

## Anodic Oxidation of Chlorinated Pesticides on BDD and PbO<sub>2</sub> Electrodes: Kinetics, Influential Factors and Mechanism Determination

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### Abstract

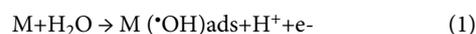
In this work, the removal of two pesticides 1, 2- dichlorobenzene and 1, 4- dichlorobenzene by electrolysis using BDD and Pb/PbO<sub>2</sub> as anodes is studied. Different operating conditions and factors affecting the treatment process including anode material, applied current density, supporting electrolyte and initial pH value were studied and optimized. Results demonstrate, as expected, that the influence of the anode material used on the degradation of pesticides was very significant in all cases. Infact electrolysis with diamond electrodes can attain the complete depletion of the pesticide and its mineralization faster than with PbO<sub>2</sub> anode. Electrolysis experiments strongly improves that the complete degradation of pesticides occurred in the presence of Na<sub>2</sub>SO<sub>4</sub> as conductive electrolyte at current density equals 20 mA cm<sup>-2</sup>. Acidic pH would accelerate dichlorobenzene degradation, whereas alkaline condition showed negative effects. The disappearance of the pesticides followed a pseudo-first-order kinetics. Reversed-phase chromatography allows detecting Catechol, 2-chlorophenol and Pyrogallol as primary aromatic intermediates of 1,2-DCB and Hydroquinone, Benzoquinone and 4-chlorophenol for 1,4-DCB. Dechlorination of these products gives chloride ions Cl<sup>-</sup>. Ion-exclusion chromatography reveals the presence of maleic, formic, fumaric, malonic, glyoxylic, acetic and oxalic acid. An oxidation mechanism is proposed in agreement with other works shown in the literature.

**Keywords:** Anodic oxidation; Dichlorobenzene; Mechanisms; Mineralization; Parametric optimization

### Introduction

Dichlorobenzene is a conventional pesticide that has been widely used on agricultural farms for several and variable purposes as preventing, destroying or repelling any pest, although it can also play the role of plant regulator and defoliant [1,2]. Dichlorobenzene is well known as a versatile herbicide that has been applied in various processes. Moreover, lowcost and good performance have increased the dichlorobenzene application worldwide. Over 600 commercial types of dichlorobenzene are produced in market for the control of weeds [3]. The extensive application of dichlorobenzene and its high solubility cause contamination of receiving waters. The presence of this herbicide has been frequently reported in drainage water and groundwater in high concentration. Dichlorobenzene is a toxic chemical that can damage human organs such as the liver and kidney [4]. In addition, it has been reported that dichlorobenzene can be carcinogenic for mammals. Hence, various methods have been developed for removing the herbicide from the aquatic environment. Such as conventional techniques (filtration, coagulation, flocculation, sedimentation and biological processes), adsorption, membrane processes, chemical oxidation, etc [5]. Its stability and toxicity have caused increased use of advanced oxidation processes (AOPs) for its degradation [6]. Advanced oxidation processes often apply a chemical oxidant for generating reactive radicals to destruct the organic compounds. Hydroxyl radical (\*OH), a powerful oxidant (E<sub>0</sub>=2.7 V

[6], is the main oxidative agent in AOPs. There are several techniques used for generating the hydroxyl radical, including chemical, photochemical, sonochemical, and electrochemical processes [7-10]. Presently, increasing attention has been paid to the anodic oxidation for degrading the environmental pollutants. In this process pollutants can be oxidized by two principal mechanisms; direct electrochemical reaction via electron transfer between anode and molecule, and indirect oxidation via oxidants generated on the anode, called also mediated oxidation, in fact highly reactive and strongly oxidant heterogeneous hydroxyl radicals M(\*OH) are produced on the anode surface (M) by electrochemical oxidation of water, according to reaction (1), using high O<sup>2</sup>-overvoltage anodes such as boron-doped diamond (BDD) and PbO<sub>2</sub> [11-14]:



The \*OH/M(\*OH) obtained is nonselective, very powerful oxidizing agents that oxidize dichlorobenzene to CO<sub>2</sub>, water and inorganic ions [15-18].

In our previous studies, anodic oxidation process was successfully applied to the degradation of different organic pollutants [19-21] and pesticides such as isothiazolin-3-ones, thiamethoxam and 2-chlorophenol [22-24]. The aim of this work was to evaluate the potential application of anodic oxidation process using BDD and PbO<sub>2</sub> anodes for the removal of a chlorinated pesticides that has not been studied until now such as 1, 2-dichlorobenzene (1, 2-DCB) and 1, 4-dihlorobenzene (1, 4-DCB). Initially, the influence of operating parameters on the degradation rate such as anode material, applied

current, pH and types of the supporting electrolyte was studied. The degradation of 1, 2-DCB and 1, 4-DCB were followed by high performance liquid chromatography (HPLC) analysis.

The decay of organic matter in the solution was followed by total organic carbon (TOC) measurements that permitted the evaluation of the mineralization efficiency. Besides, the identification of the degradation products of the dichlorobenzene was accomplished using gas chromatography coupled with mass spectrometry (GC-MS) equipment and ion-exclusion HPLC. Finally, a plausible mineralization pathway of 1, 2-DCB and 1, 4-DCB by  $\cdot\text{OH}/\text{M}(\cdot\text{OH})$  were proposed.

## Materials and Methods

### Electrodes preparation

PbO<sub>2</sub> was deposited galvanostatically on the pretreated lead substrate by electrochemical anodization of lead in oxalic acid solution (100 g L<sup>-1</sup>) at 25°C. This acid solution was electrolyzed galvanostatically for 30 min at ambient temperature using an anodic current density of 100 mA cm<sup>-2</sup>. The cathode was stainless steel (austenitic type), the two electrodes were concentric with the lead electrode as axial. This arrangement gave the formation of a regular and uniform deposit [25].

BDD films were provided by CSEM and synthesized on a conductive p-Si substrate (1 mm, Siltronix) via a hot filament, chemical vapor deposition technique (HF-CVD). The temperature of the filament was from 2440°C to 2560°C and that of the substrate was monitored at 830°C. The reactive gas used was 1% methane in hydrogen containing 1–3 ppm of trimethylboron. The gas mixture was supplied to the reaction chamber at a flow rate of 5 L min<sup>-1</sup> to give a growth rate of 0.24 μm h<sup>-1</sup> for the diamond layer. This procedure gave a columnar, randomly textured, polycrystalline diamond film, with a thickness of about 1 μm and a resistivity of 15 mΩ cm (± 30%) onto the conductive p-Si substrate [26].

### Electrolysis of dichlorobenzene solutions

Galvanostatic electrolyses were carried out at BDD and PbO<sub>2</sub> electrodes, with current density ranging from 0 to 40 mA cm<sup>-2</sup>. Runs were performed at 20°C. Solutions of 25 mg L<sup>-1</sup> of pure dichlorobenzene were used. Electrolysis was done with 50 mmol L<sup>-1</sup> of different types of electrolytes NaCl and Na<sub>2</sub>SO<sub>4</sub> with pH around 3.0 – 12.0. All electrolyses were conducted in an open, one-compartment and thermostated cylindrical cell containing a 230 mL solution stirred with a magnetic bar. The anode was a 25 cm<sup>2</sup> BDD. For comparative purposes, a 25 cm<sup>2</sup> PbO<sub>2</sub> was also employed as anode. The cathode was always a 25 cm<sup>2</sup> graphite bar. The interelectrode gap was about 3 cm. The current and potential measurements were carried out using digital multimeter.

### Analytical techniques

Dichlorobenzene and all other intermediates were either reagent or analytical grade from Sigma-Aldrich. Anhydrous sodium sulfate used as background electrolyte was analytical grade from Fluka. All solutions were prepared with water from a Millipore Milli-Q system (conductivity <6 × 10<sup>-8</sup> S cm<sup>-1</sup>). The temperature of the electrolyte was fixed by using a water thermostat. The current density for the electrolysis was kept at the desired level with an Amel 2053 potentiostat-galvanostat. The solution pH was measured with a Crison

2000 pH-meter. Total Organic Carbon (TOC) amounts in aqueous solutions were obtained with a Shimadzu VCSH carbon analyzer. During all experiments, samples were collected and immediately measured without using any filter. Chemical oxygen demand (COD) data were obtained with a Merck Model SQ118 spectrophotometer after digestion of samples in a Merck Model TR-300 thermoreactor. dichlorobenzene and all other intermediates were identified by reversed-phase chromatography with a water system composed of a Waters 600 HPLC liquid chromatography fitted with a Spherisorb ODS2 5 μm, 150 × 4.6 mm column, at room temperature, and coupled with a waters 996 photodiode array detector selected at 230 nm, controlled through a Millennium-32 program<sup>®</sup>. These analyses were made by injecting 20 μL aliquots into the chromatograph and circulating a 70/30 (v/v) Methanol/water mixture at 0.8 mL min<sup>-1</sup> as mobile phase. Generated carboxylic acids were followed by ion-exclusion chromatography by injecting 20 μL samples into the above HPLC system with a SUPELCOGEL C-610H, 250 × 4.6 mm column, at 35°C from Bio-Rad. For these measurements, the photodiode detector (L-2400) was selected at 210 nm and the mobile phase was 4 mmol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 0.2 mL min<sup>-1</sup>. Inorganic ions were analysed by ion chromatography using a Dionex ICS-1000 Basic Ion Chromatography system fitted with an IonPac AS4A-SC, 25 cm × 4 mm anion-exchange column. These measurements were conducted by injecting 25 μL samples and using a mobile phase composed of 1.8 mmol L<sup>-1</sup> of sodium carbonate and 1.7 mmol L<sup>-1</sup> of sodium bicarbonate at the flow rate of 0.8 mL min<sup>-1</sup>.

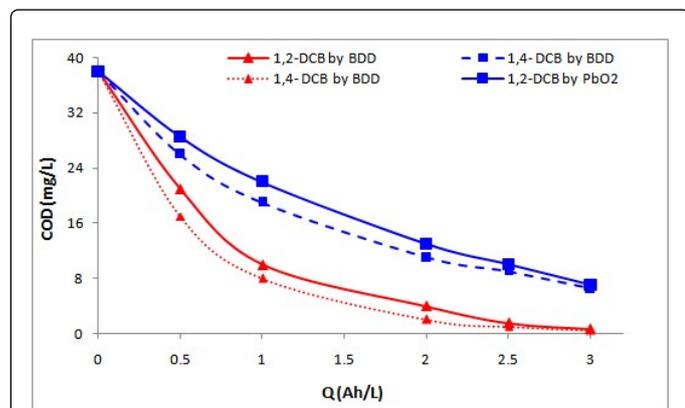
## Results and Discussion

The optimization of operating conditions and factors affecting the treatment process, such as the nature of the anode, applied current density, supporting electrolyte and initial pH value are essential for efficient degradation of chlorinated pesticides like 1, 2-DCB and 1, 4-DCB by direct electrochemical oxidation. The optimal value of pH has been studied and determined, it was showed to be definitely around the value of 3. Thus, the influence of other parameters was studied to determine operating conditions for an optimal degradation of the dichlorobenzene from aqueous solution.

### Effect of experimental parameters on dichlorobenzene mineralization

**Effect of the anode material:** Anode material plays a very important role on anodic oxidation process, when pollutants are mineralized by direct electron transfer reactions or action of hydroxyl radicals generated from the water discharge along with other oxidants. In this manner, a wide variety of electrode materials have been investigated recently (Pt, PbO<sub>2</sub>, BDD, carbon-graphite, etc.) [27]. To compare the performance of different anodes studied in this work namely BDD and PbO<sub>2</sub>, a series of electrolysis have been performed for the degradation of 1, 2-DCB and 1, 4-DCB applying a constant current of 20 mA cm<sup>-2</sup> and the results are reported in Figure 1. Comparing the abatement percentages of the oxidation and mineralization of 1, 2-DCB and 1, 4-DCB, it can be observed that the COD removal rate in BDD anode cell was much greater than those in PbO<sub>2</sub> anode cell for the both pesticides. At the end of treatment, COD was almost completely removed in BDD anode cell, while 79% of the initial COD were only removed with PbO<sub>2</sub> anode in the same period (Figure 1). It meant that the mineralization capacity of BDD anode was much stronger than that of PbO<sub>2</sub> anodes. This behavior can be explained by the different reactivity of the electrogenerated hydroxyl radicals. We speculate that

on BDD, which is well known to have weak adsorption properties due to its inert surface, hydroxyl radicals are very weakly adsorbed and consequently they are very reactive toward organics oxidation. On the contrary, lead dioxide is hydrated and hydroxyl radicals are expected to be more strongly adsorbed on its surface and consequently less reactive [28].



**Figure 1:** Chemical oxygen demand removal for the anodic oxidation of 230 mL of solution with 0.16 mM of 1, 2-dichlorobenzene and 1, 4-dichlorobenzene in 50 mM Na<sub>2</sub>SO<sub>4</sub> of pH 3.0. (▲) BDD and (■) PbO<sub>2</sub> anodes and a graphite cathode (all them of 25 cm<sup>2</sup> area) operating at 20 mA cm<sup>-2</sup> and at T=20°C.

**Effect of type of electrolyte:** The presence of electrolytes increases the conductivity, diminishes the resistance and thus, lessens the energy cost of the process. Chloride and sulphate salts are two of the most used electrolytes for electrochemical treatment. Infact, anodic oxidation of aqueous solutions containing chloride and sulphate anions promotes the formation of hypochlorites and persulphates respectively, and that these chemical species are very powerful oxidant with high standard reduction potentials [16,29].

If sodium sulphate is used as supporting electrolyte the peroxydisulphate anions will be present in the solution, following the reaction (2) Whereas when the supporting electrolyte is sodium chloride, Cl<sup>-</sup> is expected to be oxidized either by direct electron transfer at anode surface or by a reaction with OH in the vicinity of electrode, reactions (3)- (9):

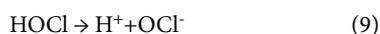
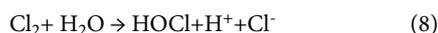
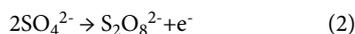
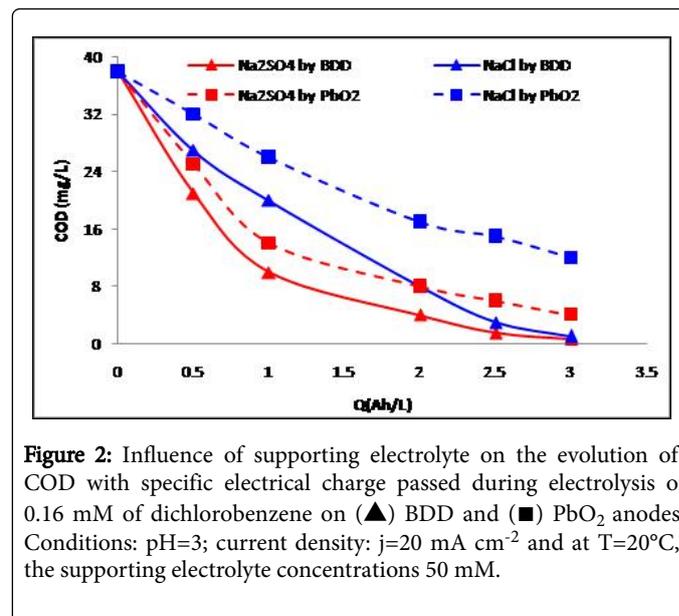


Figure 2 shows the influence of nature of supporting electrolyte (NaCl and Na<sub>2</sub>SO<sub>4</sub>) on the evolution with Q of COD during galvanostatic electrolyses (j=20 mA cm<sup>-2</sup>) of 0.16 mmol L<sup>-1</sup> of 1, 2-DCB and 1, 4-DCB at 20°C. It can be seen that the complete mineralization of two pesticides matter is achieved in the presence of the two electrolytes. The graph shows that the abatement of the COD

of dichlorobenzene in the presence of Na<sub>2</sub>SO<sub>4</sub> is more rapid than in the presence of NaCl. This suggests that in solutions containing sulfate ion, in addition to hydroxyl radicals, other oxidants may be electrogenerated. This indicates that hydroxyl radical is mainly responsible for the mineralization of dichlorobenzene and its oxidation intermediates. Thus, sodium sulphate was selected as the supporting electrolyte in this work.

**Effect of current density:** The effect of the applied current on the degradation of dichlorobenzene was studied at current density ranging from 4 and 40 mA cm<sup>-2</sup> for anodic oxidation with BDD and PbO<sub>2</sub> anodes. Results obtained are shown in Figure 3. It appears from Figure 3a and 3b that the nature of the anode influences significantly degradation of 1, 2-DCB: Anodic oxidation with BDD degrades 1, 2-DCB more efficiently than Anodic oxidation with PbO<sub>2</sub>. Indeed, 1, 2-DCB completely disappeared with 98–99% COD removal in 5 h with the BDD anode at 20 mA cm<sup>-2</sup> current density, while its complete disappearance in 7 h with PbO<sub>2</sub> anode under same conditions. The same phenomenon is observed within the degradation of 1, 4-DCB Figure 3c and 3d but with a mineralization rate slightly superior regarding 1, 2-DCB. The larger acceleration of COD abatement with time when Applied current density rises is expected by the concomitant generation of more amounts of M(·OH) [30].



**Figure 2:** Influence of supporting electrolyte on the evolution of COD with specific electrical charge passed during electrolysis of 0.16 mM of dichlorobenzene on (▲) BDD and (■) PbO<sub>2</sub> anodes; Conditions: pH=3; current density: j=20 mA cm<sup>-2</sup> and at T=20°C, the supporting electrolyte concentrations 50 mM.

In anodic oxidation, the pesticide degradation may be subjected to current control or mass transfer control. Initially, the COD concentration was relatively large, and accordingly its reduction rate was subjected to the current control. In this case, COD decreased linearly with the charge loading. In the case of the COD reduction rate that was subjected to the mass transfer control, only part of current supplied was used to oxidize pollutants, while the rest current was wasted for generation of oxygen. Therefore, the residual COD increased as the current density increased at a given charge loading. It was found that the amount of polymeric products increased with a rise in current density. The experimental results above suggest that the usage of different current densities at different oxidation stages is a good practice in industrial applications.

**Effect of pH value:** Solution pH is an important factor for wastewater treatment. In anodic oxidation, there are many reports on

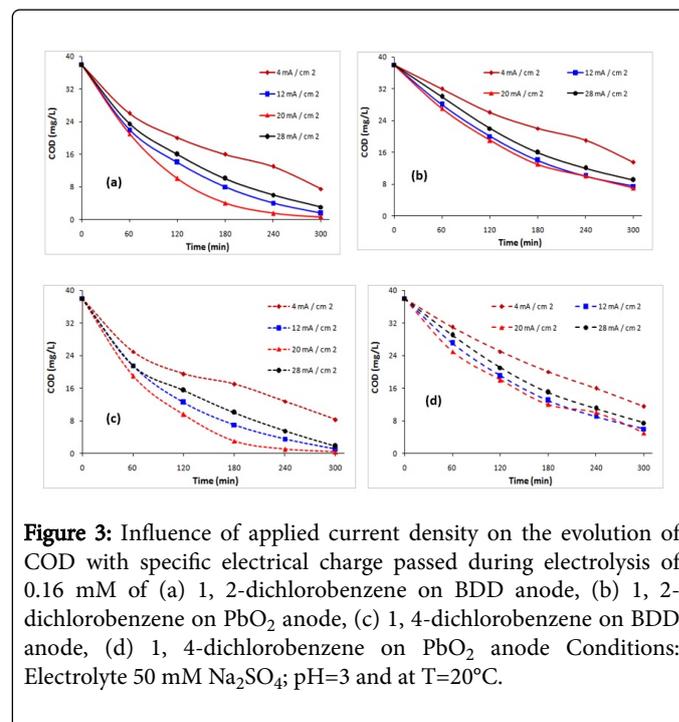
the influence of solution pH, but the results are diverse and even contradictory due to different organic structures and electrode materials [31]. Some authors reported that the oxidation process is more favorable in acidic media where a maximum generation of hydroxyl radicals was observed [32]. In contrast, others indicated that the efficiency of the process was increased in alkaline media [33]. According to this literature, it can be concluded that the effect of pH strongly depends on the nature of the investigated organics and of the supporting electrolyte. Therefore, the effect of pH on the degradation rate of 1, 2-DCB and 1, 4-DCB were studied at large pH range from acidic to basic. Aqueous solutions of DCB (25 mg L<sup>-1</sup>) were electrolyzed at pH values of 3 and 12 (Figure 4). As can be seen from this figure, the degradation of DCB in the acid medium is more efficient than the degradation in alkaline and neutral medium. This effect may be due to the extensive oxidation and/or chemical modification of the electrode surface, which suggests a change in the surface properties. Moreover, the solution was not buffered at the working pH value, the latter progressively decreased during the reaction presumably due to the formation of oxidized by-products. In fact, COD reduction attains more than 98% at pH=3.0 with a total disappearance of the color but it does not exceed 84% at pH=12.0. This is very important because industrial wastewater may have different pH values.

In pH=12.0, we observe that the solutions become a little bit turbid after oxidation. This indicates the formation of polymeric intermediate products by the hydroxyl group of DCB that makes the degradation much more difficult [17,34].

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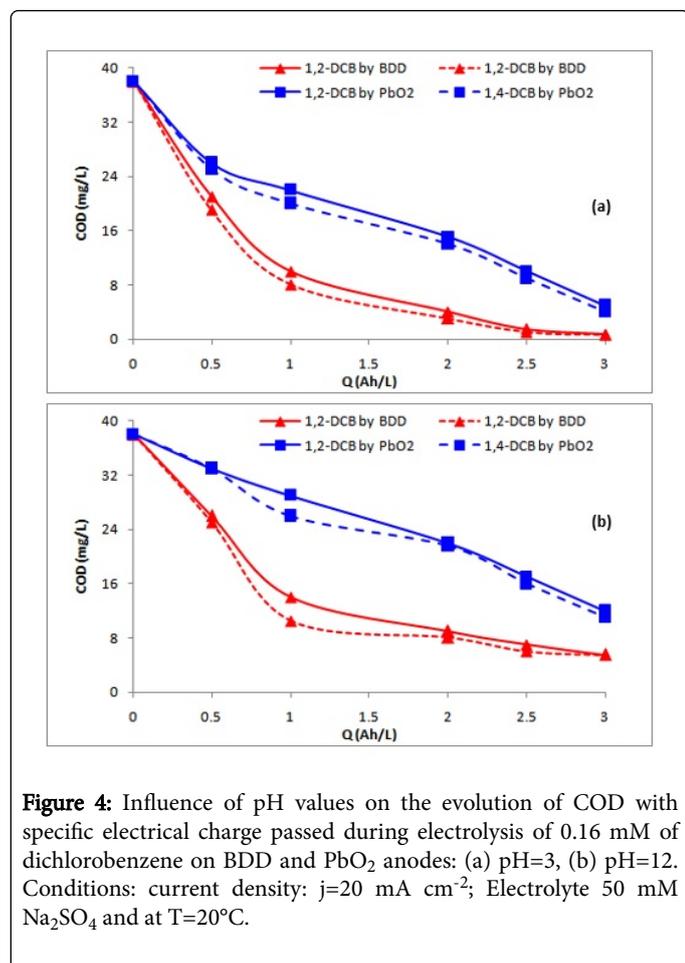
**Figure 3:** Influence of applied current density on the evolution of COD with specific electrical charge passed during electrolysis of 0.16 mM of (a) 1, 2-dichlorobenzene on BDD anode, (b) 1, 2-dichlorobenzene on PbO<sub>2</sub> anode, (c) 1, 4-dichlorobenzene on BDD anode, (d) 1, 4-dichlorobenzene on PbO<sub>2</sub> anode Conditions: Electrolyte 50 mM Na<sub>2</sub>SO<sub>4</sub>; pH=3 and at T=20°C.

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### Decay kinetics of dichlorobenzene

The kinetics of the reaction of initial pollutants with BDD (<sup>•</sup>OH) or PbO<sub>2</sub> (<sup>•</sup>OH) under the above operating conditions was followed by reversed-phase HPLC. The change of concentration of these compounds with electrolysis time is given in Figure 5. As can be seen, all dichlorobenzenes are removed at similar rate with BDD, disappearing from the medium at the same time close to 240 min. It is worth noting that the time required for total removal of 1, 2-DCB and 1, 4-DCB with BDD is very similar to that needed for their overall mineralization, indicating that dichlorobenzene persist in solution up to the end of the combustion process and they are degraded in parallel to their by-products by BDD (<sup>•</sup>OH). However, Figure 5 shows that 1, 2-DCB and 1, 4-DCB appears to be destroyed at slower rate using a PbO<sub>2</sub> anode and completely removed in a time much more than 240 min. It is well known that <sup>•</sup>OH formed at BDD remains mainly free on its surface where it attacks non-selectively and directly organics, whereas this radical is adsorbed on the PbO<sub>2</sub> surface, where it reacts selectively and more slowly with adsorbed organics [35]. According to this behavior, several authors recently reported that phenol, o-substituted phenols and nitrophenol pesticide are more rapidly destroyed with BDD than with PbO<sub>2</sub> using small conventional electrolytic cells [36].

The above concentration decays were well-fitted to a pseudo first-order kinetic equation and the excellent straight lines thus obtained are depicted in the inset panel of Figure 5. This suggests the production of a constant  $\cdot\text{OH}$  concentration at each anode during electrolysis, which is much higher than that of the initial pollutant reacting with it either on the PbO<sub>2</sub> surface or in the vicinity of the BDD electrode [15,37]. From this analysis, a similar pseudo-first-order rate constant ( $k_1$ ) of  $1.89 \times 10^{-4} \text{ s}^{-1}$  (square regression coefficient  $R^2=0.9993$ ) for 1, 4-DCB and  $1.93 \times 10^{-4} \text{ s}^{-1}$  ( $R^2=0.9990$ ) for 1, 2-DCB was determined for BDD, whereas a slightly lower  $k_1=1.53 \times 10^{-4} \text{ s}^{-1}$  ( $R^2=0.9998$ ) for 1, 2-DCB was found for PbO<sub>2</sub>. The quite analogous  $k_1$  values obtained for all dichlorobenzene using a BDD anode evidence that they undergo the same kind of attack by BDD ( $\cdot\text{OH}$ ) then leading to the production of similar primary aromatic by-products.

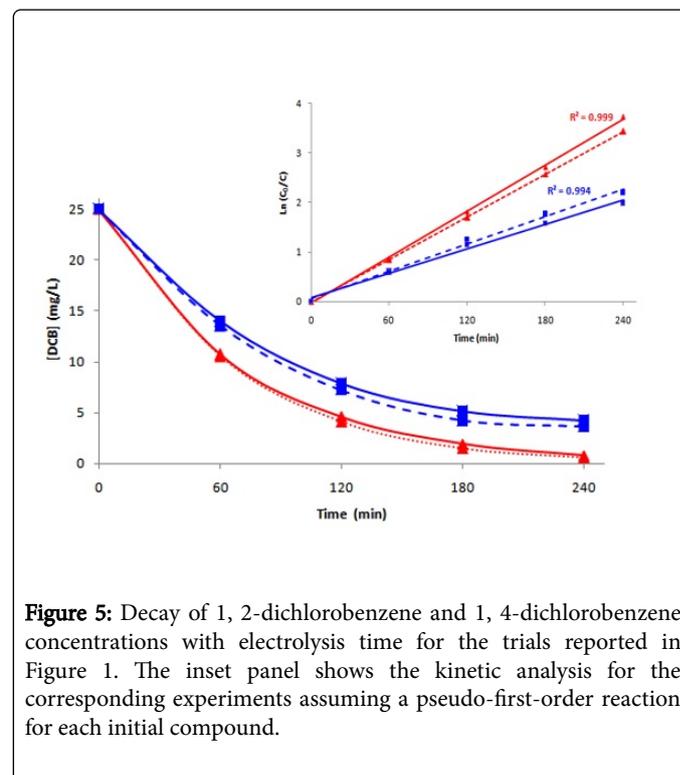


**Figure 4:** Influence of pH values on the evolution of COD with specific electrical charge passed during electrolysis of 0.16 mM of dichlorobenzene on BDD and PbO<sub>2</sub> anodes: (a) pH=3, (b) pH=12. Conditions: current density:  $j=20 \text{ mA cm}^{-2}$ ; Electrolyte 50 mM Na<sub>2</sub>SO<sub>4</sub> and at  $T=20^\circ\text{C}$ .

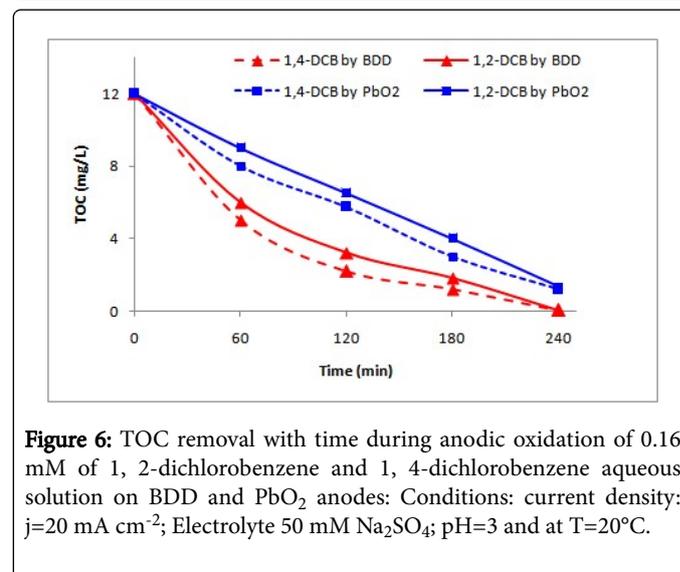
### Identification and evolution of intermediates

Changes in the concentration of 1, 2-DCB and 1, 4-DCB are important, but it is worth taking into account that the depletion of these latter does not mean total removal of the pollution problem. It is only an oxidation of the mother molecule (addition of  $-\text{OH}$  group or electron transfer) to its oxidation intermediates. For this reason, the TOC removal is a much more significant parameter, because it clearly indicates the mineralization of the pollutants, which is the complete destruction of the starting molecule and its transformation into carbon dioxide and water.

The TOC, as a function of time, is shown in Figure 6. Obviously, BDD anode is faster than PbO<sub>2</sub> in the mineralization of 1, 2-DCB and 1, 4-DCB. Reaction times required to mineralize completely the both pesticides are above 240 min for BDD anode. However, for this reaction time, less than 75% of mineralization is obtained for the electrolysis with PbO<sub>2</sub> anode.

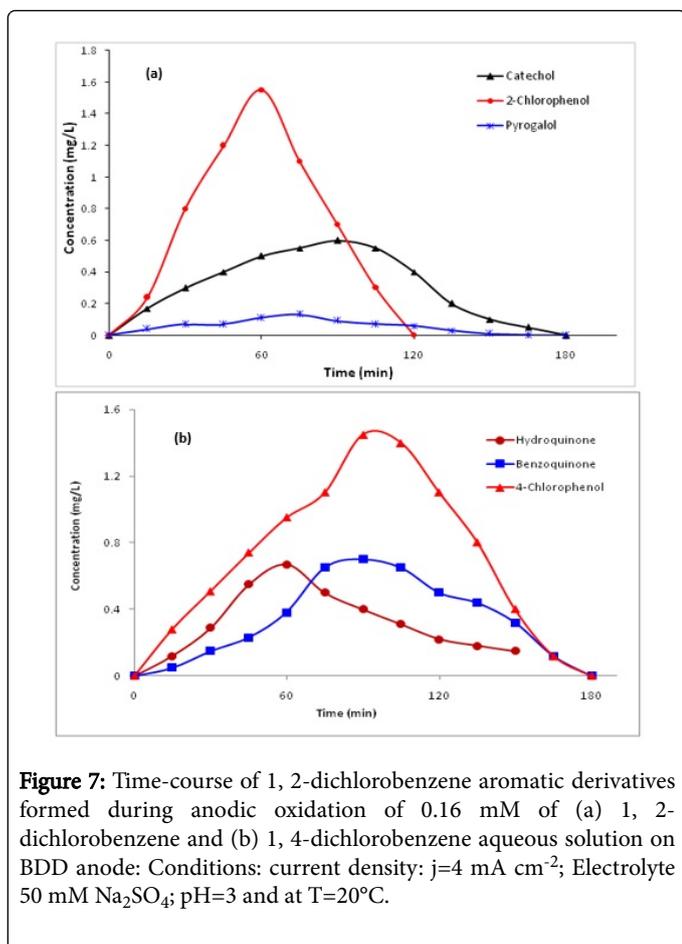


**Figure 5:** Decay of 1, 2-dichlorobenzene and 1, 4-dichlorobenzene concentrations with electrolysis time for the trials reported in Figure 1. The inset panel shows the kinetic analysis for the corresponding experiments assuming a pseudo-first-order reaction for each initial compound.



**Figure 6:** TOC removal with time during anodic oxidation of 0.16 mM of 1, 2-dichlorobenzene and 1, 4-dichlorobenzene aqueous solution on BDD and PbO<sub>2</sub> anodes: Conditions: current density:  $j=20 \text{ mA cm}^{-2}$ ; Electrolyte 50 mM Na<sub>2</sub>SO<sub>4</sub>; pH=3 and at  $T=20^\circ\text{C}$ .

The degradation of the toxic organic compounds by the anodic oxidation process can produce some aromatic intermediates that can be much more toxic than the initial product and that can pollute not only the water but also the environment. Thus, the identification of these intermediates is necessary to be able to propose a mechanism of mineralization by the attack of hydroxyl radicals [15,38].

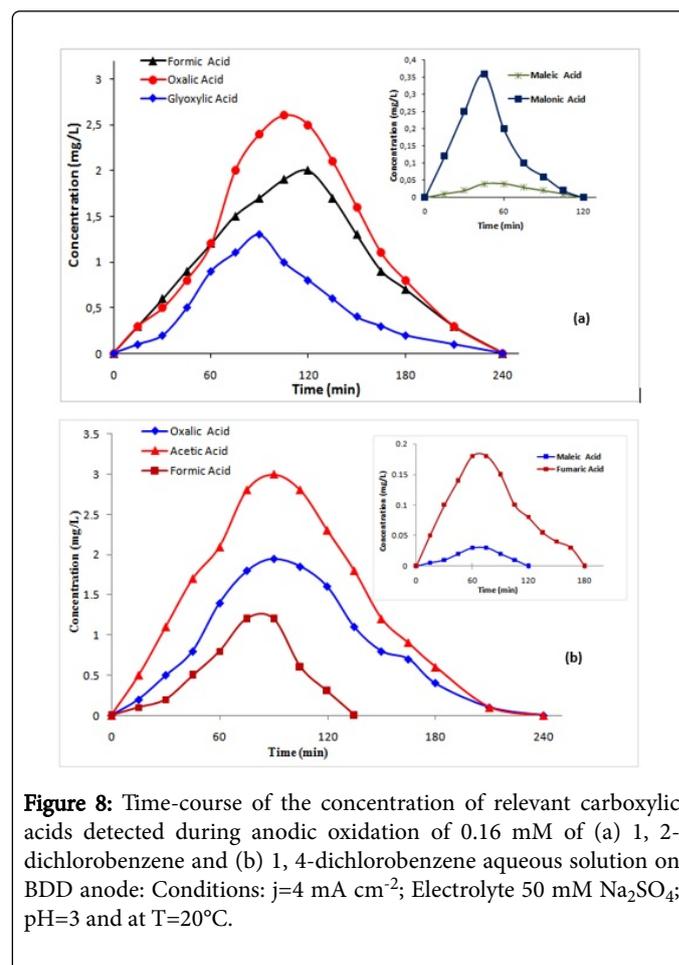


**Figure 7:** Time-course of 1, 2-dichlorobenzene aromatic derivatives formed during anodic oxidation of 0.16 mM of (a) 1, 2-dichlorobenzene and (b) 1, 4-dichlorobenzene aqueous solution on BDD anode: Conditions: current density:  $j=4 \text{ mA cm}^{-2}$ ; Electrolyte 50 mM Na<sub>2</sub>SO<sub>4</sub>; pH=3 and at T=20°C.

During anodic oxidation of 1, 2-DCB and 1, 4-DCB, main reactions are successively electrophilic addition of hydroxyl radical on the aromatic ring leading to the formation of polyhydroxylated benzene derivatives, such as Catechol, 2-chlorophenol and Pyrogallol for 1, 2-DCB and hydroquinone, benzoquinone and 4-chlorophenol for 1, 4-DCB. The evolution of these substances in aqueous medium is represented respectively in Figure 7a and 7b, in that these compounds are accumulated to the maximum 60-120 min of treatment with BDD anode, further being slowly removed to disappear in 120-180 min, that is a time similar to that needed for the total removal of the initial pollutant.

Carboxylic acids start their formation at the beginning of electrolysis as shown in Figure 8 and reach their maximum concentration between 60 and 120 min. Beyond this time, the acid concentration decreases rapidly toward vanishing which is proved in the Figure 6 where the TOC is removed in the same period. Formic, oxalic and glyoxylic acids identified during the mineralization for the 1, 2-DCB (Figure 8a) and oxalic, acetic and formic for the 1, 4-DCB (Figure 8b) were predominantly formed in initial stages, but there were also traces of fumaric and maleic. These acids are formed by the breaking of aromatic rings. On the other hand, the results obtained on the PbO<sub>2</sub> anode show (data not showed) that the concentration of these carboxylic acids decreases weakly with the electrolysis time and remain present in the solution even after 240 min of treatment. This result was already highlighted by Zazou et al. [4], Flores et al. [12] and Trelu et al. [21].

The release of Cl<sup>-</sup> ions is more important at the beginning of the electrolysis between 60 and 120 min with The BDD (Figure 9) and reaches its maximum after 120 min, and then its concentration decreases gradually to reach a value of 4 mg/L at the end of the electrolysis. This behavior can be explained by the oxidation at the anode of the Cl<sup>-</sup> ion in dichlorine Cl<sub>2</sub>, which then changes to the hypochlorous acid (HOCl) at the pH value of the medium, according to the reactions (3, 8 and 9) [4]. The time-course of Cl<sup>-</sup> concentration exhibits a very different behavior using PbO<sub>2</sub> anode, in fact the release of Cl<sup>-</sup> ions is complete at 1 h and the concentration of 15 mg/L remains constant along treatment. The same result is already reported by Duan et al. [24] for the degradation of 2-chlorophenol on PbO<sub>2</sub> anode.



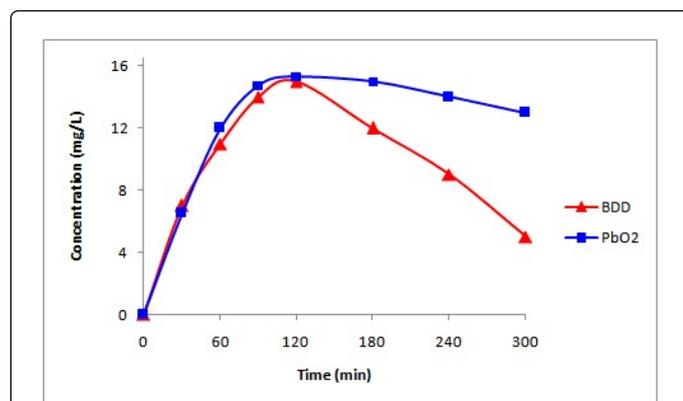
**Figure 8:** Time-course of the concentration of relevant carboxylic acids detected during anodic oxidation of 0.16 mM of (a) 1, 2-dichlorobenzene and (b) 1, 4-dichlorobenzene aqueous solution on BDD anode: Conditions:  $j=4 \text{ mA cm}^{-2}$ ; Electrolyte 50 mM Na<sub>2</sub>SO<sub>4</sub>; pH=3 and at T=20°C.

### Possible mechanism of dichlorobenzene degradation

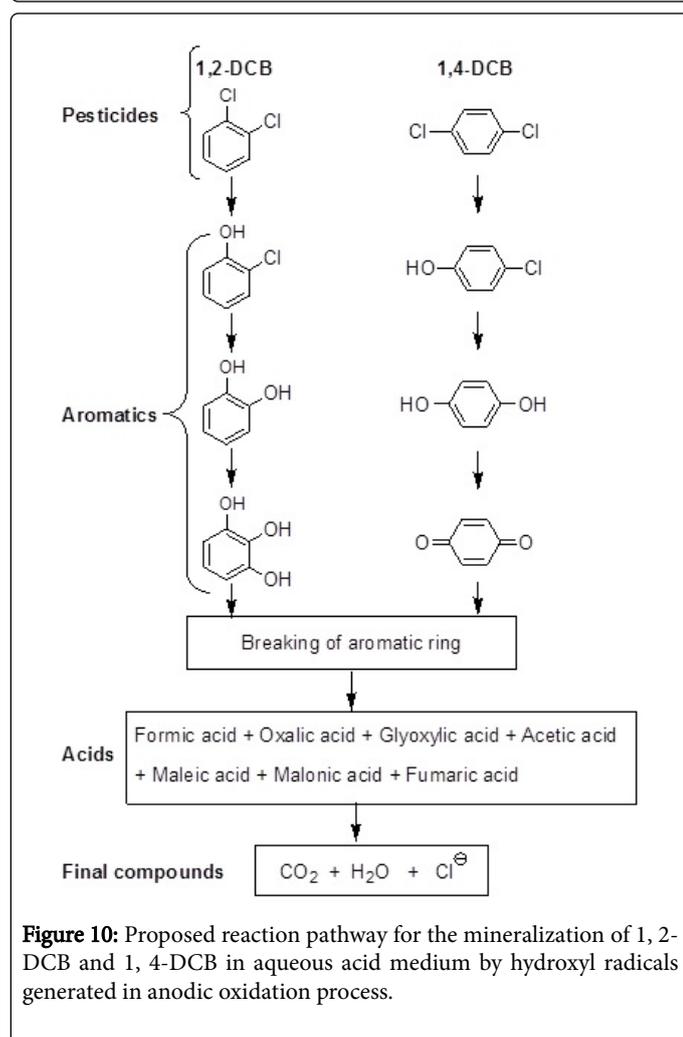
The aromatic intermediates, carboxylic acids and chloride ions formed during the mineralization reaction, as well as their evolution over time in the treatment of aqueous solutions of 1,2-DCB and 1,4-DCB by anodic oxidation, allowed to propose the following mineralization mechanism (Figure 10).

According to Figure 10, the degradation of the two pesticides takes place in a series of reactions as early as the first minutes of anodic oxidation treatment. Intermediates (A and B) were obtained from the over position of chloride ion by the attack of hydroxyl radicals. It then degrades to form the intermediates (C and D) with the release of the chlorinated inorganic ions. The intermediates (E and F) decompose to

form the carboxylic acids and then transform into CO<sub>2</sub> and H<sub>2</sub>O under the optimum mineralization conditions.



**Figure 9:** Accumulation of chloride ions detected during anodic oxidation of 0.16 mM of 1, 2-dichlorobenzene aqueous solution on BDD and PbO<sub>2</sub> anodes: Conditions:  $j=4 \text{ mA cm}^{-2}$ ; Electrolyte 50 mM Na<sub>2</sub>SO<sub>4</sub>; pH=3 and at T=20°C.



**Figure 10:** Proposed reaction pathway for the mineralization of 1, 2-DCB and 1, 4-DCB in aqueous acid medium by hydroxyl radicals generated in anodic oxidation process.

## Conclusion

Since they have a strong resistance to biodegradation and they have a higher toxicity rate, the pesticides 1,2- DCB and 1,4- DCB are classified too hazardous to the environment. Within this framework, our study showed that the direct electrochemical advanced oxidation process is so efficient that it can mineralize these latter pesticides.

Under the optimum conditions of degradation, the disappearance of these two molecules requires an electrolysis time of less than 240 min. Furthermore, the anodic oxidation method allowed the determination of the 1, 2-DCB and 1, 4-DCB rate constants ( $1.89 \times 10^{-4} \text{ s}^{-1}$  and  $1.93 \times 10^{-4} \text{ s}^{-1}$ ) respectively.

The results of the TOC and COD measurements confirmed that the anodic oxidation process with the anode BDD in Na<sub>2</sub>SO<sub>4</sub> medium with 20 mA/cm<sup>2</sup>, mineralizes 98% of the organic charge for 1,2- DCB and 1,4- DCB. On the other hand, with the anode PbO<sub>2</sub>, the mineralization rate remains lower. In both cases, the TOC of the solution decreases exponentially during processing and the mineralization is much faster at the start of treatment than at its end. Indeed, the action of hydroxyl radicals on aromatic rings is more effective than on aliphatic products that resist mineralization and their mineralization takes time. Residual carboxylic acids persist even at the end of treatment, which is environmentally safe and can be degraded by biodegradation.

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