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Degradation of the herbicide 2,4-DP by anodic oxidation, electro-Fenton and photoelectro-Fenton using platinum and boron-doped diamond anodes

Enric Brillas^{*}, Miguel Ángel Baños, Marcel Skoumal, Pere Lluís Cabot, José Antonio Garrido, Rosa María Rodríguez

Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

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Abstract

This paper reports the degradation of 2,4-DP (2-(2,4-dichlorophenoxy)-propionic acid) solutions of pH 3.0 by environmentally friendly electrochemical methods such as anodic oxidation, electro-Fenton and photoelectro-Fenton with a Pt or boron-doped diamond (BDD) anode. In the two latter techniques an O₂-diffusion cathode was used and 1.0 mM Fe²⁺ was added to the solution to give hydroxyl radical ([•]OH) from Fenton's reaction between Fe²⁺ and H₂O₂ generated at the cathode. All treatments with BDD are viable to decontaminate acidic wastewaters containing 2,4-DP since they give complete mineralization, with loss of chloride ion, at high current due to the great production of oxidant [•]OH at the BDD surface favoring the destruction of final carboxylic acids. [•]OH formed from Fenton's reaction destroys more rapidly aromatic products, making the electro-Fenton and photoelectro-Fenton processes much more efficient than anodic oxidation. UVA light in photoelectro-Fenton with BDD has little effect on the degradation rate of pollutants. The comparative procedures with Pt lead to slower decontamination because of the lower oxidizing power of this anode. The effect of current on the degradation rate and efficiency of all methods is studied. The 2,4-DP decay always follows a pseudo-first-order kinetics. Chlorohydroquinone, chloro-*p*-benzoquinone and maleic, fumaric, malic, lactic, pyruvic, acetic, formic and oxalic acids are detected as products by chromatographic techniques. A general sequence accounting for by the reaction of all these intermediates with the different oxidizing agents is proposed.

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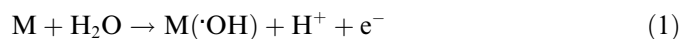
Keywords: Herbicides; Electro-Fenton; Photoelectro-Fenton; Boron-doped diamond; Electrochemical degradation; Water treatment

1. Introduction

Recently, there is great interest in the remediation of wastewaters containing aromatic organics by electrochemical techniques such as anodic oxidation and indirect electro-oxidation methods based on H₂O₂ electrogeneration. In these environmentally friendly methods hydroxyl radical ([•]OH) is largely produced as the main oxidizing agent. This radical is the second most strong oxidant known, after fluorine, having a very high standard potential ($E^{\circ}(\text{[•]OH/}$

H₂O) = 2.80 V vs. NHE) that makes it able to non-selectively react with organics to give hydroxylated or dehydrogenated derivatives until their complete mineralization, that is, their transformation into CO₂, water and inorganic ions.

In anodic oxidation (AO) organic pollutants are destroyed in an electrolytic cell by adsorbed hydroxyl radical formed as intermediate from water oxidation to O₂ at the surface of a high O₂-overvoltage anode (Marselli et al., 2003; Panizza and Cerisola, 2005) as follows:



where M([•]OH) denotes the adsorbed hydroxyl radical at the anode M. The recent use of a boron-doped diamond

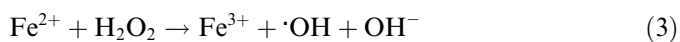
^{*} Corresponding author. Tel.: +34 93 4021223; fax: +34 93 4021231.
E-mail address: brillas@ub.edu (E. Brillas).

(BDD) thin-film electrode in AO has attracted great attention for wastewater treatment. This anode possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential windows in aqueous medium (Panizza and Cerisola, 2005). In comparison with a conventional Pt anode, the BDD electrode has much greater O_2 -overvoltage, thus producing more amount of reactive $BDD(\cdot OH)$ than $Pt(\cdot OH)$ from reaction (1) and yielding a quicker oxidation of organics. This has been confirmed from the total mineralization achieved for several organic pollutants in aqueous medium from electrolysis with a BDD electrode (Cañizares et al., 2003, 2005; Kraft et al., 2003; Marselli et al., 2003; Brillas et al., 2004a, 2005; Polcaro et al., 2004; Panizza and Cerisola, 2005; Nasr et al., 2005; Flox et al., 2006a).

Indirect electrooxidation methods based on the cathodically generation of hydrogen peroxide such as electro-Fenton (EF) and photoelectro-Fenton (PEF) are also being developed for the destruction of organic pollutants in acidic wastewaters. These techniques are performed in an electrolytic cell where H_2O_2 is continuously supplied to the contaminated solution from the two-electron reduction of O_2 at reticulated vitreous carbon (Xie and Li, 2006), carbon-felt (Oturán et al., 1999; Aaron and Oturán, 2001; Gözmen et al., 2003; Hanna et al., 2005; Irmak et al., 2006; Diagne et al., 2007) and carbon-polytetrafluoroethylene (PTFE) O_2 -diffusion (Boye et al., 2002; Brillas et al., 2004a; Flox et al., 2006b; Sirés et al., 2006, 2007) cathodes:



In the EF method a small quantity of Fe^{2+} is added to the solution to react with H_2O_2 to yield the strong oxidant $\cdot OH$ and Fe^{3+} from Fenton's reaction (Sun and Pignatello, 1993):



Reaction (3) is catalytic since it is propagated from Fe^{2+} regeneration that mainly takes place by reduction of Fe^{3+} at the cathode (Oturán et al., 1999) and/or with H_2O_2 (Boye et al., 2002). In our laboratory we have tested the electro-Fenton method using a one-compartment cell with a Pt or BDD anode where pollutants can be simultaneously oxidized by $Pt(\cdot OH)$ or $BDD(\cdot OH)$ produced at the corresponding anode from reaction (1) and $\cdot OH$ formed in the medium from Fenton's reaction (3) (Boye et al., 2002; Brillas et al., 2004a; Flox et al., 2006b; Sirés et al., 2006, 2007).

The PEF process involves the additional irradiation of the solution with UVA light to favor: (i) the photodecomposition of complexes of Fe^{3+} with generated carboxylic acids (Zuo and Hoigné, 1992; Boye et al., 2002; Flox et al., 2006b; Sirés et al., 2006, 2007) and (ii) the regeneration of Fe^{2+} with production of more amount of oxidant $\cdot OH$ from photoreduction of $Fe(OH)^{2+}$, which is the predominant Fe^{3+} species in acid medium (Sun and Pignatello, 1993):



The presence of chlorophenoxy herbicides in US and European ground waters and surface waters at relatively high contamination levels has been recently documented (Oturán et al., 1999; Albrechtsen et al., 2001; Gerecke et al., 2002). This pollution comes from their widespread use for agricultural and non-agricultural purposes generating continuously rinsate, waste product and contaminated soil in application sites. Chlorophenoxy herbicides are considered as moderately toxic towards human and animals by the World Health Organization and resist biodegradation. To avoid their dangerous accumulation in the aquatic environment, powerful oxidation methods are being developed for achieving an efficient destruction of such compounds in wastewaters.

In previous work we have reported the degradation of acidic solutions of chlorophenoxyacetic acids such as 4-chlorophenoxyacetic, 4-chloro-2-methylphenoxyacetic, 2,4-dichlorophenoxyacetic (2,4-D) and 2,4,5-trichlorophenoxyacetic at pH 3.0 by AO and EF with a BDD anode (Brillas et al., 2004a), as well as by the same methods and PEF with a Pt anode (Boye et al., 2002). A more efficient mineralization of these herbicides is always obtained using a BDD anode than a Pt one. This behavior has also been found for the AO treatment of a chlorophenoxypropionic herbicide like 2-(4-chloro-2-methylphenoxy)-propionic acid (mecoprop) in acidic and alkaline media (Flox et al., 2006a). To gain a better knowledge of the electrochemical decontamination of wastewaters containing chlorophenoxy herbicides, especially using photoelectro-Fenton with a BDD anode that has not been previously reported in the literature, we have undertaken a comparative study on the destruction of 2-(2,4-dichlorophenoxy)-propionic acid (2,4-DP or dichlorprop) in acidic aqueous medium by all these techniques using both Pt and BDD anodes. This compound is a selective pre- and post-emergent herbicide widely utilized for control of broad-leaved aquatic weeds, annual and perennial weeds in cereals, pastures, forestry and rights-of-way. For this chlorophenoxypropionic acid, a poor degradation by means of O_3 and O_3/H_2O_2 (Meijers et al., 1995; Hu et al., 2000), which is enhanced using catalyzed ozonation (Brillas et al., 2004b), has been previously described.

This paper reports the treatment of acidic synthetic wastewaters of 2,4-DP by anodic oxidation, electro-Fenton and photoelectro-Fenton using a Pt or BDD anode under comparable conditions. The effect of applied current on the degradation rate and mineralization current efficiency of all methods was examined. The influence of Fe^{2+} concentration in the electro-Fenton and photoelectro-Fenton processes was also explored. The herbicide decay and the evolution of intermediates were followed by chromatographic techniques. A general reaction sequence for 2,4-DP mineralization involving all products detected in the electrochemical methods is finally proposed.

2. Experimental

2.1. Chemicals

2,4-DP, chlorohydroquinone, chloro-*p*-benzoquinone and lactic, pyruvic, acetic, maleic, malic, fumaric and oxalic acids were reagent of analytical grade supplied by Sigma, Aldrich, Fluka and Merck. Anhydrous sodium sulfate used as background electrolyte and heptahydrated ferrous sulfate used as catalyst were analytical grade from Fluka. Solutions were prepared with high-purity water from a Millipore Milli-Q system, with resistivity >18 MΩ cm at 25 °C. The initial solution pH was adjusted to pH 3.0 with analytical grade sulfuric acid purchased from Merck. Organic solvents and other chemicals used were HPLC or analytical grade from Panreac and Aldrich.

2.2. Apparatus

Electrolyses were performed with an Amel 2053 potentiostat-galvanostat. The solution pH was measured with a Crison 2000 pH-meter. The mineralization of 2,4-DP solutions was monitored from the abatement of their total organic carbon (TOC), determined on a Shimadzu 5050 TOC analyzer. From these data, the mineralization current efficiency (MCE) for treated solutions at a given time was calculated from the following equation:

$$\text{MCE} = \frac{\Delta(\text{TOC})_{\text{exp}}}{\Delta(\text{TOC})_{\text{theor}}} \times 100 \quad (5)$$

where $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC removal and $\Delta(\text{TOC})_{\text{theor}}$ is the theoretical TOC abatement assuming that the applied charge (=current × time) is only consumed in the mineralization reaction.

The 2,4-DP decay and the evolution of its aromatic intermediates were followed by reversed-phase HPLC chromatography using a Waters 600 high-performance liquid chromatograph fitted with a Spherisorb ODS2 5 μm, 150 × 4.6 mm (i.d.), column at room temperature, coupled with a Waters 996 photodiode array detector selected at $\lambda = 280$ nm and controlled through a Millennium-32[®] program. Generated carboxylic acids were identified and quantified by ion-exclusion chromatography using the above HPLC chromatograph fitted with an Aminex HPX 87H, 300 × 7.8 mm (i.d.), column at 35 °C from Bio-Rad and selecting the photodiode array detector at $\lambda = 210$ nm. Cl^- concentration in electrolyzed solutions was determined by ion chromatography using a Shimadzu 10Avp HPLC chromatograph fitted with a Shim-Pack IC-A1S, 10 × 4.6 mm (i.d.), anion column at 40 °C and coupled with a Shimadzu CDD 10Avp conductivity detector.

2.3. Electrolytic systems

All electrolyses were conducted in an open, undivided and thermostated conic cell containing 100 ml of solution

vigorously stirred with a magnetic bar. AO treatments were carried out using either a 10 cm² Pt sheet of 99.99% purity from SEMPASA (AO-Pt method) or a BDD thin film deposited on a conductive Si sheet from CSEM (AO-BDD method) as anode and a 3 cm² graphite bar from Sofacel as cathode. EF and PEF degradations were performed with the above Pt (EF-Pt and PEF-Pt methods) or BDD (EF-BDD and PEF-BDD methods) anode and a 3 cm² carbon-PTFE electrode from E-TEK as cathode, which was fed with pure O₂ at 20 ml min⁻¹ for continuous H₂O₂ electrogeneration from reaction (2). The preparation of the O₂-diffusion cathode has been described elsewhere (Boye et al., 2002). For the PEF trials, a Philips 6 W fluorescent black light blue tube was placed at the top of the open cell, at 7 cm above the solution. The tube emitted UVA light in the wavelength region between 300 and 420 nm, with $\lambda_{\text{max}} = 360$ nm, supplying a photoionization energy input to the solution of 140 μW cm⁻², as detected with a NRC 820 laser power meter working at 514 nm.

Comparative treatment of solutions containing 217 mg l⁻¹ 2,4-DP (corresponding to 100 mg l⁻¹ TOC) and 0.05 M Na₂SO₄ at pH 3.0 by the above methods was carried out at a constant current of 100, 300 and 450 mA. The value of pH 3.0 was chosen since it is close to the optimum pH of 2.8 for Fenton's reaction (3) (Sun and Pignatello, 1993). For the EF and PEF degradations, a Fe²⁺ concentration between 0.5 and 2.0 mM was added to the solution, since these catalyst contents were found to be very efficient for the EF-Pt treatment of other aromatics (Boye et al., 2002; Flox et al., 2006b; Sirés et al., 2006). All trials were carried out at 35 °C, which is the maximum temperature to operate with the open cell without significant water evaporation from solution (Boye et al., 2002).

2.4. Analytical procedures

Samples withdrawn from electrolyzed solutions were filtered with 0.45 μm PTFE filters from Whatman before analysis. Reproducible TOC values were obtained by injecting 100 μl aliquots into the TOC analyzer using the non-purgeable organic carbon method. All HPLC analyses were carried out by injecting 20 μl aliquots into the chromatograph. The mobile phase for reversed-phase chromatography was a 50:45:5 (v/v/v) methanol/phosphate buffer (pH 2.5)/pentanol mixture circulating at 1.0 ml min⁻¹, whereas for ion-exclusion chromatography, it was 4 mM H₂SO₄ at 0.6 ml min⁻¹. For Cl^- measurements, a 2.4 mM tris(hydroxymethyl)aminomethane and 2.5 mM phthalic acid solution at pH 4.0 was used as mobile phase at 1.5 ml min⁻¹.

3. Results and discussion

3.1. Comparative TOC removal

The oxidation power of the different electrochemical methods was tested by electrolyzing 217 mg l⁻¹ 2,4-DP

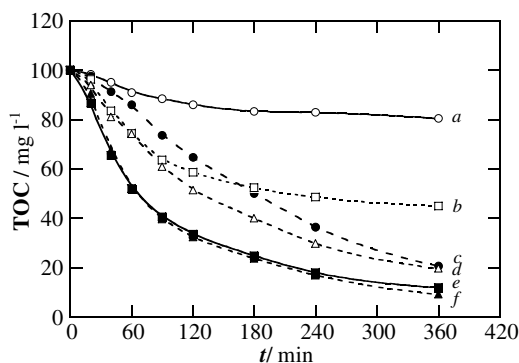


Fig. 1. TOC removal with electrolysis time for the degradation of 100 ml of 217 mg l⁻¹ 2,4-DP solutions in 0.05 M Na₂SO₄ of pH 3.0 at 100 mA and at 35 °C. Method: (a, ○) anodic oxidation with a 10 cm² Pt anode and a 3 cm² graphite cathode (AO-Pt); (b, □) electro-Fenton with a Pt anode, a 3 cm² O₂-diffusion cathode and 1.0 mM Fe²⁺ in solution as catalyst (EF-Pt); (c, ●) anodic oxidation with a 3 cm² BDD anode and a graphite cathode (AO-BDD); (d, △) photoelectro-Fenton with a Pt anode and 1.0 mM Fe²⁺ and 6 W UVA light of λ_{max} = 360 nm as catalysts (PEF-Pt); (e, ■) electro-Fenton with a BDD anode and 1.0 mM Fe²⁺ (EF-BDD); and (f, ▲) photoelectro-Fenton with a BDD anode, 1.0 mM Fe²⁺ and UVA light (PEF-BDD).

solutions of pH 3.0 at 100 mA and at 35 °C for 6 h. For the EF and PEF treatments, 1.0 mM of catalyst Fe²⁺ was added to the starting solution. In all these trials the solution pH remained practically constant, slightly decreasing to a final value of 2.8–2.9 due to the formation of acid products. The TOC decay with time for such experiments is shown in Fig. 1. Table 1 also collects the corresponding percentage of TOC removal found after 1 and 4 h of electrolysis.

Fig. 1 evidences that a lower decontamination is always attained for the treatments with Pt than comparatively with BDD. When electrolyses are prolonged for 6 h, the oxidation power increases in the sequence: AO-Pt < EF-Pt < AO-BDD < PEF-Pt < EF-BDD ≤ PEF-BDD. However, the relative TOC decay between AO-BDD and EF-Pt is opposite at short electrolysis times (see Table 1).

The AO-Pt method has the lowest oxidation power since it only yields 20% mineralization at 6 h (see curve a of Fig. 1), indicating the formation of a low amount of Pt(OH) from reaction (1) with ability to transform the organic pollutants into CO₂. In contrast, the AO-BDD method leads to a slow, but continuous, degradation (see curve c of Fig. 1) up to 79% of final decontamination. Table 1 shows that after 1 h of this treatment, 14% mineralization is reached, a value much lower than 25% of EF-Pt. That means that at the early stages of such electrolyses pollutants react more quickly with the high amount of ·OH produced in the medium from Fenton's reaction (3) in EF-Pt than with BDD(·OH) generated from reaction (1) in AO-BDD. A different trend is found after 4 h of both treatments (see Table 1), since TOC is reduced by 63% using AO-BDD, but only by 48% in EF-Pt. The latter method does not yield much higher decontamination at 6 h (see curve b of Fig. 1). The lower oxidation power of EF-Pt

Table 1

Percentage of TOC removal and mineralization current efficiency calculated from Eq. (5) for the treatment of 100 ml of 217 mg l⁻¹ 2,4-DP solutions of pH 3.0 at 35 °C by different electrochemical methods under selected conditions

Method	Applied current (mA cm ⁻²)	After 1 h of treatment		After 4 h of treatment	
		%TOC removal	MCE	%TOC removal	MCE
AO-Pt	100	9	8.1	17	3.8
	300	10	3.0	23	1.7
	450	12	2.4	26	1.2
AO-BDD	100	14	12	63	14
	300	24	7.1	82	6.1
	450	35	6.9	97	4.8
EF-Pt ^a	100	25	23	48	11
	300	46	13	57	4.2
	450	51	10	63	3.1
EF-BDD ^a	100	48	43	82	18
	300	57	16	88	6.6
	450	65	13	97	4.7
PEF-Pt ^a	100	26	24	70	15
	300	42	12	90	6.7
	450	54	10	91	4.5
PEF-BDD ^a	100	48	43	83	18
	300	58	17	93	6.9
	450	69	13	98	4.8

^a The starting solution contained 1.0 mM Fe²⁺ as catalyst.

than AO-BDD at long electrolysis time can then be related to the formation of stable complexes of Fe³⁺ with generated carboxylic acid that can not be destroyed by ·OH and Pt(OH) (Boye et al., 2002; Brillas et al., 2004). The photodecomposition of these complexes under UVA irradiation (Zuo and Hoigné, 1992) can explain the higher degradation rate for PEF-Pt (see curve d of Fig. 1) than AO-BDD, although a similar TOC decay close to 80% is attained at the end of both treatments. Fig. 1 also shows that the 2,4-DP solution is more rapidly degraded by EF-BDD (curve e) and PEF-BDD (curve f) up to reach a final TOC removal of 88% and 91%, respectively. A slightly faster degradation can be observed for PEF-BDD than EF-BDD from 90 min of electrolysis, indicating that it has the highest oxidation power. The little influence of UVA light on pollutant mineralization in the indirect electro-oxidation methods with BDD suggests that organics are preferentially oxidized with ·OH and BDD(·OH) than photodecomposed.

The effect of applied current on the oxidation power of the above treatments was further studied and selected results are given in Table 1. These data show a gradual increase in TOC removal with raising current from 100 to 450 mA in all cases. This enhancement of the oxidation power of all methods can be associated with a faster destruction of pollutants by the increase in rate of reaction (1) to produce more quantity of adsorbed Pt(OH) or BDD(·OH), as well as the accumulation of more H₂O₂ from reaction (2) (Boye et al., 2002) leading to the generation of

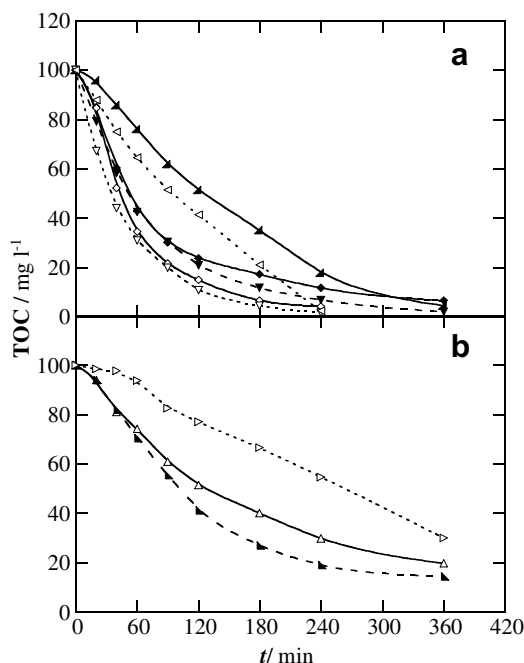


Fig. 2. Effect of experimental parameters on TOC abatement of 100 ml of 217 mg l⁻¹ 2,4-DP solutions in 0.05 M Na₂SO₄ of pH 3.0 at 35 °C. In plot (a), treatment by: AO-BDD at (▲) 300 mA and (◄) 450 mA; EF-BDD with 1.0 mM Fe²⁺ at (◆) 300 mA and (◇) 450 mA; and PEF-BDD with 1.0 mM Fe²⁺ at (▼) 300 mA and (▽) 450 mA. In plot (b), degradation by PEF-Pt with a Fe²⁺ concentration in solution of: (■) 0.5 mM; (Δ) 1.0 mM; and (▷) 2.0 mM at 100 mA.

higher amount of $\cdot\text{OH}$ from Fenton's reaction (3). Fig. 2a shows that overall mineralization (>97% TOC reduction) is reached after 4 h of all treatments with BDD at 450 mA due to the greater production of BDD($\cdot\text{OH}$) at high current. Results of Fig. 2a also evidence a slightly higher degradation rate for PEF-BDD than EF-BDD at all currents, thus confirming the little effect of UVA light when a BDD anode is used in the indirect electrooxidation methods. In contrast, the comparative use of a Pt anode always yields slower mineralization of 2,4-DP. After 6 h of electrolysis at 450 mA, for example, the solution TOC is reduced by 35% in AO-Pt, 65% in EF-Pt and 94% in PEF-Pt. These results allow concluding that all methods with BDD are viable and useful for the effective and total decontamination of acidic wastewaters containing 2,4-DP.

The possible influence of Fe²⁺ concentration from 0.5 to 2.0 mM in the indirect electrooxidation methods was also investigated. As an example, the TOC-time plots determined for the PEF-Pt treatments of a 217 mg l⁻¹ 2,4-DP solution at 100 mA are depicted in Fig. 2b. A gradual decay in TOC abatement can be observed when Fe²⁺ content increases, leading to a final mineralization of 86%, 80% and 71% for 0.5, 1.0 and 2.0 mM Fe²⁺, respectively. This tendency can be accounted for by the slower degradation of pollutants due to the progressive waste of $\cdot\text{OH}$ with increasing amount of Fe²⁺ by the following non-oxidizing reaction (Sun and Pignatello, 1993):

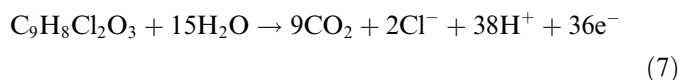


A similar behavior was also found for the EF-Pt, EF-BDD and PEF-BDD treatments. These findings indicate that a low Fe²⁺ content between 0.5 and 1.0 mM is sufficient to yield an efficient production of $\cdot\text{OH}$ from Fenton's reaction (3) in all indirect electrooxidation methods tested.

3.2. Mineralization current efficiency

The mineralization process of 2,4-DP implies its overall dechlorination. Ion chromatograms for all treated solutions at 100 mA revealed that initial chlorine is completely lost in the form of Cl⁻ ion. For the treatments with Pt, this ion is accumulated up to a steady concentration of 66 mg l⁻¹, equal to the initial chlorine content of the solution. In the treatments with BDD, however, Cl⁻ is released and further slowly removed due to its oxidation to Cl₂ on this anode (Kraft et al., 2003).

The mineralization reaction of the herbicide then involves its conversion into CO₂ and Cl⁻, as primary inorganic ion, and can be written as follows:



Reaction (7) was taken to calculate the efficiency for treated solutions from Eq. (5). The MCE-specific charge (Q , in A h l⁻¹) plots thus obtained for the treatments reported

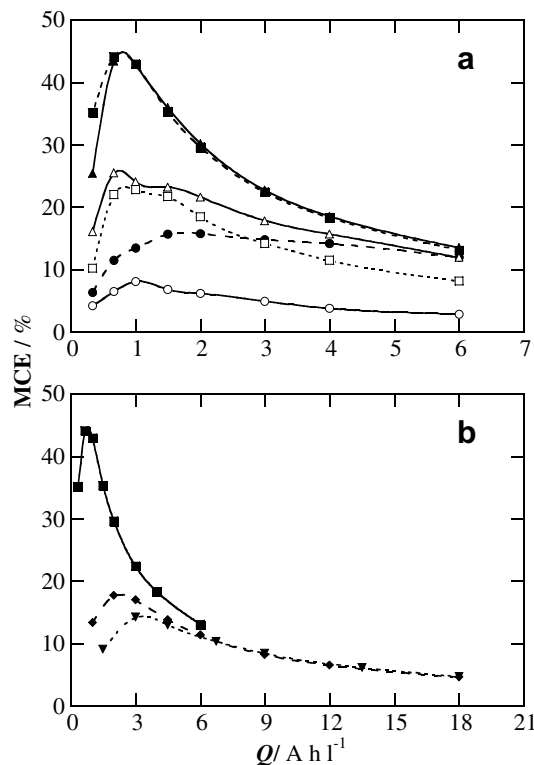


Fig. 3. Mineralization current efficiency calculated from Eq. (5) versus applied specific charge. Plot (a) corresponds to the experiments reported in Fig. 1 for 217 mg l⁻¹ 2,4-DP solutions of pH 3.0 at 100 mA. Plot (b) corresponds to the degradation of the same solution by EF-BDD with 1.0 mM Fe²⁺ in solution at (■) 100 mA; (◆) 300 mA; and (▼) 450 mA.

in Fig. 1 at 100 mA are presented in Fig. 3a. As can be seen, the efficiency increases at the beginning of all processes up to 0.67–1.5 A h l⁻¹ (40–90 min), indicating the initial formation of products that are easily mineralized with Pt(·OH), BDD(·OH) and/or ·OH. At higher Q the MCE value usually undergoes a dramatic drop due to the production of hardly oxidizable species such as carboxylic acids. The highly powerful EF-BDD and PEF-BDD methods show similar efficiencies, with a maximum value close to 44%, given the great reactivity of ·OH and BDD(·OH). A similar maximum of about 24% MCE is also attained for EF-Pt and PEF-Pt, as expected if ·OH formed from Fenton's reaction (3) in the main oxidizing agent at the beginning of both treatments. When electrolysis is prolonged, the PEF-Pt method becomes more efficient because of the photodecomposition of Fe³⁺ complexes under the action of UVA light. On the contrary, the initial efficiencies for the two AO methods are much smaller due to the lower degradation ability of Pt(·OH) and BDD(·OH) than ·OH. At $Q > 1$ A h l⁻¹ the MCE value for AO-BDD does not vary practically, suggesting a constant destruction rate of pollutants with BDD(·OH).

Table 1 collects selected MCE values at 1 h and 4 h of all treatments at 100, 300 and 450 mA. An inspection of these data allows concluding that all methods are less efficient with raising current at each electrolysis time. As illustrated in Fig. 3b for the EF-BDD process, a strong decay of MCE also takes place at a given specific charge when current increases. This loss in efficiency seems contradictory to the faster degradation found for all processes as current rises (see Fig. 2a). This apparent contradiction can be explained if higher current causes the generation of more amount of ·OH, Pt(·OH) and/or BDD(·OH) accelerating the destruction of pollutants with time, but with the consumption of higher specific charge because the non-oxidizing reactions of such oxidants takes place in larger extent. Thus, in AO-Pt Pt(·OH) can be more rapidly oxidized to O₂ by reaction (8) and recombined into H₂O₂ by reaction (9) whereas in AO-BDD BDD(·OH) can yield a larger proportion of O₂, also being enhanced the production of weaker oxidants such as S₂O₈²⁻ and O₃ formed from the anodic oxidation of SO₄²⁻ by reaction (10) and H₂O by reaction (11), respectively (Panizza and Cerisola, 2005). In the indirect electrooxidation methods a larger proportion of ·OH can be destroyed by reaction (6) due to the enhancement of reaction (3), along with the corresponding relative decay of Pt(·OH) or BDD(·OH).



3.3. 2,4-DP decay

A preliminary test was made by exposing 100 ml of a solution containing 217 mg l⁻¹ of the herbicide, 20 mM

H₂O₂ and 0.05 M Na₂SO₄ of pH 3.0 to UVA illumination at 35 °C. The 2,4-DP concentration in this trial was determined by reversed-phase chromatography, where it displayed a well-defined peak with a retention time (t_r) of 10.2 min. No change in herbicide content in such solution was found for 3 h, indicating that it is not directly oxidized with H₂O₂ neither photolyzed with UVA light. Consequently, in the indirect electrooxidation methods tested this compound can only react with Pt(·OH) or BDD(·OH) produced at the corresponding anode surface from reaction (1) and ·OH in the medium from reaction (3) and/or (4).

The kinetics of the destruction of 2,4-DP for the different treatments was then comparatively studied under the conditions given in Fig. 1. The change of herbicide concentration with time for the AO-Pt and AO-BDD methods at 100 mA is presented in Fig. 4a. As can be seen, 2,4-DP is slowly removed in both cases, disappearing from the medium in 180 or 300 min using a Pt or BDD anode, respectively. The higher destruction rate in AO-Pt can be ascribed to the adsorption of much more quantity of the herbicide on Pt than BDD, thus favoring its reaction with Pt(·OH) in relation to BDD(·OH). This behavior seems surprising if one takes into account that only the BDD anode is able to mineralize all organic pollutants (see Figs. 1 and 2) because of the production of much higher amount of reactive BDD(·OH). This effect of the anode is less apparent in

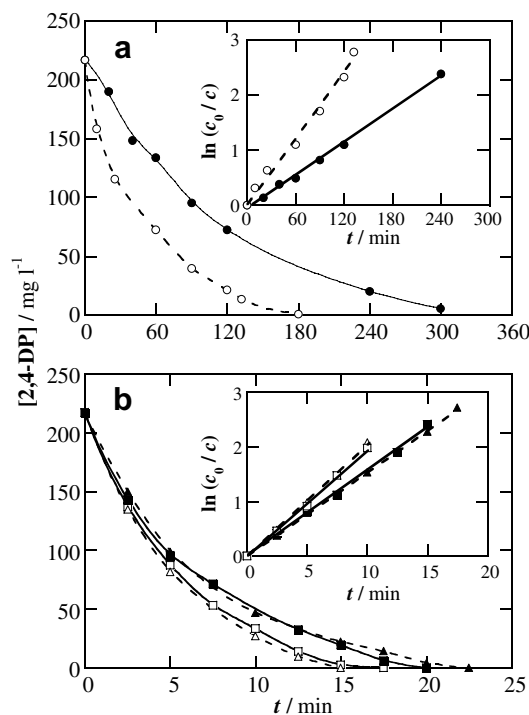


Fig. 4. 2,4-DP decay with electrolysis time during the treatment of 100 ml of 217 mg l⁻¹ herbicide solutions in 0.05 M Na₂SO₄ of pH 3.0 at 100 mA and at 35 °C. In plot (a), methods: (○) AO-Pt; and (●) AO-BDD. In plot (b), methods: (□) EF-Pt; (Δ) PEF-Pt; (■) EF-BDD; and (▲) PFE-BDD, all of them with 1.0 mM Fe²⁺ in solution. The inset panels show the corresponding kinetic analysis assuming that 2,4-DP follows a pseudo-first-order reaction.

Fig. 4b, where the herbicide concentration decay for the EF-Pt, PEF-Pt, EF-BDD and PEF-BDD methods at 100 mA is depicted. Under these conditions, this compound is very rapidly removed, disappearing in 15–17 min using Pt and a slightly longer time of 20–22 min using BDD. The little change in the decay rate for electro-Fenton and photo-electro-Fenton at each anode indicates a small participation of reaction (4) to produce $\cdot\text{OH}$. The much faster destruction of 2,4-DP in these treatments than in the two anodic oxidation ones then confirms that $\cdot\text{OH}$ generated in the medium from Fenton's reaction (3) is the main oxidant in all indirect electrooxidation methods, at least at short electrolysis times.

The concentration decays given in Fig. 4a and b fit well with a kinetic equation related to a pseudo-first-order reaction of the herbicide. The excellent straight lines thus obtained are shown in the corresponding inset panel of the above figures. From this kinetic analysis, a pseudo-first-order rate constant (k) of $3.2 \times 10^{-4} \text{ s}^{-1}$ (square regression coefficient (R^2) = 0.990) for AO-Pt is found, a twice-value than $1.7 \times 10^{-4} \text{ s}^{-1}$ (R^2 = 0.997) determined for AO-BDD. Similarly, the k -value rises from $2.6 \times 10^{-3} \text{ s}^{-1}$ (R^2 = 0.996) for EF-BDD to $3.3 \times 10^{-3} \text{ s}^{-1}$ (R^2 = 0.998) for EF-Pt and from $2.5 \times 10^{-3} \text{ s}^{-1}$ (R^2 = 0.998) for PEF-BDD to $3.5 \times 10^{-3} \text{ s}^{-1}$ (R^2 = 0.9996) for PEF-Pt. The slight increase in k for electro-Fenton and photoelectro-Fenton using Pt instead of BDD can be associated with the destruction of more amount of 2,4-DP by $\text{Pt}(\cdot\text{OH})$ than $\text{BDD}(\cdot\text{OH})$, although the major part of this compound reacts with the great $\cdot\text{OH}$ concentration formed from Fenton's reaction (3), as stated above. The insignificant change in k when the solution is irradiated by UVA light in the photoelectro-Fenton processes agrees with the fact that the herbicide is not directly photolyzed.

3.4. Identification and time-course of intermediates

Reversed-phase HPLC chromatograms of the 2,4-DP solutions degraded at 100 mA showed the presence of two additional absorption peaks related to chlorohydroquinone at t_r = 2.13 min and its oxidation product chloro-*p*-benzoquinone at t_r = 2.69 min. Note that another possible primary product as 2,4-dichlorophenol was undetected in this analysis. This aromatic has been identified during the anodic oxidation and electro-Fenton treatments of 2,4-D as a result of direct hydroxylation on its C(1) position with loss of glycolic acid (Brillas et al., 2004). It seems that the presence of a propionic group in 2,4-DP favors the consecutive dihydroxylation at similar rate of its C(1) and C(4) positions, with loss of lactic acid and Cl^- , leading to chlorohydroquinone.

The evolution of chlorohydroquinone and chloro-*p*-benzoquinone determined via calibration with external standards is shown in Fig. 5a and b, respectively. Both compounds are largely accumulated in AO-Pt, reaching 33 and 48 mg l^{-1} after 90 and 120 min of electrolysis, respectively, suggesting that they correspond to the main

degradation path of 2,4-DP. At 360 min of this treatment, they still persist in the medium because of their slower destruction with $\text{Pt}(\cdot\text{OH})$ than 2,4-DP, which disappears in 180 min (see Fig. 4a). For AO-BDD, about 5 mg l^{-1} of both products are accumulated as maximum, only remaining ca. 2 mg l^{-1} of chlorohydroquinone at 360 min. These results indicate a quicker destruction of both aromatics by BDD($\cdot\text{OH}$) than Pt($\cdot\text{OH}$), contrary to 2,4-DP, probably because they are adsorbed in smaller extent on Pt. In contrast, chlorohydroquinone and chloro-*p*-benzoquinone are rapidly formed and removed in less than 40 min by all indirect electrooxidation methods, as expected if they undergo a faster reaction with $\cdot\text{OH}$ in the medium.

Ion-exclusion chromatograms of the same treated solutions allowed detecting peaks associated with carboxylic acids such as oxalic (t_r = 6.75 min), maleic (t_r = 8.14 min), pyruvic (t_r = 9.08 min), malic (t_r = 9.79 min), lactic (t_r = 12.0 min), formic (t_r = 13.9 min), acetic (t_r = 15.2 min) and fumaric (t_r = 15.9 min). Maleic, malic and fumaric acids come from the oxidative breaking of the aryl moiety of aromatic products, being independently transformed into oxalic acid (Boye et al., 2002; Flox et al., 2006b). Formic acid is also formed during the oxidation of longer carboxylic acids. Oxalic and formic acids are further mineralized to CO_2 as ultimate carboxylic acids. On the other hand, lactic acid is expected to be released during the hydroxylation of 2,4-DP, as pointed out above. To clarify its oxidation path, solutions containing 100 mg l^{-1} of pure lactic, pyruvic or acetic acids in 0.05 M Na_2SO_4 of pH 3.0 were separately degraded at 100 mA and at 35 °C by AO-BDD and the evolution of their products were followed by ion-exclusion chromatography. These trials revealed that lactic acid yields pyruvic acid, followed by the conversion of this acid into acetic acid, which is degraded to oxalic acid.

As can be seen in Fig. 5c, maleic acid is continuously accumulated in AO-Pt due to the low oxidation power of $\text{Pt}(\cdot\text{OH})$, whereas it is removed after 90 min of EF-Pt and 120 min of PEF-Pt. This evidences the most effective reaction of this acid with $\cdot\text{OH}$ in the medium, being its degradation accelerated by UVA light probably due to the photolysis of its complexes with Fe^{3+} . When BDD is used, this acid is only detected in AO-BDD, where it is removed in 300 min. Maleic acid is then efficiently destroyed by BDD($\cdot\text{OH}$) and its additional faster reaction with $\cdot\text{OH}$ prevents its accumulation in EF-BDD and PEF-BDD. A similar behavior was found for fumaric and malic acids. Formic acid also showed the same trend, but it was undetected in AO-Pt due to the hard degradation of precedent longer acids by $\text{Pt}(\cdot\text{OH})$. On the other hand, lactic acid is only largely accumulated in AO-Pt, disappearing in 240 min. Its oxidation product, pyruvic acid, is much more slowly degraded in all methods. Fig. 5d shows that this acid attains 11 mg l^{-1} from 120 min of AO-Pt, whereas in AO-BDD it reaches 2.4 mg l^{-1} at 60 min and practically disappears at 360 min. In contrast, pyruvic acid is removed after 60 min of EF-Pt and PEF-Pt and 90 min of EF-BDD and PEF-BDD. These results indicate clearly that the

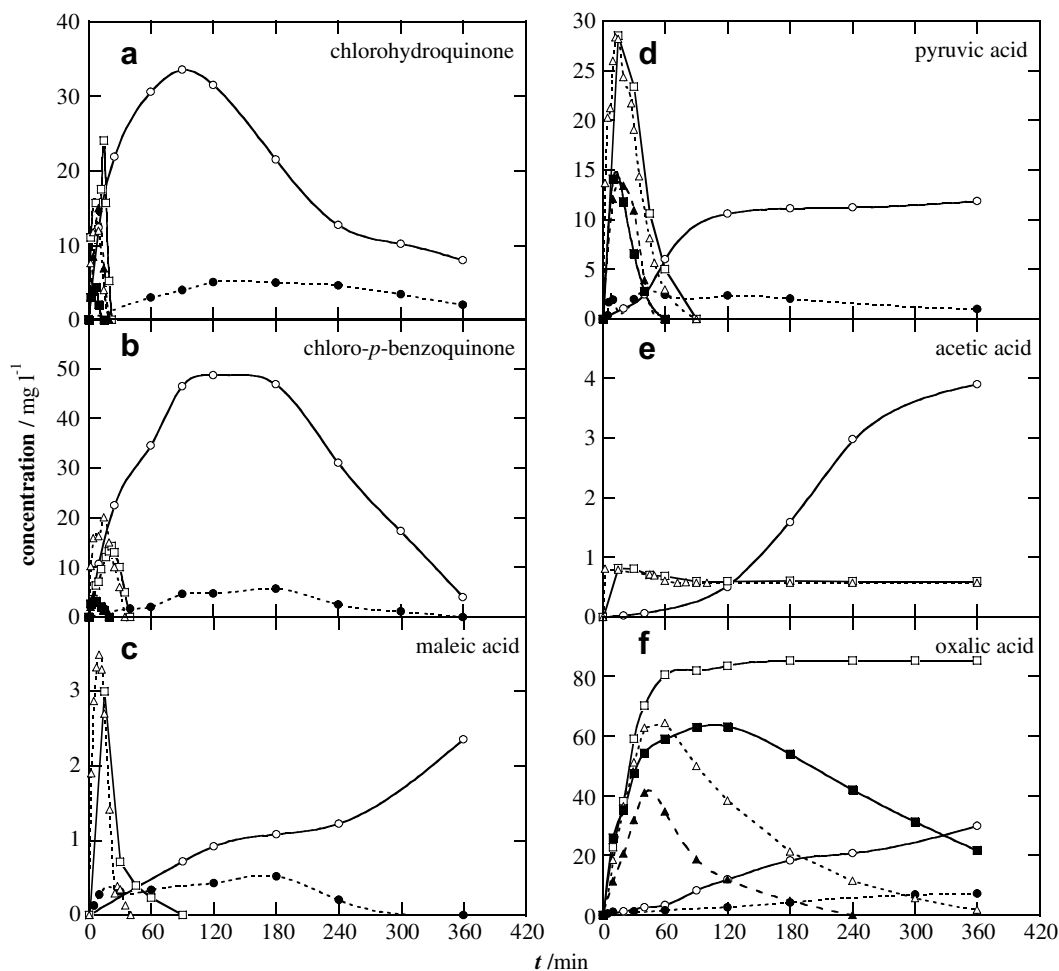


Fig. 5. Evolution of the concentration of selected intermediates detected during the degradation of 100 ml of 217 mg l⁻¹ 2,4-DP solutions in 0.05 M Na₂SO₄ of pH 3.0 at 100 mA and at 35 °C by: (○) AO-Pt; (●) AO-BDD; (□) EF-Pt; (Δ) PEF-Pt; (■) EF-BDD; and (▲) PFE-BDD. The latter four treatments were carried out with 1.0 mM Fe³⁺ in solution. Plots correspond to: (a) chlorohydroquinone; (b) chloro-*p*-benzoquinone; (c) maleic acid; (d) pyruvic acid; (e) acetic acid; and (f) oxalic acid.

degradation of pyruvic acid is unaffected by UVA light, taking place by reaction with both $\cdot\text{OH}$ and BDD($\cdot\text{OH}$), but not with Pt($\cdot\text{OH}$). A different behavior was found for acetic acid coming from pyruvic acid oxidation. Fig. 5(e) evidences that acetic acid is only accumulated using Pt, where its content increases gradually to ca. 4 mg l⁻¹ at the end of AO-Pt and attains a steady value of 0.6 mg l⁻¹ from 60 min of EF-Pt and PEF-Pt. The persistence of acetic acid under these conditions agrees with the fact that 2,4-DP is not completely mineralized in PEF-Pt. Traces of this acid were detected at the early stages of the treatments with BDD, corroborating its quick reaction with BDD($\cdot\text{OH}$).

Fig. 5f shows that in AO-Pt oxalic acid is progressively accumulated to 30 mg l⁻¹ at 360 min, as expected if it is not destroyed by Pt($\cdot\text{OH}$). The inability of this oxidant to degrade most carboxylic acids can then explain the lowest oxidation power of this method. For AO-BDD, an accumulation lower than 7 mg l⁻¹ for oxalic acid can be observed since it is mineralized with BDD($\cdot\text{OH}$) while is generated. This confirms the high oxidizing power of AO-BDD at long time and its ability to completely mineralize

2,4-DP at high current (see Fig. 2a). Fig. 5f also evidences that oxalic acid remains stable in EF-Pt with a steady concentration of 85 mg l⁻¹, indicating that its Fe³⁺ complexes are not oxidized neither $\cdot\text{OH}$ nor Pt($\cdot\text{OH}$). These complexes are slowly removed by BDD($\cdot\text{OH}$) in EF-BDD to attain a final content of 21 mg l⁻¹ at the end of electrolysis. The faster reaction of this oxidant with all products with raising current then yields the total mineralization of 2,4-D by this method (see Fig. 2a). In contrast, the PEF-Pt and PEF-BDD treatments lead to the complete destruction of Fe³⁺-oxalato complexes since they are photodecarboxylated by UVA light (Zuo and Hoigné, 1992). As can be seen in Fig. 5f, the destruction rate of these complexes is greater in PEF-BDD, as expected if they are also oxidized with BDD($\cdot\text{OH}$). This positive synergetic effect explains the highest oxidation power of the latter method.

A simple balance mass of the final solution treated by EF-Pt at 100 mA reveals that TOC related to the remaining acetic (0.01 mg l⁻¹) and oxalic (23 mg l⁻¹) acids is much lower than 48 mg l⁻¹ experimentally determined (see Fig. 1). That means that this final solution contains

about 25 mg l^{-1} of TOC corresponding to other undetected products that are hardly oxidizable by $\cdot\text{OH}$. These species are then destroyed by $\text{BDD}(\cdot\text{OH})$ and/or photodecomposed by UVA light in the faster processes taking place in PEF-Pt, EF-BDD and FEF-BDD.

3.5. Proposed reaction sequence

A plausible general path for 2,4-DP mineralization in acid medium by all electrochemical treatments tested is proposed in Fig. 6. This sequence involves all products

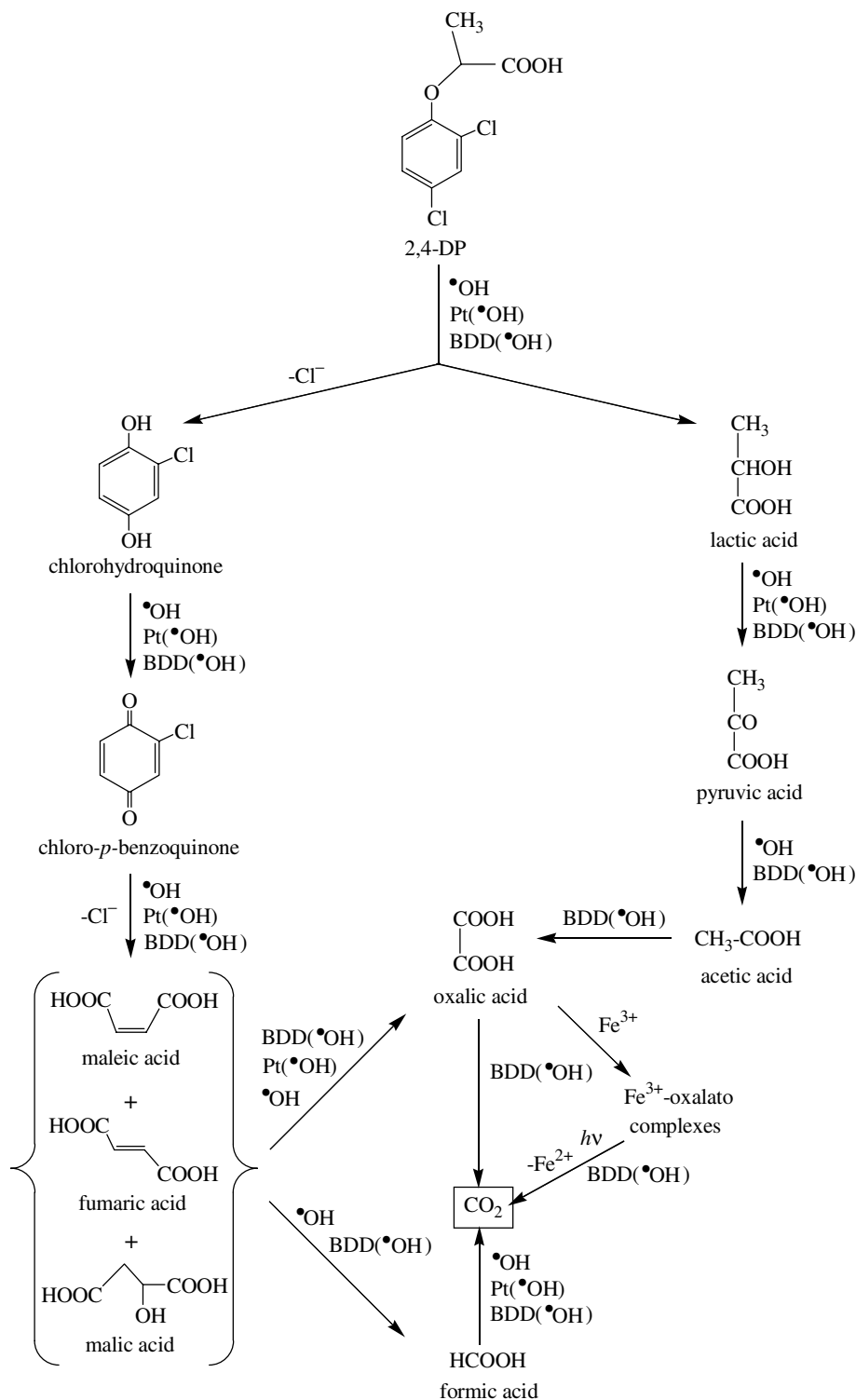


Fig. 6. Proposed general reaction sequence for the mineralization of 2,4-DP in acid medium by anodic oxidation and by electro-Fenton and photoelectro-Fenton with electrogenerated H_2O_2 using Fe^{2+} and UVA light as catalysts. The oxidant hydroxyl radical is denoted as $\cdot\text{OH}$ when formed from Fenton's reaction, whereas it is symbolized as $\text{Pt}(\cdot\text{OH})$ and $\text{BDD}(\cdot\text{OH})$ when produced from water oxidation at the Pt and BDD anode surface, respectively.

detected in this work and for sake of simplicity, the main oxidizing agents ($\cdot\text{OH}$, $\text{Pt}(\cdot\text{OH})$ and $\text{BDD}(\cdot\text{OH})$) are only specified. Other parallel degradation reactions of some products and their complexes with Fe^{3+} with weaker oxidants such as H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, O_3 , etc. are also possible.

The process is initiated by consecutive dihydroxylation on the C(1) and C(4) positions of the herbicide by $\cdot\text{OH}$, $\text{Pt}(\cdot\text{OH})$ and $\text{BDD}(\cdot\text{OH})$ leading to the formation of chlorohydroquinone, with loss of lactic acid and Cl^- . Further oxidation of chlorohydroquinone gives chloro-*p*-benzoquinone, which is subsequently degraded to a mixture of malic, fumaric and maleic acids with release of Cl^- . These latter acids are rapidly transformed into formic and oxalic acid with $\cdot\text{OH}$ and $\text{BDD}(\cdot\text{OH})$, but they are much more slowly oxidized with $\text{Pt}(\cdot\text{OH})$. In fact, formic acid is not generated in AO-Pt, although once produced in the other methods, it can be mineralized to CO_2 by all oxidizing agents. The parallel destruction of the initially generated lactic acid yields acetic acid via pyruvic acid. However, pyruvic acid can only be degraded with $\cdot\text{OH}$ and $\text{BDD}(\cdot\text{OH})$ and acetic acid with the latter oxidant. Similarly, oxalic acid is only transformed into CO_2 by $\text{BDD}(\cdot\text{OH})$. In the EF and PEF processes Fe^{3+} -oxalato complexes are also formed, remaining stable under EF-Pt conditions, although they are mineralized by $\text{BDD}(\cdot\text{OH})$ in EF-BDD or photodecarboxylated under UVA irradiation in the PEF processes, with loss of Fe^{2+} , as proposed by Zuo and Hoigné (1992).

Probably, Fe^{3+} -acetato complexes are also produced in the indirect electrooxidation methods, being destroyed by $\text{BDD}(\cdot\text{OH})$ but not photodegraded by UVA light, since they persist during the PEF-Pt treatment (see Fig. 5e). Our results evidence the formation of complexes of Fe^{3+} with other acids such as maleic, fumaric, malic and formic, which are photodecomposed by UVA light.

4. Conclusions

It has been demonstrated that anodic oxidation, electro-Fenton and photoelectro-Fenton with a BDD anode are viable methods to decontaminate acidic wastewaters containing 2,4-DP. These electrochemical techniques yield overall mineralization at high current due to the great production of oxidant $\text{BDD}(\cdot\text{OH})$ favoring the destruction of final carboxylic acids. $\cdot\text{OH}$ formed from Fenton's reaction (3) destroys more rapidly aromatic products, thus making the electro-Fenton and photoelectro-Fenton processes much more efficient than anodic oxidation. UVA light in photoelectro-Fenton with BDD has little influence on the degradation rate of pollutants. The alternative use of a Pt anode in the same methods under comparable conditions leads to slower decontamination because of the lower oxidizing power of $\text{Pt}(\cdot\text{OH})$. The increase in current accelerates the degradation of all pollutants, but with the consumption of more specific charge. The initial chlorine is released as Cl^- , which is stable in the treatments with Pt and oxidized to Cl_2 at the BDD anode. The 2,4-DP

decay always follows a pseudo-first-order kinetics. Chlorohydroquinone and chloro-*p*-benzoquinone are detected as aromatic intermediates and maleic, fumaric, malic, lactic, pyruvic, acetic, formic and oxalic acids are identified as carboxylic acids. Acetic acid is destroyed by the oxidant $\text{BDD}(\cdot\text{OH})$, but not by $\text{Pt}(\cdot\text{OH})$. Oxalic acid and Fe^{3+} -oxalato complexes are also converted into CO_2 by $\text{BDD}(\cdot\text{OH})$, whereas the latter complexes are simultaneously photodecarboxylated under UVA irradiation in photoelectro-Fenton.

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