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Electrochemical degradation of a chlorophenoxy propionic acid derivative used as an herbicide at boron-doped diamond

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ABSTRACT

The electrochemical degradation of *diclofop-methyl* (DM), an herbicide deriving from aryloxy propionic acid, was carried out by galvanostatic electrolysis at boron-doped diamond electrode. The oxidation process leads in an early step to the cleavage of the aryloxy propionic ester bond and the formation of 4-(2,4-dichlorophenoxy) phenol (P1). The subsequent oxidation of P1 resulted in a quantitative mineralization of DM. Measuring the reduction in chemical oxygen demand and total organic carbon during the electrolysis shows that the mineralization efficiency increases with decreasing current densities. As a result, two mechanistic pathways were proposed for DM electrochemical degradation. The first one is a direct electro-oxidation of the starting molecule leading to the breakdown of aromatic ether bonds. A second evidenced competitive pathway uses electrogenerated hydroxyl radicals as mediators in the mineralization process of DM.

Keywords: BDD; Diclofop-methyl; Electrochemical degradation; Hydroxyl radical

1. Introduction

The massive use of pesticides in agriculture contributes to the risk of increased pollution of the environment. Much research has been undertaken to develop effective ways to solve this problem. Thus, several processes have been implemented for the degradation of these toxic substances. The advanced oxidation processes (AOP) are very promising methods in this field. They are based on mineralization of organic compound by chemical or electrochemical reactions generating powerful oxidizing agents.

Methyl-2-[4-(2,4-dichlorophenoxy) phenoxy] propionate named diclofop-methyl (DM) is a selective systemic herbicide used for the post-emergence control of wild oats and the annual grass weeds. The corresponding chemical structure (Fig. 1) is related to other widely used chlorinated aryloxy phenoxy propionate herbicides.

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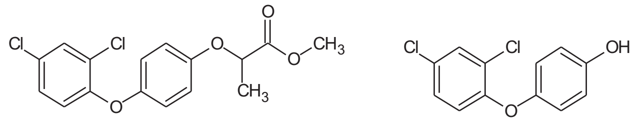

DM DP

Fig. 1. Chemical structures of DM and its metabolite 4-(2,4-dichlorophenoxy) phenol (DP).

The degradation of DM has been the subject of several studies using biological processes [1–3]. The results show that such methods lead to incomplete mineralization. Furthermore, DM breakdown products may contribute to the environmental risks. This has been demonstrated especially for 4-(2,4-dichlorophenoxy) phenol (product DP in Fig. 1), which has higher acute toxicity than the parent compound [3].

In contrast, the degradation of DM with chemical processes was not sufficiently investigated except the study by Gomathi Devi et al. reporting the photocatalytic degradation of DM in the presence of semiconductor [4]. This work resulted in the mineralization of DM when particles of $TiO_2/TiBaO_3$ semiconductor are illuminated by UV radiation. The authors proposed a process involving radicals such as $^{\cdot}OH$, $H^{\cdot}$, O_2. The intervention of these radicals and in particular $^{\cdot}OH$ has often been suggested in the degradation process of organic matter under various chemical and electrochemical conditions [5–7]. Thus, hydroxyl radical seems to play a key role in the mechanism of degradation due to a strong oxidizing power allowing it to destroy organic molecules rapidly and non-selectively. Such effectiveness is explained by the high oxidation potential ($E^0_{OH^{\cdot}}/H_2O - 2.7\,V/NHE$) and also by the ability of $^{\cdot}OH$ to transfer oxygen atom to organic molecules [8]. The production of hydroxyl radical was often carried out using Fenton's reagent which can be electrogenerated by the processes called electro-Fenton and photoelectro-Fenton [9–14]. $^{\cdot}OH$ radical can also be obtained directly by the discharge of water on different types of anodes. The AOP are precisely those based on the use of powerful oxidizing agents, especially hydroxyl radicals, to destroy harmful molecules. In this context, significant progress was recorded by using a new type of electrode based on conducting boron-doped diamond (BDD). The BDD anode is characterized by high overvoltage of oxygen evolution favorable to significant production of hydroxyl radical. Its efficiency in the degradation of organic compounds has been reported in many studies [15–32].

In this work, we were interested in the electrochemical degradation of DM which can be considered as a model molecule of widely used herbicides. Such organic pollutants are not readily biodegradable because of their quite complex chemical structures. We report the electrochemical degradation of DM in acidic aqueous medium using BDD anode. Monitoring of the electrolysis solution permits to highlight the role of hydroxyl radicals in the mineralization process.

2. Experimental

2.1. Electrochemical procedures

The voltammetric study is performed with a Voltalab 80 analyzer from Radiometer. The working electrode consisted of a BDD sheet ($4\,mm^2$ surface) plunged in $1\,M$ H_2SO_4 solution. The auxiliary electrode is a platinum wire. The reference is a saturated calomel electrode (SCE).

The galvanostatic electrolyses in sulfuric medium are performed in a one compartment cell equipped with a BDD sheet as anode and a platinum grid as the cathode, both have $4\,cm^2$ surface. Different current densities are used. The values are comprised between 5 and $30\,mA/cm^2$. The electrolysis solutions are evaporated then extracted with chloroform before chromatographic analysis.

The boron-doped diamond (Si/BDD) electrodes are provided and synthesized by the Swiss Centre for Electronics and Microtechnology SA Neuchatel-Switzerland using the hot filament chemical vapors deposition (HF-CVD) technique on conducting p-Si. The obtained film thickness is about 1 mm.

The instantaneous current efficiency (ICE) is calculated using the following equation [30]:

$$\mathrm{ICE} = FV(\mathrm{COD}_{t+\Delta t} - \mathrm{COD}_t)/8I\Delta t$$

F is the Faraday constant (96487 C), V is the volume of electrolyte (dm^3), COD_t and $COD_{t+\Delta t}$ are the chemical oxygen demand (COD) (g of $O_2\,dm^{-3}$) at times t and $t + \Delta t$ (s), respectively, I is the current intensity (A), and 8 is a dimensional factor for unit consistence [32 g of O_2 $(mol\,O_2)^{-1}/4\,mol\,e^-$ $(mol\,O_2)^{-1}$].

2.2. Total organic carbon and COD analysis

Degradation by galvanostatic electrolysis of DM on BDD anode is followed by measuring the decrease in COD and total organic carbon (TOC) during the treatment. COD is determined using a Hanna (HI 83212) type analyzer while TOC is measured using a TOC-VCSH Shimatzu type analyzer.

2.3. GC/MS analysis

The extracts of DM electrolysis are analyzed by gas chromatography/mass spectrometry. The GC separation was performed with an Agilent (6890 N) type chromatograph using a silica capillary column of 5% phenyl methyl siloxane (30 m × 0.25 mm in diameter, 0.2 µm film thickness). The temperature varies between 40 and 325℃ at a rate of 6℃ mn^{-1}. The mass spectrometric analysis is made with a 5957B type Agilent spectrometer. The mass spectrometer was operated with electron impact ionization at 70 eV. The conditions analysis was as follows: the temperature of the injector was 250℃, the ion source and the analyzer were held at 230 and 280℃, respectively. The carrier gas was helium with flow rate at 1.2 mL min^{-1}.

2.4. Chemical

DM of analytical grade was purchased from Fluka. The characterization of the electrolysis products of DM is achieved by mass spectrometry. The corresponding mass data are given below:

- P1: *m/z*: {254 (100%), 256 (65%), 258 (11%): molecular cluster}, 184 (30%)
- P2: *m/z*: 104 (100%, molecular peak), 90(40%)
- P3: *m/z*: {162 (100%), 164 (66%), 166 (11%): molecular cluster}, 98 (26%), 64 (38%)
- P4: *m/z:* 110 (100%: molecular peak), 80 (30%), 54 (88%)
- P5: *m/z:* 108 (100%, molecular peak), 83 (38%), 54 (86%)
- P6: *m/z:* 144 (100%), 146 (31%): molecular cluster
- P7: *m/z:* 126 (100%: molecular peak), 110 (42%), 56 (48%)

Products P6 and P7 are obtained in the prolonged galvanostatic electrolysis on BDD anode beside all other products.

3. Results and discussion

3.1. Electrochemical degradation of DM on BDD anode in sulfuric acid

Before proceeding to the degradation of DM by exhaustive electrolysis in sulfuric acid medium, we examined first its voltammetric behavior on a BDD anode. The voltammogram given in Fig. 2 shows a single broad anodic peak located at 2.03 V/SCE. It is likely that the oxidation of DM in sulfuric medium involves several overlapping peaks of oxidation giving rise to an apparent single broad peak.

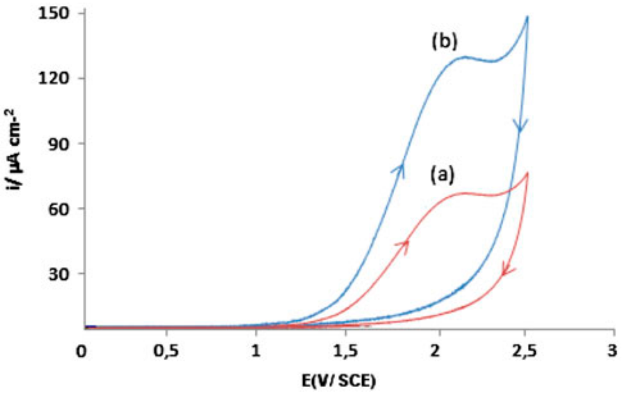

Fig. 2. Cyclic voltammogram of DM on a BDD anode (4 mm^2) in sulfuric acid 1 M. $v = 100$ mV s^{-1}; (a) $C = 10^{-3}$ M; (b) $C = 2.10^{-3}$ M.

The electrochemical degradation of DM was achieved by galvanostatic electrolysis. GC analysis of the electrolysis solution at different times showed a progressive decrease in DM and the transient formation of several oxidation products P1-P7 given in Table 1. The identification is based on mass spectrometric results when compared with those of authentic samples.

Chromatograms recorded during electrolysis indicated that 4-(2,4-dichlorophenoxy) phenol (P1) is formed first and then it gradually decreases forming 2,4-dichlorophenol (P3), 1,4-hydroquinone (P4), and quinone (P5). Subsequent products: 1,2,4-benzenetriol (P6) and 2-chloro-1,4-hydroquinone (P7) appear later and disappear at the end of electrochemical treatment revealing a quantitative degradation of the starting material.

P6 and P7 products are plausibly obtained by hydroxylation of P4 and P3, respectively. Therefore, the oxidation process involves very probably hydroxyl radicals which are generated by the discharge of water on the BDD anode. In addition, the intervention of ·OH could account for the observed ultimate mineralization. Thus, we may transpose the model proposed by Comninellis et al. who have concluded that the discharge of water generating hydroxyl radical results in concomitant organic oxidation and oxygen evolution illustrated in the following scheme: [33–38].

[1] $\mathrm{BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + 1e^-}$
[2] $\mathrm{BDD\ (\cdot OH) + R \rightarrow BDD + m\ CO_2 + n\ H_2O}$
[3] $\mathrm{BDD\ (\cdot OH) \rightarrow BDD + ½\ O_2 + H^+ + 1e^-}$

Thus, the degradation of DM on BDD anode in sulfuric acid medium seems to occur via two pathways:

Table 1
Products of anodic oxidation of DM on BDD in H_2SO_4 1 M

Product	Retention time (min)
2-Hydroxy-propanoic acid methyl ester (P2)	3.6
1,4-Hydroquinone (P4)	4.2
Quinone (P5)	4.8
1,2,4-Benzenetriol (P6)	6.2
2-Chloro-1,4-hydroquinone (P7)	8.9
2,4-Dichlorophenol (P3)	11.2
4-(2,4-Dichlorophenoxy) phenol (P1)	33.1
DM (starting material)	37.2

- A direct electron transfer,
- An indirect oxidation mediated by hydroxyl radicals whose result is given in reaction [2].

The second pathway occurs when the electrolysis is sufficiently advanced. It competes with the first process when the imposed current becomes superior to the diffusion limiting current of the electroactive species allowing the discharge of water. The corresponding scheme is shown in Fig. 3.

A similar behavior has been described in precedent studies for chlorophenoxy propionic acid derivatives such as clorofibric acid [34] and mecoprop [37] when treated by anodic oxidation at BDD anode. The proposed pathway starts similarly with breaking of the C(1)-O phenoxy bond leading to 4-chlorophenol which undergoes subsequently dechlorination and hydroxylation with hydroxy radical.

3.2. Current efficiency

The monitoring of the mineralization process was performed by measuring the COD, TOC, and by UV–visible absorption spectrophotometry.

Fig. 4 shows the evolution of COD during electrolysis with three different current densities. It was found that the rate of mineralization increases with decreasing current densities. Thus, the lowest value (5 mA/cm^2) led to 95% COD elimination after 6 h indicating that process [2] of mineralization is favored. At high current densities, recombination of $^{\cdot}OH$ radicals into less effective oxidizing agents (reaction [3]) becomes predominant.

An analysis of the ICE confirmed this assumption. It was found that for the lowest current density (5 mA/cm^2), ICE is about 100% at the beginning of treatment and then decreases exponentially (insert in Fig. 4). Whereas for higher densities (10 and 30 mA/cm^2), the

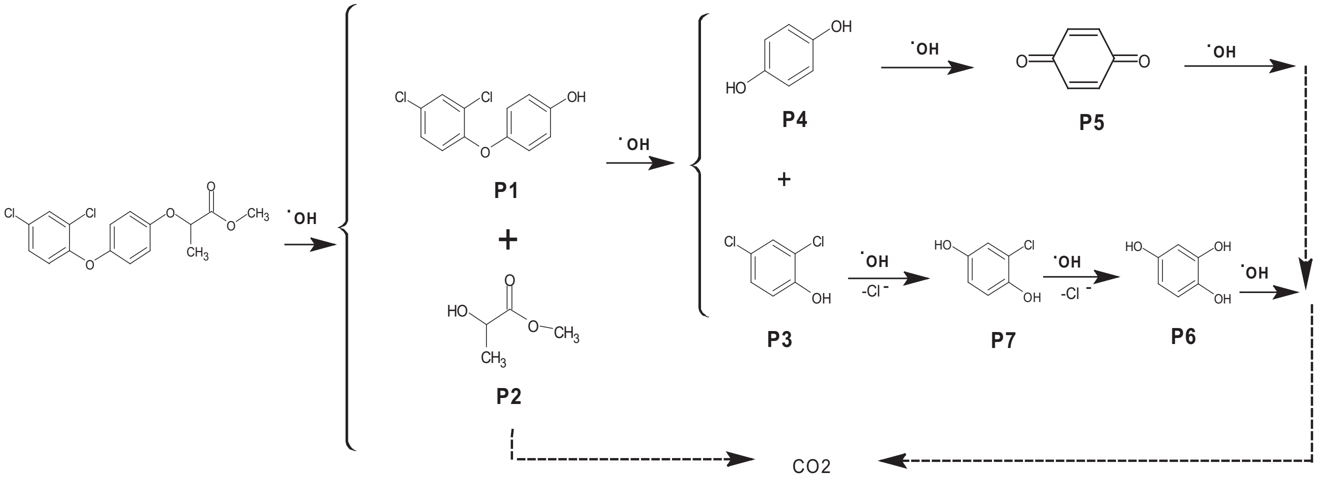

Fig. 3. Postulated degradation process of DM mediated by $^{\cdot}OH$ in galvanostatic electrolysis with BDD anode.

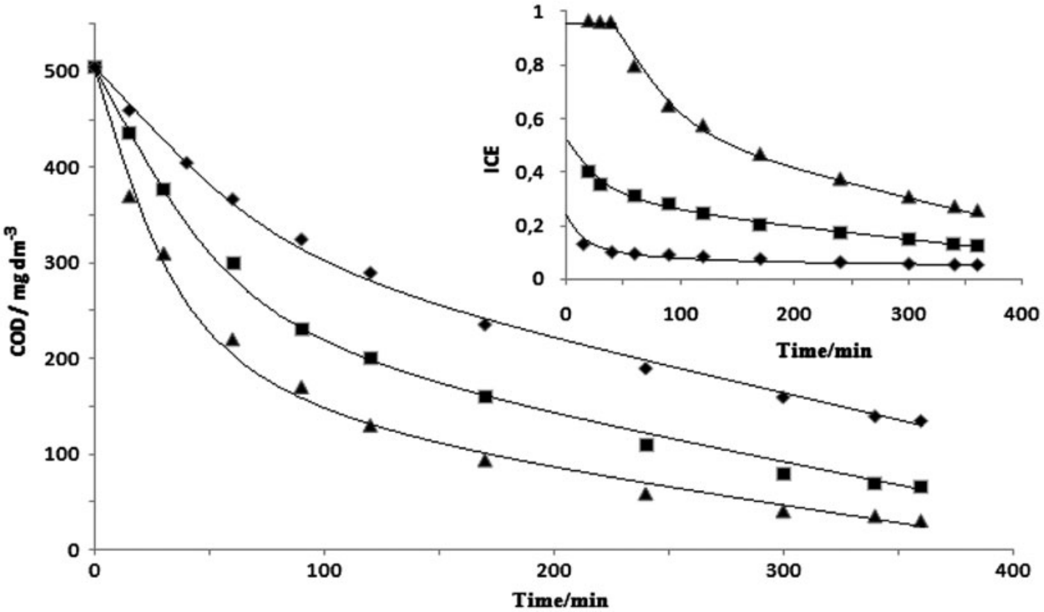

Fig. 4. COD and ICE (insert) during electrolysis on BDD of 1 mM DM in 1 M H_2SO_4. Current density: 5 mA/cm^2 (▲); 10 mA/cm^2(■); 30 mA/cm^2(◆).

decay is only exponential. These results suggest that for low current densities and at the beginning of the electrolysis, the degradation of DM starting material is due to a direct electron transfer. For longer times, as well as for high current densities, secondary electrochemical reactions involving the solvent or may be the supporting electrolyte can occur leading to a decrease in the faradic efficiency [39–40]. Indeed, reactions such as oxygen evolution may arise gradually as the concentration of substrate studied decreases.

The mineralization process by electrolysis on BDD was confirmed by monitoring the decrease in TOC. Fig. 5 shows a rapid elimination of TOC at the beginning of the electrochemical treatment which is attributable to a rapid degradation of the cyclic intermediates. A slow down was observed later may be due to more time-consuming mineralization of aliphatic intermediates [31].

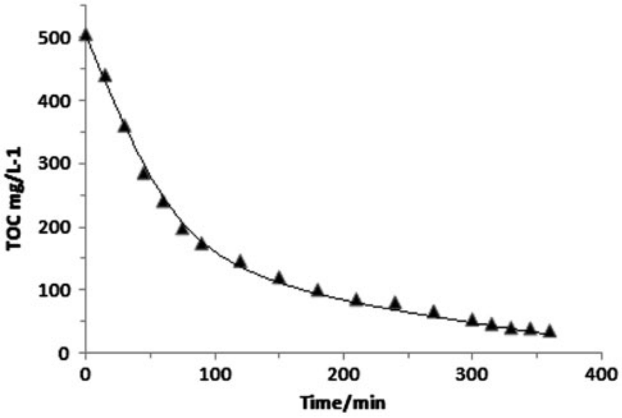

Fig. 5. Evolution of TOC during electrolysis on BDD of DM (C = 10^{-3} M) in H_2SO_4 1 M, current density 5 mAcm^{-2}.

The kinetics of degradation of the aromatic compounds was studied by recording UV–visible spectra of the solution at different electrolysis advancements (Fig. 6).

The absorption decay at 200 nm is related to the evolution of aromatic intermediates. A linear variation of log (A_0/A_t) is obtained indicating a first-order degradation. The result indicates that the rate constant obtained is approximately $1.2\,10^{-3}\,\text{min}^{-1}$. The same behavior was described for clorofibric acid [34]. In fact, a pseudo-first-order rate constant of the same order of magnitude was found for this compound with BDD anode ($k = 1.3 \times 10^{-4}\,\text{s}^{-1}$). The results confirm the intervention of $^{\cdot}$OH with a large excess in the non-selective degradation of organic material.

4. Conclusion

Exhaustive electrolysis of DM aryloxy propionic acid derivative on BDD anode resulted in its quantitative mineralization. Several intermediates were identified resulting from the cleavage of aromatic ether bonds. The transient formation of hydroxylated intermediates suggests the involvement of hydroxyl radicals. The kinetics of the degradation process were

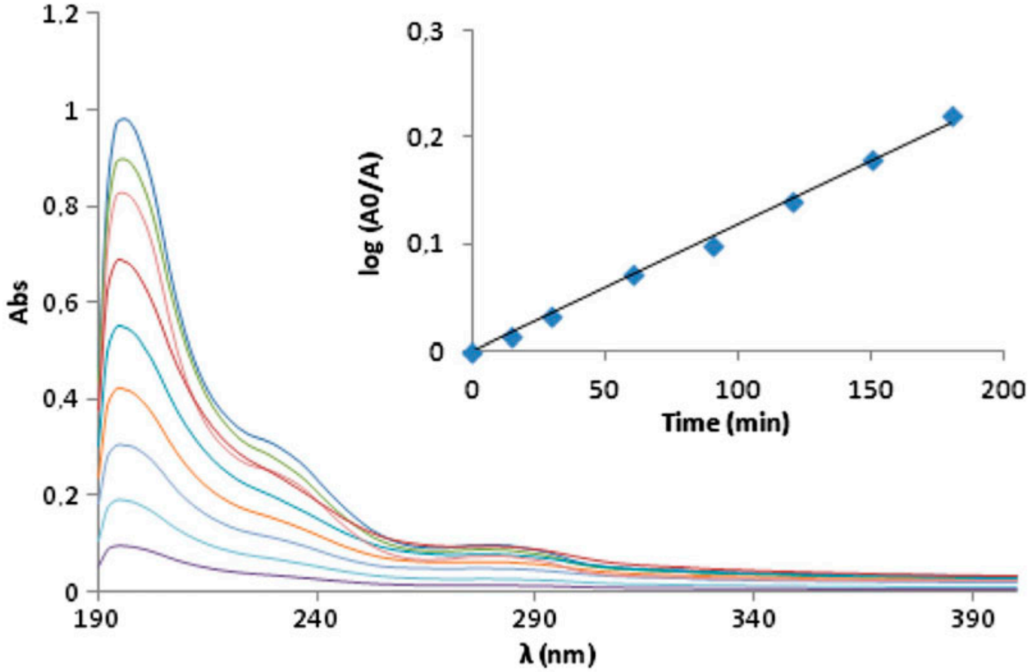

Fig. 6. Evolution of UV–visible spectra during galvanostatic electrolysis of DM on BDD anode, H_2SO_4 1 M, Current density = 5 mA/cm^2.

followed by COD, TOC, and UV–visible spectrometry. It was found that the electrochemical treatment is the most effective and rapid when the current density is low. A mechanistic scheme of the electrochemical degradation of DM on BDD was proposed. It involves a direct electron transfer process together with an indirect oxidation mediated by hydroxyl radicals leading to the ultimate mineralization.

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