}$  PTFE filters supplied by Whatman. The mineralization of the herbicide solution was monitored from their TOC decay, determined on a Shimadzu VCSN analyzer. Reproducible TOC values with an accuracy of  $\pm 2\%$  were obtained by injecting 50  $\mu\text{L}$  samples to the analyzer. For a given trial at constant  $I$  (in A), the MCE value at time  $t$  (in h) was then determined from Eq. (5) [38,39]:

$$\text{MCE (\%)} = \frac{nFV_s\Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 mlt} \times 100 \quad (5)$$

where  $F$  is the Faraday constant (96,487 C mol $^{-1}$ ),  $V_s$  is the solution volume (in L),  $\Delta(\text{TOC})_{\text{exp}}$  is the experimental TOC decay (in mg L $^{-1}$ ),

$4.32 \times 10^7$  is a conversion factor to homogenize units (3600 s h $^{-1}$   $\times$  12,000 mg mol $^{-1}$ ) and  $m$  is the number of carbon atoms of 2,4-D (8 atoms). The number of electrons ( $n$ ) consumed per each molecule was taken as 30 assuming that mineralization involves its conversion into  $\text{CO}_2$  and  $\text{Cl}^-$  ion, as reported elsewhere [48]:



The specific energy per unit TOC mass (EC) was calculated from Eq. (7) [39]:

$$\text{EC (kW h g}^{-1} \text{ TOC)} = \frac{E_{\text{cell}} I t}{V_s \Delta(\text{TOC})_{\text{exp}}} \quad (7)$$

where  $E_{\text{cell}}$  is the average cell voltage (V).

The herbicide decay was followed by reversed-phase HPLC chromatography. This analysis was made by injecting 20  $\mu\text{L}$  samples into a Waters 600 LC fitted with a Thermo Electron Corporation Hypersil ODS2 5  $\mu\text{m}$ , 150 mm  $\times$  3 mm, column at room temperature and coupled with a Waters 996 photodiode array detector selected at  $\lambda = 282$  nm. A 50:50 (v/v) acetonitrile/water (phosphate buffer of pH 3) solution at 0.6 mL min $^{-1}$  was used as eluent and a good chromatographic peak related to 2,4-D was displayed at a retention time ( $t_r$ ) of 2.65 min. Generated carboxylic acids were identified and quantified by ion-exclusion HPLC using the same LC fitted with a Bio-Rad Aminex HPX 87H, 300 mm  $\times$  7.8 mm, column at 35 °C and setting the photodiode detector at  $\lambda = 210$  nm. For this analysis, 20  $\mu\text{L}$  samples were also injected into the LC and the mobile phase was a 4 mM  $\text{H}_2\text{SO}_4$  solution circulating at 0.6 mL min $^{-1}$ .

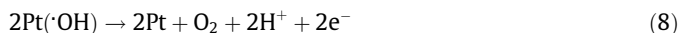
### 3. Results and discussion

#### 3.1. EO and EF degradation using a Pt/air-diffusion cell

A first experiment was made by electrolyzing 2.5 L of a 92 mg L<sup>-1</sup> 2,4-D solution (40 mg L<sup>-1</sup> TOC) in 0.05 M Na<sub>2</sub>SO<sub>4</sub> of pH 3.0 using the recirculation flow plant equipped with a single Pt/air-diffusion cell operating at 2.0 A, 35 °C and flow rate of 200 L h<sup>-1</sup> for 300 min. The temperature of 35 °C was chosen since it is the maximum value that allows working the plant without significant water evaporation from the solution. In this EO trial, the solution pH remained practically constant, but the solution TOC decayed very slowly, being reduced by less than 4 mg L<sup>-1</sup> (<10% mineralization) at the end of the electrolysis (data not shown). This poor decontamination indicates that 2,4-D and its oxidation products are very slowly degraded by Pt(OH) and/or generated H<sub>2</sub>O<sub>2</sub> because of their small oxidation ability [19,21,22].

The above 2,4-D solution was further treated in the same electrolytic system under EF conditions. To do this, 0.5 mM Fe<sup>2+</sup> was added to the initial solution to produce the more potent oxidant ·OH in the bulk from Fenton's reaction (4). This Fe<sup>2+</sup> concentration was selected because it has been found as optimal for similar degradations of other aromatics [14,15,39]. The effect of applied current on the EF treatment of a 92 mg L<sup>-1</sup> 2,4-D solution was then examined to clarify the role of this variable to regulate the generation of the oxidizing species.

Fig. 2a depicts the TOC decay determined for *I* values ranging between 0.5 and 2.0 A. The decontamination process became faster with raising *I* up to 180 min, whereupon TOC was slowly reduced reaching a quite similar mineralization of 54%, 57% and 58% after 300 min of electrolysis at 0.5, 1.0 and 2.0 A, respectively. In all cases, the final pH dropped to values of 2.6–2.7, suggesting the formation of acidic products like short-chain carboxylic acids which yield Fe(III) complexes that are hardly removed by Pt(OH) and ·OH in the bulk [14]. A similar proportion of recalcitrant by-products were then produced by this EAOP regardless of the applied *I*. The increase in mineralization rate at the starting stages of the EF process at higher *I* can be related to a faster destruction of easily oxidizable starting molecule and by-products as a result of the quicker production of Pt(OH) from the acceleration of the reaction (1) at the Pt anode and primordially, of H<sub>2</sub>O<sub>2</sub> from the greater rate of reaction (3) yielding more amounts of ·OH from Fenton's reaction (4). However, Fig. 2b highlights that MCE decreased gradually as *I* rose, as expected if the relative proportion of the above generated oxidizing agents decayed progressively enhancing their parasitic reactions and inhibiting the mineralization process due to the fall in degradation events. These waste reactions involve, for example, the oxidation of Pt(OH) to O<sub>2</sub> at the anode from reaction (8) and the reaction of ·OH with either H<sub>2</sub>O<sub>2</sub> to yield the weaker oxidant hydroperoxyl radical (HO<sub>2</sub>) or Fe<sup>2+</sup> from reactions (9) and (10), respectively [14,17,32].



According to this behavior, Fig. 2b shows that the highest efficiencies were obtained at 0.5 A, with a maximum MCE value of 34% at 60–90 min of treatment. For all these trials, MCE decreased drastically at long electrolysis time due to the generation of more recalcitrant by-products and the loss of organic matter [17]. The opposite trend was found for the specific energy, as can be seen in Fig. 2c. Thus, the lowest costs were determined for 0.5 A, varying from 0.16 to 0.26 kW h g<sup>-1</sup> TOC by prolonging the electrolysis time

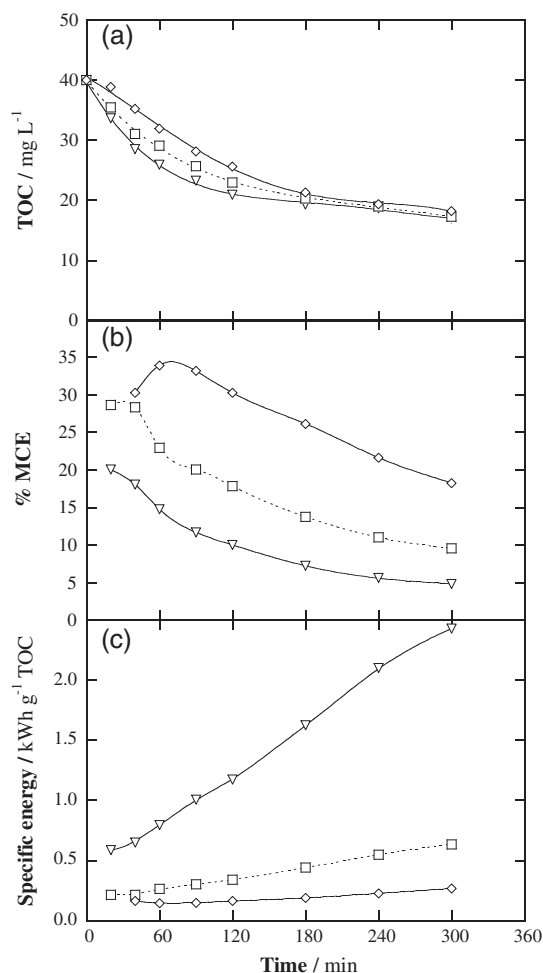


Fig. 2. (a) TOC abatement, (b) mineralization current efficiency and (c) specific energy per unit TOC mass for the treatment of 2.5 L of a 92 mg L<sup>-1</sup> 2,4-D (40 mg L<sup>-1</sup> TOC) solution in 0.05 M Na<sub>2</sub>SO<sub>4</sub> with 0.5 mM Fe<sup>2+</sup> at pH 3.0 and 35 °C by electro-Fenton (EF) process using a flow plant with a Pt/air-diffusion cell with 20 cm<sup>2</sup> electrode area at flow rate of 200 L h<sup>-1</sup>. Applied current: (◇) 0.5 A, (□) 1.0 A and (▽) 2.0 A.

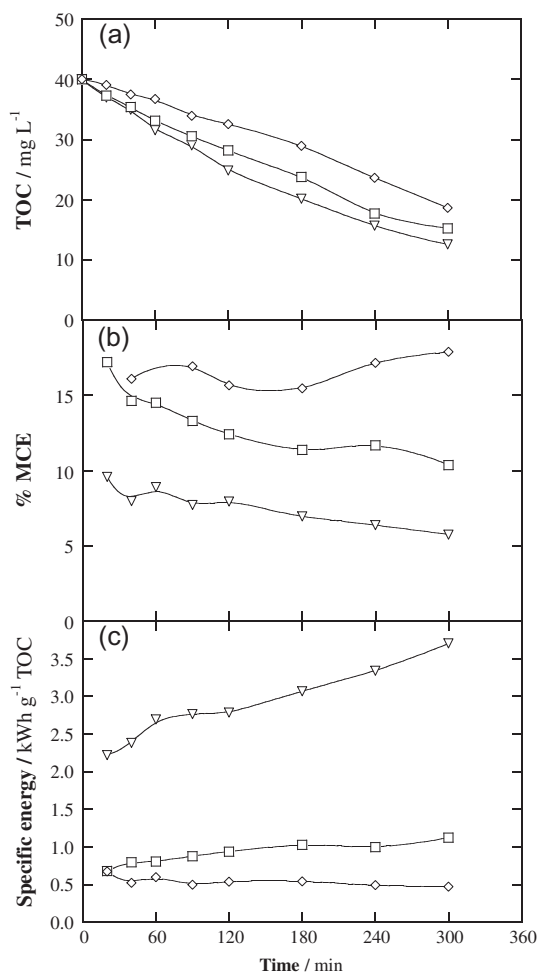
to 300 min. For 1.0 A, the specific energy rose from 0.21 to 0.63 kW h g<sup>-1</sup> TOC, whereas for 2.0 A, values as high as 2.43 kW h g<sup>-1</sup> TOC were finally obtained. These findings indicate that low currents are preferable to be provided to the single Pt/air-diffusion cell to yield higher MCE values and lower specific energies for achieving similar mineralization degree by EF.

#### 3.2. EO and EF treatments using a BDD/BDD cell

The solution containing 92 mg L<sup>-1</sup> 2,4-D at pH 3.0 was further degraded by EO and EF using the recirculation flow plant with a single BDD/BDD cell under the same conditions as used for the Pt/air-diffusion one. In the experiments performed with the BDD/BDD cell by both EAOPs, the solution pH was not regulated since it decayed slightly up to 2.6–2.8 at 300 min, suggesting again the formation of acidic by-products from herbicide degradation.

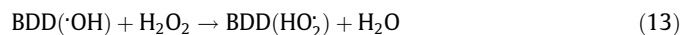
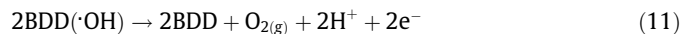
Fig. 3a shows that the EO process always led to a gradual TOC removal of the 2,4-D solution, which increased with increasing *I*. At the end of these electrolyses, 53%, 62% and 69% of mineralization for 0.5, 1.0 and 2.0 A, respectively, were obtained, values much higher than those found for the Pt/air-diffusion cell (see Fig. 2a). The greater oxidation power of the BDD/BDD cell in EO can be explained by the higher amounts of oxidant BDD(OH) formed from reaction (2) [17,18]. The quicker mineralization rate when *I* rises





**Fig. 3.** (a) TOC removal, (b) mineralization current efficiency and (c) specific energy per unit TOC mass vs. electrolysis time for 2.5 L of a 92 mg L<sup>-1</sup> 2,4-D solution in 0.05 M Na<sub>2</sub>SO<sub>4</sub> with 0.5 mM Fe<sup>2+</sup> at pH 3.0 and 35 °C degraded by electrochemical oxidation (EO) using a flow plant with a BDD/BDD cell at flow rate of 200 L h<sup>-1</sup>. Applied current: (◇) 0.5 A, (□) 1.0 A and (▽) 2.0 A.

can then be related to the concomitant acceleration of reaction (2) producing more reactive BDD(·OH) that destroys more rapidly organics. Nevertheless, less relative proportion of this radical was generated with increasing *I* causing a progressive fall in MCE, as shown in Fig. 3b. This phenomenon is due to the increase in rate of its waste reactions, pre-eminently its oxidation to O<sub>2</sub> by reaction (11), its dimerization to H<sub>2</sub>O<sub>2</sub> by reaction (12) and its reaction with the latter species via reaction (13) [17,19]:



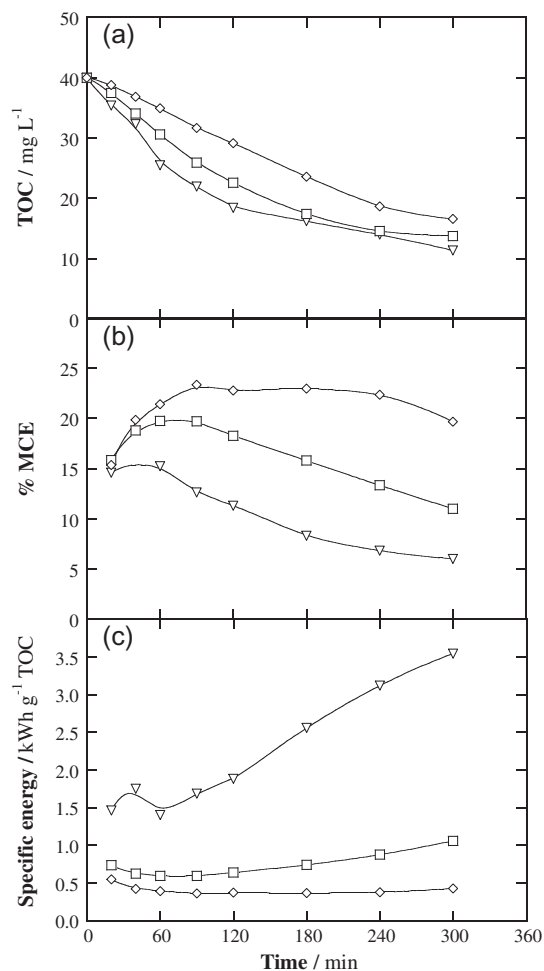
BDD(·OH) formation can also be partially inhibited by the larger acceleration of reactions (14) and (15) at the BDD anode giving rise to other weaker oxidants like persulfate ion (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) from the SO<sub>4</sub><sup>2-</sup> ion of the electrolyte and ozone, respectively [17,29–31].



The MCE values shown in Fig. 3b for 0.5 A fluctuated between 16% and 18%, indicating that organics are mineralized at practically the same rate using this low *I* in EO. In contrast, the efficiency

dropped more rapidly, from 17% to 10% and from 9.6% to 5.7%, for the higher currents of 1.0 and 2.0 A, respectively. This tendency suggests the quicker production of persistent by-products as *I* rises, which are then hardly destroyed, mainly by BDD(·OH), with prolonging electrolysis. As expected, the evolution of the specific energy followed the opposite trend and it increased strongly with raising *I*. Fig. 3c highlights that the lowest consumptions varied between 0.47 and 0.60 kWh g<sup>-1</sup> TOC at 0.5 A. For the higher *I* of 2.0 A, however, final values as high as 3.70 kWh g<sup>-1</sup> TOC were found. These results indicate that low currents yield high efficiencies with small specific energies, although the herbicide is less extensively mineralized.

The EF degradation of the same 92 mg L<sup>-1</sup> 2,4-D solution with 0.5 mM Fe<sup>2+</sup> was comparatively assessed in the recirculation flow plant with the single BDD/BDD cell. As can be seen in Fig. 4a, TOC was reduced by 59%, 66% and 72% operating at 0.5, 1.0 and 2.0 A, respectively, values higher than those found for the EO process made with the same cell (see Fig. 3a) and the EF degradation with the Pt/air-diffusion one (see Fig. 2a). The superiority of EF using the BDD/BDD cell can be accounted for by the combined action of BDD(·OH) produced at the anode surface from reaction (2) and ·OH formed in the bulk from Fenton's reaction (4) to more effectively react with the herbicide and its oxidation products, enhancing the degradation process. Nevertheless, this EAOP did



**Fig. 4.** (a) TOC decay, (b) mineralization current efficiency and (c) specific energy per unit TOC mass for the EF degradation of 2.5 L of a 92 mg L<sup>-1</sup> 2,4-D solution in 0.05 M Na<sub>2</sub>SO<sub>4</sub> with 0.5 mM Fe<sup>2+</sup> at pH 3.0 and 35 °C using a flow plant with a BDD/BDD cell with 20 cm<sup>2</sup> electrode area at flow rate of 200 L h<sup>-1</sup>. Applied current: (◇) 0.5 A, (□) 1.0 A and (▽) 2.0 A.

not allow total mineralization and a large proportion of persistent by-products still remained in the solution after 300 min of electrolysis.

Fig. 4b presents the time course of MCE for the above EF trials. The fall of efficiency with rising  $I$  can be related to the loss of relative quantities of  $\text{BDD}(\cdot\text{OH})$  by the preponderance of its waste reactions (11)–(15), as well as  $\cdot\text{OH}$  by the faster parasite reactions (9) and (10). Compared to the EO process (see Fig. 3b), slightly higher efficiencies with similar trends can be observed in Fig. 4b for EF at each applied  $I$ . The highest MCE values varied between 20% and 23% during most treatment at 0.5 A. Consequently, lower specific energies were also determined for EF, with minimum values between 0.36 and 0.42  $\text{kW h g}^{-1}$  TOC at the lowest  $I$  of 0.5 A, as shown in Fig. 4c. Again, the EF treatment became more favorable operating at low current, although higher mineralization was achieved at higher  $I$  but with loss of efficiency and greater specific energy.

The aforementioned study on the EO and EF degradation of 2.5 L of a  $92 \text{ mg L}^{-1}$  2,4-D solution of pH 3.0 in the recirculation flow plant allowed concluding that the use of a BDD/BDD cell allowed higher decontamination than a Pt/air-diffusion one. This is indicative of a greater ability of  $\text{BDD}(\cdot\text{OH})$  compared to  $\cdot\text{OH}$  to mineralize the products formed from 2,4-D oxidation. In the BDD/BDD cell, however, much lower amounts of  $\text{H}_2\text{O}_2$  and hence of  $\cdot\text{OH}$  are produced. To explore the oxidation ability of an EF system with a BDD anode and high  $\text{H}_2\text{O}_2$  production, the treatment of 2,4-D solutions in the plant was extended by coupling both cells, as schematized in Fig. 1c. The effect of  $I$  and herbicide concentration on such process is detailed in subsection below.

### 3.3. EF degradation with the coupled Pt/air-diffusion-BDD/BDD cell

The trials with the coupled Pt/air-diffusion-BDD/BDD cell were carried out by providing the same  $I$  at each reactor. Fig. 5a depicts the gradual TOC abatement determined for several equal individual currents during the EF degradation of the  $92 \text{ mg L}^{-1}$  herbicide solution with  $0.5 \text{ mM Fe}^{2+}$  at pH 3.0. Maximum TOC reductions of 53%, 58% and 63% were found after 180, 120 and 90 min of electrolysis at 0.5 A/0.5 A, 1.0 A/1.0 A and 2.0 A/2.0 A, respectively. No more TOC was removed at longer time. That means that using both coupled cells, the EF process was strongly enhanced and stable by-products were accumulated in much shorter time compared to the single systems where organics were degraded at less up to 300 min (see Figs. 2a and 4a). From the decontamination achieved, however, one can infer that the oxidation ability of the coupled cell was quite similar to that of the Pt/air-diffusion one, but much smaller than of the BDD/BDD one. This behavior suggests that 2,4-D is more rapidly degraded by  $\cdot\text{OH}$  in the bulk than by  $\text{Pt}(\cdot\text{OH})$  and  $\text{BDD}(\cdot\text{OH})$ , yielding final by-products that are slowly destroyed by these oxidants. For the single Pt/air-diffusion cell and the coupled system where a large and similar amount of  $\cdot\text{OH}$  is produced, a major proportion of analogous persistent by-products could be formed from the predominant attack of  $\cdot\text{OH}$  over intermediates and their slower destruction by  $\text{Pt}(\cdot\text{OH})$  and/or  $\text{BDD}(\cdot\text{OH})$  led to a similar TOC reduction in both cases. In contrast, the preponderant oxidation of aromatics by  $\text{BDD}(\cdot\text{OH})$  using the single BDD/BDD cell gives rise to more quantities of intermediates that are easily mineralized by this radical, thereby being the most potent EAOP for 2,4-D degradation.

The expected drop in MCE and rise in specific energy at higher current for the above trials with the coupled cell, as a result of the larger acceleration of the parasitic reactions (8)–(15) of the main oxidizing agents  $\text{Pt}(\cdot\text{OH})$ ,  $\text{BDD}(\cdot\text{OH})$  and  $\cdot\text{OH}$ , are shown in Fig. 5b and c, respectively. When the maximum mineralization was reached, efficiencies of 14%, 11% and 8.7% with specific energies of 0.47, 0.74 and  $1.90 \text{ kW h g}^{-1}$  TOC were found for 0.5 A/0.5 A,

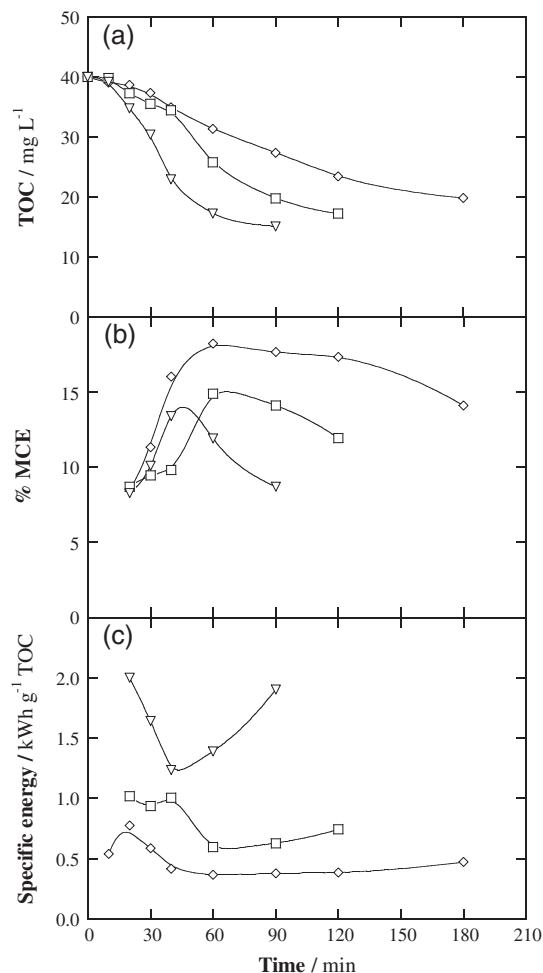


Fig. 5. (a) TOC decay, (b) mineralization current efficiency and (c) specific energy per unit TOC mass for the EF process of 2.5 L of a  $92 \text{ mg L}^{-1}$  2,4-D solution in  $0.05 \text{ M Na}_2\text{SO}_4$  with  $0.5 \text{ mM Fe}^{2+}$  at pH 3.0 and  $35^\circ\text{C}$  using a flow plant with a coupled Pt/air-diffusion-BDD/BDD system at flow rate of  $200 \text{ L h}^{-1}$ . Applied current to both cells: (◇) 0.5 A/0.5 A, (□) 1.0 A/1.0 A and (▽) 2.0 A/2.0 A.

1.0 A/1.0 A and 2.0 A/2.0 A, respectively, which are good results when compared to those found for the single cells in view of the shorter times applied. For example, the single Pt/air-diffusion cell yielded 11% efficiency and  $0.55 \text{ kW h g}^{-1}$  TOC to obtain 53% mineralization in 240 min at 1.0 A (see Fig. 2), whereas the single BDD/BDD one led to a similar TOC reduction with 17% efficiency and  $0.70 \text{ kW h g}^{-1}$  TOC in 180 min at 1.0 A (see Fig. 4b and c). By comparing these data with those determined for the coupled cell after 180 min at 0.5 A/0.5 A (i.e., the same total  $I$  of 1.0 A), one can infer that this system can be valuable for the EF degradation of 2,4-D because it gives a more rapid TOC removal up to maximum mineralization with an acceptable MCE value and an specific energy even inferior to that of single cells.

The influence of herbicide concentration between 92 and  $370 \text{ mg L}^{-1}$  (near saturation) on the EF performance with the coupled cell was assessed at 2.0 A/2.0 A. The changes of TOC, MCE and specific energy up to maximum TOC reduction for these assays are shown in Fig. 6a–c, respectively. Fig. 6a shows an increasing mineralization of 63%, 74% and 83% with raising 2,4-D content of 92, 196 and  $276 \text{ mg L}^{-1}$ , followed by a drastic fall up to 62% TOC removal at the highest concentration of  $370 \text{ mg L}^{-1}$ . Since the same production of main oxidants,  $\text{Pt}(\cdot\text{OH})$ ,  $\text{BDD}(\cdot\text{OH})$  and  $\cdot\text{OH}$ , is expected at the same current, the gradual rise in mineralization up to  $276 \text{ mg L}^{-1}$  can be related to a progressive deceleration of their waste reactions (8)–(15) because the above radicals can react

more preferentially with the raising amounts of organics present in solution, thus enhancing the mineralization process. The formation of more persistent by-products, probably by condensation of aromatic intermediates, due to the presence of a higher organic load could explain the subsequent loss of mineralization at 370 mg L<sup>-1</sup>. This behavior is also reflected in the current efficiencies and specific energies, which present their best values of 14–15% (see Fig. 6b) and 1.10–1.15 kW h g<sup>-1</sup> TOC (see Fig. 6c) after 90 min of treatment of 196 and 276 mg L<sup>-1</sup> 2,4-D. In this concentration range, the EF process then possesses the highest oxidation ability to decontaminate the herbicide solution.

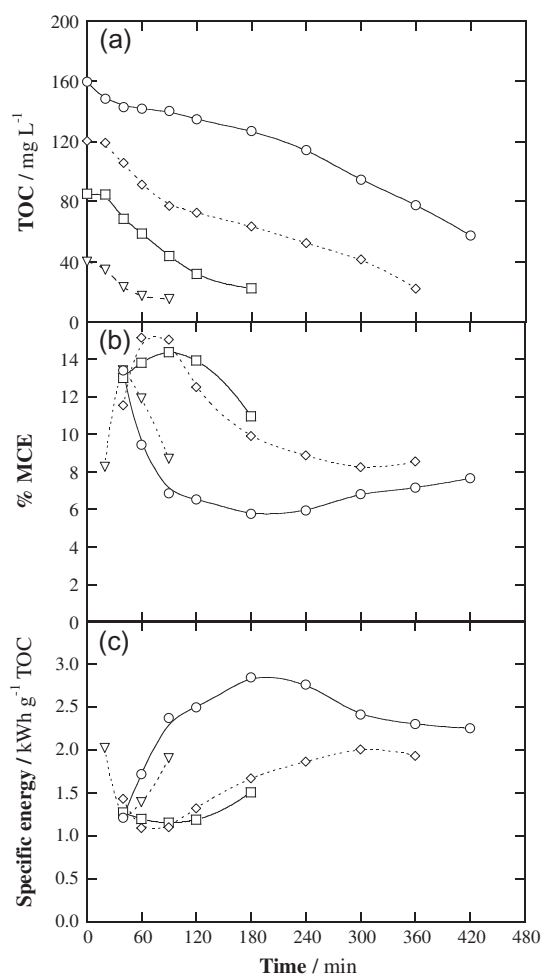
### 3.4. Decay kinetics of 2,4-D and evolution of carboxylic acids using single and coupled cells

The kinetics of the reaction of 2,4-D with the generated oxidizing agents (mainly Pt(·OH), BDD(·OH) and ·OH) was followed by analyzing the decay of its concentration in the electrolyzed solution by reversed-phase HPLC. Fig. 7a shows that in EO with the BDD/BDD cell at 2.0 A, 300 mg L<sup>-1</sup> of herbicide at pH 3.0 were continuously removed by the attack of BDD(·OH) up to their disappearance at approximately 120 min. When EF with 0.5 mM Fe<sup>2+</sup> was performed with the Pt/air-diffusion cell at 2.0 A, a much faster

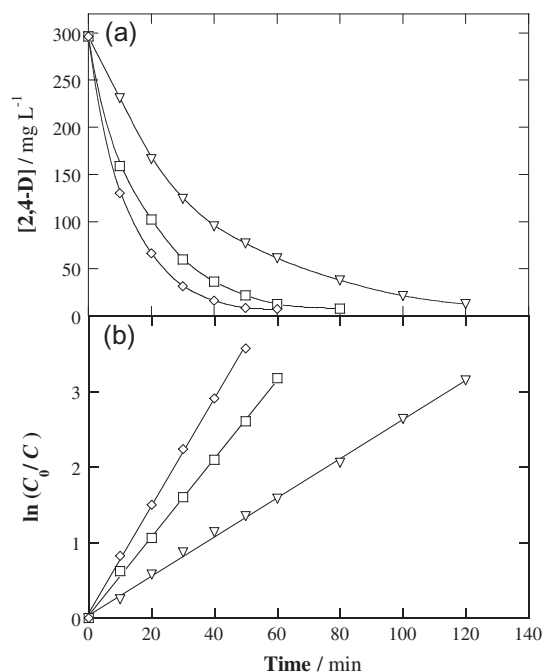
destruction of 2,4-D can be observed in Fig. 7a, disappearing in about 80 min. This indicates a quicker reaction of 2,4-D with ·OH. Fig. 7a also shows that the drop of the herbicide was slightly more rapid using the coupled cell at 2.0 A/2.0 A because the oxidizing species formed in each individual cell acted simultaneously and it was totally removed in only 60 min. All these results corroborate the existence of a much quicker reaction of 2,4-D, and by extension its aromatic derivatives, with ·OH in the bulk, as stated above.

The above concentration decays were analyzed by kinetic equations related to simple reaction orders and excellent linear correlations were found for a pseudo-first-order reaction, as presented in Fig. 7b. This analysis allowed determining an increasing apparent rate constant ( $k_1$ ) of  $4.3 \times 10^{-4} \text{ s}^{-1}$  ( $R^2 = 0.998$ ) for EO with a BDD/BDD cell,  $8.6 \times 10^{-4} \text{ s}^{-1}$  ( $R^2 = 0.9990$ ) for EF with a Pt/air-diffusion one and  $1.18 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9990$ ) for EF with the coupled cell. Note that the latter  $k_1$  value is close to the sum of the two first ones, as expected if 2,4-D is destroyed independently by the action of oxidizing agents produced by both separated cell. The fact that its decay always obeys a pseudo-first-order reaction suggests that it reacts with a constant amount of each generated hydroxyl radical in each electrolytic system checked. Moreover, when the BDD anode is used in EO, this behavior also indicates a control of the process by mass transport of the herbicide towards the anode [17].

The destruction of 2,4-D by hydroxyl radicals yields aromatic derivatives like 2,4-dichlorophenol, 4,6-dichlororesorcinol and 4-chlorohydroquinone with release of its lateral group as glycolic acid [6,43,48]. Further cleavage of the benzenic moiety of these products with loss of Cl<sup>-</sup> ion leads to a mixture of short-linear carboxylic acids [48]. Based on this previous work, the generated carboxylic acids during the EO and EF degradations of 2.5 L of a 92 mg L<sup>-1</sup> herbicide solution of pH 3.0 in the recirculation flow plant using single and coupled cells were identified and quantified



**Fig. 6.** Effect of herbicide concentration on (a) TOC abatement, (b) mineralization current efficiency and (c) specific energy per unit TOC mass vs. electrolysis time for the EF treatment of 2.5 L of 2,4-D solutions in 0.05 M Na<sub>2</sub>SO<sub>4</sub> with 0.5 mM Fe<sup>2+</sup> at pH 3.0 and 35 °C using a flow plant with a coupled Pt/air-diffusion-BDD/BDD cell at 2.0 A/2.0 A and flow rate of 200 L h<sup>-1</sup>. Initial 2,4-D content: (○) 370 mg L<sup>-1</sup> (near saturation), (◇) 276 mg L<sup>-1</sup>, (□) 196 mg L<sup>-1</sup> and (▽) 92 mg L<sup>-1</sup>.

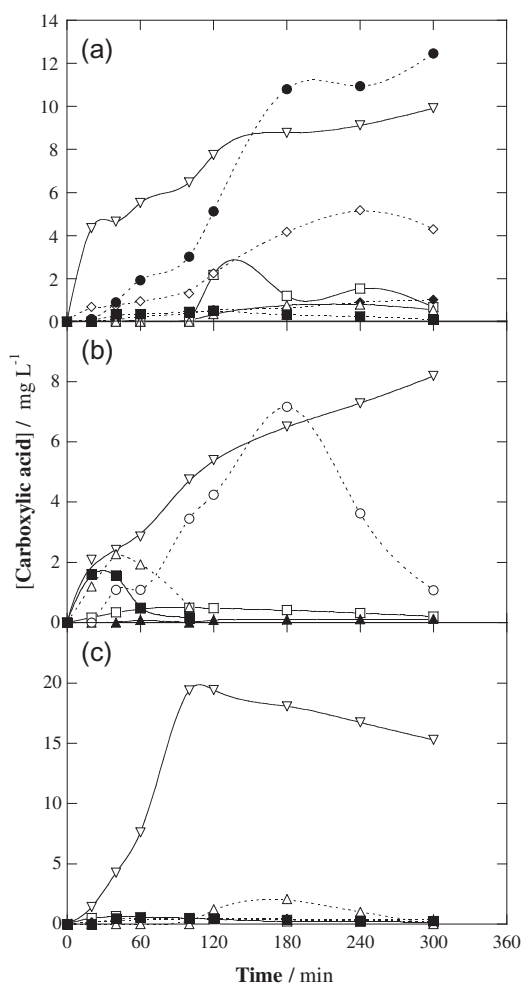


**Fig. 7.** (a) Decay of 2,4-D concentration with electrolysis time during the degradation of 2.5 L of 300 mg L<sup>-1</sup> 2,4-D solutions in 0.05 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0 and 35 °C using the recirculation flow plant at flow rate of 200 L h<sup>-1</sup>. Method: (▽) EO using a BDD/BDD cell at 2.0 A, (□) EF with 0.5 mM Fe<sup>2+</sup> using a Pt/air-diffusion cell at 2.0 A and (◇) EF with 0.5 mM Fe<sup>2+</sup> using the coupled Pt/air-diffusion-BDD/BDD system at 2.0 A/2.0 A. (b) Kinetic analysis assuming a pseudo-first order reaction for 2,4-D.



by ion-exclusion HPLC. Oxalic ( $t_r = 6.6$  min), maleic ( $t_r = 8.2$  min), glyoxylic ( $t_r = 9.2$  min), malic ( $t_r = 9.5$  min), succinic ( $t_r = 11.3$  min), glycolic ( $t_r = 12.1$  min), formic ( $t_r = 13.7$  min), fumaric ( $t_r = 14.1$  min) and acetic ( $t_r = 15.2$  min) acids were detected. While glyoxylic acid is expected to be formed from the oxidation of the initially released glycolic acid, succinic, malic, maleic, fumaric and acetic acids proceed from the oxidative degradation of aromatic intermediates [14,22,39,40]. Further oxidation of all the above acids yields oxalic and formic acids, which are ultimate products since they are directly transformed into  $\text{CO}_2$  [21,29].

Fig. 8a reveals the accumulation of small amounts of a large variety of carboxylic acids during the EO process with the single BDD/BDD cell at 2.0 A, pre-eminently succinic, acetic and oxalic acids. At the end of this treatment, all these by-products contributed in  $10.41 \text{ mg L}^{-1}$  of TOC, corresponding to an 83% of the organic content of the final solution (see Fig. 3a). This means that the formation of carboxylic acids is the main degradative way of 2,4-D under the action of  $\text{BDD}(\cdot\text{OH})$  in EO. In contrast, Fig. 8b shows that EF with a Pt/air-diffusion cell at 2.0 A yielded less quantities of carboxylic acids, with malic and oxalic acids as major components. The total content of all the acids at 300 min was equivalent to  $2.70 \text{ mg L}^{-1}$  of TOC and represented only a 16% of the organic load of the electrolyzed solution (see Fig. 2a). These findings are



**Fig. 8.** Evolution of the concentration of (▽) oxalic, (□) maleic, (◇) succinic, (◆) formic, (●) acetic, (Δ) glyoxylic, (■) glycolic, (○) malic and (▲) fumaric, produced during the degradation of 2.5 L of  $92 \text{ mg L}^{-1}$  2,4-D solutions in  $0.05 \text{ M Na}_2\text{SO}_4$  at pH 3.0 and  $35^\circ\text{C}$  using the recirculation flow plant at flow rate of  $200 \text{ L h}^{-1}$ . Method: (a) EO with a BDD/BDD cell at 2.0 A, (b) EF with  $0.5 \text{ mM Fe}^{2+}$  using a Pt/air-diffusion cell at 2.0 A and (c) EF with  $0.5 \text{ mM Fe}^{2+}$  using the coupled Pt/air-diffusion-BDD/BDD system at 2.0 A/2.0 A.

indicative of the preponderant generation of other unidentified recalcitrant products instead of carboxylic acids when 2,4-D is degraded by  $\text{Pt}(\cdot\text{OH})$  and mainly  $\cdot\text{OH}$  in this EF system. A similar behavior can be observed in Fig. 8c when the coupled cell at 2.0 A/2.0 A was used for EF. In this case, oxalic acid was also the major by-product and all the accumulated acids at 90 min of electrolysis for reaching maximum TOC reduction yielded  $5.8 \text{ mg L}^{-1}$  of TOC, only corresponding to 38% of the organic content of the treated effluent (see Fig. 5a). Accordingly, a larger proportion of other unidentified persistent by-products was accumulated in the medium, as expected if the attack of  $\cdot\text{OH}$  on intermediates is much quicker than that of  $\text{Pt}(\cdot\text{OH})$  and  $\text{BDD}(\cdot\text{OH})$  due to the high  $\text{H}_2\text{O}_2$  production at the air-diffusion cathode. This agrees with the similar mineralization degree achieved in the single Pt/air-diffusion and the coupled cells, suggesting a similar degradative route in both cases. The large stability of the final by-products remaining in coupled system can be easily confirmed from Fig. 8c, since oxalic acid was very slowly removed when the EF process was prolonged up to 300 min because it forms  $\text{Fe(III)}$  complexes that can only be hardly destroyed by  $\text{BDD}(\cdot\text{OH})$  [14].

#### 4. Conclusions

It has been demonstrated that a  $92 \text{ mg L}^{-1}$  2,4-D solution of pH 3.0 can be decontaminated in larger extent by EO and EF using a recirculation flow plant equipped with a single BDD/BDD cell instead of a single Pt/air-diffusion one. This is due to the higher ability of generated  $\text{BDD}(\cdot\text{OH})$  in the former cell to mineralize organic intermediates than the great amounts of  $\cdot\text{OH}$  produced in the latter one. For the most potent BDD/BDD cell, the EF process at 0.5 A yielded 59% mineralization with 23% efficiency and  $0.42 \text{ kW h g}^{-1}$  TOC specific energy after 300 min of electrolysis. The use of a coupled Pt/air-diffusion-BDD/BDD cell with equal individual current in EF gave similar mineralization degree to that found for a single Pt/air-diffusion one at the same total  $I$  although in much shorter electrolysis time. In all the systems, TOC was reduced more rapidly by increasing  $I$  in each cell, but with a loss in current efficiency and a greater specific energy due to the concomitant quicker acceleration of waste reactions of hydroxyl radicals. The opposite trend was found for the coupled cell operating under EF conditions at 2.0 A/2.0 A when the herbicide content rose up to  $276 \text{ mg L}^{-1}$ . In this case, TOC was reduced by 83% in 360 min attaining the best results of 15% efficiency and  $1.10 \text{ kW h g}^{-1}$  TOC after 90 min of treatment. The 2,4-D decay always obeyed a pseudo-first-order reaction. Its apparent rate constant for EF with a Pt/air-diffusion cell was double than for EO with a BDD/BDD one, whereas their sum corresponded to the rate constant found for EF with the coupled cell. The final solution of the EO process with a BDD/BDD cell contained a mixture of carboxylic acids as major component. In contrast, the predominant degradation of aromatics via  $\cdot\text{OH}$  in the EF processes with both, the Pt/air-diffusion and coupled cells, led to a major formation of other undetected recalcitrant products with accumulation of carboxylic acids in much lesser extent.

#### Conflict of interest

The authors declare no conflict of interest.

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