The effect of the sp^3/sp^2 carbon ratio on the electrochemical oxidation of 2,4-D with p-Si BDD anodes

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Abstract

Boron-doped diamond films on silicon substrates (p-Si BDD) with different sp^3/sp^2 carbon ratios are systematically varied in electrodes used to oxidize 2,4-dichlorophenoxyacetic acid (2,4-D) in synthetic wastewater containing chlorides. 2,4-D is completely mineralized during the electrolysis. A higher sp^3/sp^2 ratio in the anode results in a more rapid and efficient oxidative removal of 2,4-D. Chlorinated compounds such as 4-chlororesorcinol, 2-chlorophenol, and 2,4-dichlorophenol form as intermediates during the oxidative treatment. Although these compounds are completely depleted during the electrolysis, their maximum observed concentrations decrease as the sp^3 content increases in the anode. On the contrary, higher maximum concentrations are observed for non-chlorinated intermediates, especially hydroquinone, and there is a greater formation of chlorates and perchlorates in chloride-containing solutions as the sp^3 content increases in the anode.

Keywords

Boron-doped diamond, sp^3/sp^2 ratio, electrolysis, pesticide, 2-4-D, perchlorate

Highlights

- The efficiency of the electrolysis of 2,4-D depends on the sp^3/sp^2 ratio of the diamond anode.
- A higher sp^3/sp^2 ratio lowers the energy required to mineralize the pesticide.
- The sp^3/sp^2 ratio influences the concentration but not the type of intermediates produced.
- Chlorate and perchlorate production is favored at higher sp^3/sp^2 ratios.

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Introduction

Electro-oxidation with diamond anodes carried out at the laboratory or bench scale has been demonstrated to be a very effective treatment for the removal of various types of organic pollutants typically resilient to removal by other technologies, such as dyes, pharmaceutics, phthalates and pesticides [1]. In this context, compared with carbonaceous, platinum and metal oxide electrodes, conductive diamond-coated electrodes exhibit exemplary properties such as high overpotential for water electrolysis, excellent chemical and electrochemical stability, satisfactory conductivity and the ability to generate various powerful oxidants depending on the wastewater composition and the operational conditions [2, 3]. These excellent properties are attributed to the production and weak adsorption of hydroxyl radicals $HO^{\bullet}$ [4], which results in a low electrochemical activity of the oxygen evolution reaction and, consequently, in a high chemical reactivity for the oxidation of organics [5]. However, the intensive study of the applications of diamonds in environmental remediation [6-8], few studies have assessed the properties of the diamond coating in terms of the remediation process performance. Thus, many important features are known to influence the efficiency of diamond electrode performance, such as the doping type and level, morphological features, non-diamond impurity content, crystallographic orientation, and surface group functionalities (H, O, F, etc.), and one of the most significant is certainly the sp^3/sp^2 ratio.

Diamond is an extremely hard crystalline form of carbon, with each carbon atom tetrahedrally bonded to four other sp^3 hybridized carbons. By doping the deposited diamond film grown by chemical vapor deposition (CVD) with impurities such as boron, nitrogen, or fluoride, the wide gap of diamond (5.5 eV) can be reduced, producing a semiconductor material. According to the literature, the most interesting doping agent is boron. In the synthetic boron-doped diamond (BDD), boron acts as an electron acceptor

due to an electron deficiency in its external shell imparting p-type semiconducting properties. The effect of boron doping has been studied by many authors. An interesting contribution from Bogdanowicz [9] involved the impact of the [B]/[C] ratio (boron/carbon ratio) in a Si/BDD electrode on the efficiency of the electrochemical oxidation of the reactive dye Rubin F-2B 9. Electrodes with [B]/[C] = 10000 attained a higher electroactivity than those with [B]/[C] = 2000, and the former electrodes were much more efficient in the degradation of the dye. These differences were explained in terms of the surface microstructure of the diamond films and the relatively low surface resistivity. These results also suggest that a higher boron concentration might contribute to the enhancement of electric forces responsible for the electro-generation of oxidants. Similar conclusions were drawn from the study of the dye reactive orange (RO) 16 [10]. This work demonstrated that the diamond electrodes doped with the greatest amount of boron exhibited the highest performance for similar contents of non-diamond carbon. The presence of graphite in the sample with a higher boron percentage may be hidden beneath by the other nearby band features. However, a small volume of randomly distributed non-diamond carbon atoms may form different conduction routes that contribute to the performance of this electrode.

These results illustrate the significance of not only the boron content but also the sp^2 carbon content in electrolytic performance. It is important to consider that diamond coatings are synthesized under conditions in which graphite synthesis is competitive, and non-diamond components may also be incorporated into their structure. Studies have demonstrated that these aggregates can be associated with amorphous regions that contain sp^2 graphite domains. Comninellis's group intensively studied the electron transfer kinetics of composite diamond (sp^3) – graphite (sp^2) electrodes in various works [11-13] [14-17]. Their results demonstrated that the graphite particles deposited on the electrode

surface promote this outer-sphere reaction by acting as charge transfer mediators between the redox couple and the electrode surface. Consequently, the decrease in electrode activity after anodic polarization may be explained by the corrosion of the graphitic (sp^2) active species initially present on the electrode surface. After these pioneering studies, Enache [18] showed that the diamond electrode background current and the working potential window are influenced by the electroactivity of these non-diamond carbon impurities, and Migliorini [19] demonstrated the influence of methane addition to the gas phase for different doping levels on BDD films grown on titanium substrates. The sp^2 phase increased with CH_4 addition for all films studied. For highly doped films, this diamond grain decrease favored sp^2 carbon incorporation at the diamond grain boundaries. Regarding the same topic, Guinea et al. also studied the effect of the sp^3/sp^2 ratio [20] in the degradation of enrofloxacin, demonstrating that this ratio has a crucial effect on the efficiency of the degradation; tailoring new electrodes for special applications could be a topic of a great interest in the development of environmental electrochemistry. Similar results were obtained by de Araujo [21] in a recent study in which the influence of the sp^3/sp^2 ratio on the degradation of rhodamine B (RhB) was assessed. Electrolysis performed by diamonds with a lower content of sp^3 carbon led to less abrupt oxidation curves, favoring the electrochemical conversion of RhB. In the presence of higher contents of diamond carbon, total organic carbon (TOC) decayed more rapidly, and a sort of electrochemical combustion may be justified.

Previous works have demonstrated that electrode characteristics and the relation between the conductivity of the BDD film and the level of impurities present is important to attain higher electrode efficiencies in electrochemical applications. These are not the only factors affecting the performance of electrolysis with diamonds; the diamond's properties

also influence the production of oxidants [22, 23], in which the thickness of the coating was found to play a very important role.

However, further is necessary to clarify this point, and the present work assessed the performance of Si/BDD with different sp^3-sp^2 ratios in the electrolytic removal of a model pesticide from water. Synthetic wastewater containing solutions of the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) and sodium chloride were used. The influence of the sp^3/sp^2 ratio on pesticide removal and chloride oxidation was evaluated during the electrolysis. Pesticide remediation is a major environmental issue [24] [25] [26]. Typically, these substances exhibit bio-recalcitrant properties and high toxicity and persist in the environment. In addition, they can be easily transported by several mechanisms and may therefore contaminate groundwater by leaching through the soil and surface water through runoff. The herbicide 2,4-D is the most commonly used acidic phenoxy herbicide in agriculture, forestry, and lawn care and is used to a lesser extent in parks, golf courses, and gardening. 2,4-D is highly water-soluble (i.e., 900 mg/L at 25 °C) and can be detected in surface water and ground water even long after its use [27]. Conventional methods for wastewater treatment such as coagulation or biological treatment are unsatisfactory or ineffective in the removal of 2,4-D from wastewater. For this reason, many technologies are currently being studied and developed to efficiently destroy this pollutant, and electrolysis with BDD is among the most promising.

Materials and methods

2.1. Chemicals

All chemicals, including sodium sulfate and sodium chloride from Fluka (Spain) and 2,4-D, hydroquinone, 1,4-benzoquinone, 4-chlororesorcinol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol from Sigma-Aldrich (Spain) were of analytical

grade and used as received. HPLC-grade acetonitrile (Sigma-Aldrich, Spain) was used as the mobile phase. Double-deionized water (Millipore Milli-Q system, resistivity = 18.2 MΩ cm at 25 ºC) was used to prepare all solutions.

2.2 Experimental setup

All electrolytic tests were carried out in a single-compartment electrochemical flow cell. Boron-doped diamond electrodes supplied and characterized by Adamant Technologies (Switzerland) synthesized the monocrystalline p-type Si substrate (thickness 2 mm, resistivity 100 mΩ cm) with a diamond coating of 2–3 μm by the hot filament chemical vapor deposition technique (HF CVD). The diamond quality and the boron level were analyzed by micro-Raman scattering spectroscopy, and the certificate of analysis was signed by the testing engineer (reference number: 24026); the electrodes used as the anode all had a boron concentration of 500 ppm and had the following distinct sp^3/sp^2 ratios: BDD_1 = 165, BDD_2 = 176, BDD_3 = 206, BDD_4 = 225, BDD_5 = 262 and BDD_6 = 323. A BDD electrode with an sp^3-sp^2 ratio of 176 was used as the cathode. Both electrodes were circular (100 mm diameter), covering a geometric area of 70 cm^2. The BDD electrode was polarized for 10 min in a 1 M Na_2SO_4 solution at 15 mA cm^{-2} prior to the electrolysis assays.

Galvanostatic electrolysis was carried using 0.6 dm^3 of a solution containing 100 mg dm^{-3} 2,4-D at natural pH (3.5). Aqueous sodium chloride (0.05 M) was used as the supporting electrolyte. The solution was recirculated between the cell and an auxiliary tank at a constant flow rate (26.4 dm^3 h^{-1}) to favor mixing conditions, gas stripping and temperature regulation. A heat exchanger coupled with a controlled thermostatic bath was used to maintain the temperature at 25 ºC.

2.3 Analysis procedures and methods

All samples taken from the electrolyzed solutions were filtered through Whatman® nylon membrane filters (0.45 µm) before analysis. Measurements of pH were carried out with an InoLab WTW pH meter. The decay of the herbicide and the evolution of its aromatic products were followed by reversed-phase chromatography and measurements of TOC and chemical oxygen demand (COD). The chromatography system was an Agilent 1100 series coupled a UV detector. A Phenomenex Gemini 5 µm C18 analytical column was used. The mobile phase consisted of 60 % acetonitrile/40 % water with 2 % acetic acid (flow rate of 0.4 cm^3 min^{-1}). The UV detection wavelength was 280 nm, the temperature was maintained at 25 ºC, and the injection volume was 20 µL. The TOC concentration was monitored on a Multi N/C 3100 Analytik Jena analyzer. The COD was monitored using Spectroquant® standard kits in a range of 0-150 mg dm^{-3} (1.18751.0001) from Merck. These solutions were oxidized by digestion for 2 h at 150 ºC in an ECO 25 block thermoreactor (Velp Scientifica). After the ambient temperature was reached, the absorbance of the samples was read at 600 nm in a spectrophotometer (Hach DR 2000). Samples with a chloride concentration above 2 g dm^{-3} were diluted as recommended. Chloride anions (Cl^-, ClO_3^-, ClO_4^-) were determined by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column, a mobile phase of 2.5 mM phthalic acid at pH 4.0 and a flow rate of 1×10^{-3} dm^3 min^{-1}. The detection limit was 0.007 mg dm^{-3} for both chlorate and perchlorate. Hypochlorite ($HClO^-$) was determined by titration with 0.001 M As_2O_3 in 2.0 M NaOH. Samples were pretreated by adding 2×10^{-3} dm^3 of 2.0 M NaOH to increase the pH.

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Results and discussion

Figure 1 shows the changes in the concentration of 2,4-D during the six treatment tests with different sp^3/sp^2 ratios in BDD electrodes. Complete pesticide removal is attained for all electrodes studied. A higher diamond content results in a faster and more efficient

decay of 2,4-D in the bulk electrolysis. An increase in the sp^3/sp^2 ratio from 165 to 323 improves the 2,4-D removal from 69.7 % to 93.5 % for an electric charge of Q = 15.09 kA h dm^{-3}. In terms of the energy costs (taking into account the resulting cell voltage in the galvanostatic electrolysis), the calculated energy requirement to attain complete removal with the highest sp^3/sp^2 ratio is approximately 157 kWh m^{-3}. On the contrary, the energy required for total depletion increases to 244 kWh m^{-3} with the lowest diamond content, meaning that the process is 55.4% more expensive in terms of energy consumption. This observation indicates that tailoring electrodes for each application could become the most important in future applications. At this point, the inset of the figure shows the changes in the cell potential during the six electrolytic tests. In all tests, the cell voltage decreases slightly during the electrolytic treatments down to a constant value. The changes are more pronounced in the initial stage of the electrolytic tests, within a range 0-5 Ah dm^{-3}. This is a typical behavior in most electrochemical remediation tests, and it can be related to the important change in the conductivity of the electrolyte. Comparing the values of the cell voltage obtained, there is not a clear trend caused by the diamond/graphite carbon ratio, except that electrolysis using the anode with the highest sp^3/sp^2 ratio obtained the worst results. The ohmic resistances in the diamond electrodes are more closely related to the boron content and the other parameters than to the sp^3/sp^2 ratio, as has been noted in previous works [28, 29]. No influence of this higher resistance is observed on the oxidation efficiency [28], and, in the present study, the boron content of the electrodes was nearly the same.

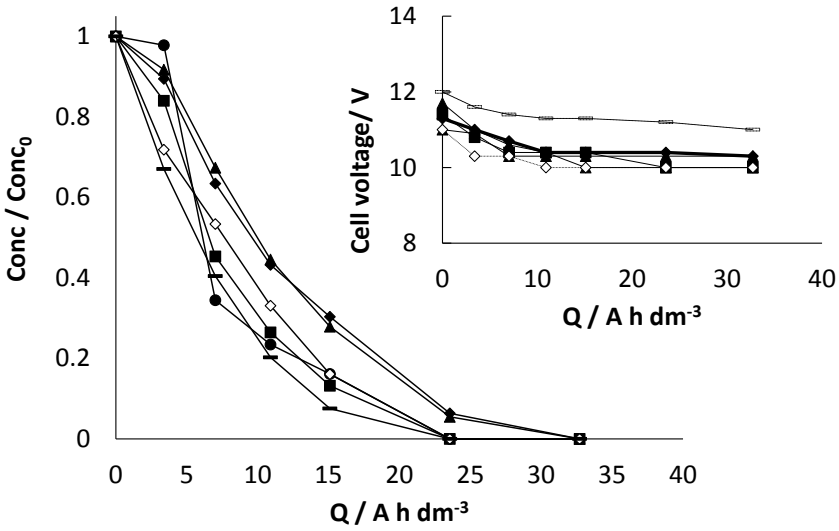

Figure 1. Relative [2,4-D] decay as a function of the applied charge per unit volume of the electrolyzed solution (Q) during the electrochemical oxidation of synthetic wastewater in a single-compartment electrochemical flow cell equipped with electrodes with an sp^3/sp^2 ratio of (♦) 165, (▲) 176, (●) 206, (■) 225, (◊) 262 and (-) 323. Inset: changes in the cell voltage during the electrolysis tests. Conditions: 100 mA cm^{-2} and 25 °C.

Depletion of the pesticide is an interesting parameter, but it does not inform the complete progress of the treatment as for TOC and COD. Figure 2 shows the effect of the graphite/diamond ratio on the decay of COD and TOC. Both parameters are completely depleted during treatments with all studied electrodes, indicating that these electrodes are very effective not only in the degradation of this pesticide but also in the degradation of its intermediates. Complete mineralization can be attained regardless of the sp^3/sp^2 ratio of the diamond coating (within a range of 165-323). This result can be explained in terms of the high production of hydroxyl radicals and other oxidants on the electrode surface. When using chloride as the supporting electrolyte, the expected oxidants are hypochlorite,

chlorite, chlorate and perchlorate, with perchlorate as the final product in the oxidation of chlorides with diamond anodes [30-33]. Formation of these species will be discussed further because it is heavily debated in the literature [34, 35] and is the main drawback to the electrolysis of wastewater due to their hazardous features. Regarding their effect on oxidation, although chlorate and perchlorate are known to be stronger oxidants than hypochlorite (and gaseous chlorine), their role is less effective at room temperature because of their well-known slower kinetics.

Figure 2a shows that the decay of the COD changes very rapidly, and total depletion is obtained with a very low current charge. This can be explained in terms of the presence of chlorides and the formation of a high concentration of chlorinated oxidants. At this point, it is important to keep in mind that COD measurements are significantly affected by the chloride content. In terms of mineralization, the decay of TOC is softer than that of the COD, as observed in Figure 2b. However, complete mineralization is attained at low applied electric charge. The most efficient removal is achieved using the BDD with highest diamond content. Hence, the sp^3 content speeds up the degradation process and, hence, decreases the Q required for total removal. Thus, complete mineralization is obtained at specific charge of 15.09 kAh m^{-3} using the electrode with an sp^3/sp^2 ratio of 323, whereas the electrode with an sp^3/sp^2 ratio of 165 requires 32.70 kA h m^{-3}. In terms of TOC removal while changing the sp^3/sp^2 ratio, the improvement in the charge required for mineralization is even higher than that reported for the removal of the only the pesticide molecule and reaches 116.7%, again illustrating the necessity of tailoring anode electrodes for each particular application.

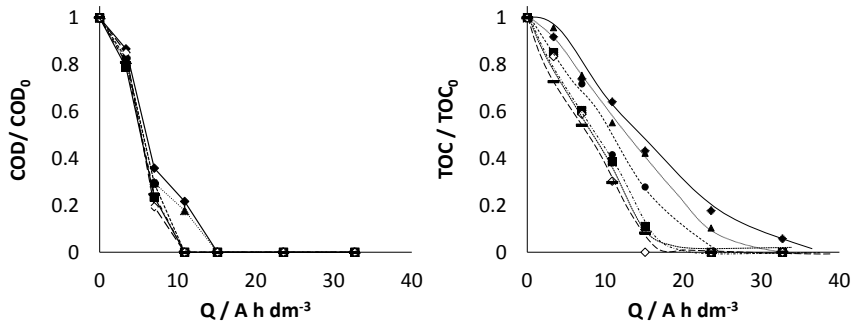

Figure 2. (a) Relative *COD* and (b) *TOC* decay as a function of the applied charge per unit volume of electrolyzed solution (Q_{ap}) during the electrochemical oxidation of synthetic wastewater with a single-compartment electrochemical flow cell equipped with electrodes with sp^3-sp^2 ratios of (♦) 165, (▲) 176, (●) 206, (■) 225, (◊) 262 and (-) 323. Conditions: 100 mA cm^{-2} and 25 °C.

When experimental data are plotted in semi-logarithmic scales (not shown), straight lines are attained. This result is expected in light of previous studies and indicates that the rate is controlled by mass transport limitations, by mediated electro-oxidation or by a combination of both bottlenecks [36-39]. The reduced slope in the beginning of the curves of concentration vs. Q and TOC vs. Q could be attributed to the competition between the oxidation of organics by direct transfer and hydroxyl radical-mediated reactions and the production of ClO_x compounds. Table 1 shows the values obtained for the kinetic constant calculated for the removal of TOC by fitting experimental data to first order kinetics. The kinetic constant clearly increases with the sp^3/sp^2 ratio, and fitting regression coefficients are indicative of the coexistence of different oxidation mechanisms because of their moderate values.

Table 1. Pseudo-first order kinetic constants calculated for TOC removal.

	TOC	
sp^3/sp^2 ratio	K_{TOC}	R^2
165	0.0103	0.96
176	0.0134	0.87
206	0.0186	0.84
225	0.0213	0.94
262	0.0261	0.89
323	0.0262	0.95

Table 2 shows the maximum concentration of the aromatic intermediates detected by HPLC in the six tests. 2,4-Dichlorophenol is the main (in terms of concentration) and first (in terms of oxidation progress) intermediate formed after 2,4-D oxidation. The monitored maximum concentration decreased with the increase in the sp^3 content. The same behavior can be observed (in this case, with a higher fluctuation) for 2-chlorophenol. However, for hydroquinone, the observation is completely opposite, and higher concentrations are observed when the sp^3 content increases. This indicates that, even though the sp^3/sp^2 ratio of the diamond coating does not affect the types of intermediates formed, it affects the efficiency and rate of dechlorination. A higher content of sp^3 diamond favors the rapid dechlorination of 2,4-D (and other chlorinated intermediates) and leads to the transient accumulation of hydroquinone in the bulk. The main intermediates detected were 4-chlororesorcinol, 2-chlorophenol, 2,4-dichlorophenol, and hydroquinone, and this speciation agrees with that observed in previous studies [40-43].

Table 2. Maximum concentrations (mg dm^{-3}) of aromatic intermediates detected.

Intermediate	sp^3/sp^2 ratio					
	165	176	206	225	262	323
4-Chlororesorcinol	9.83	11.62	11.57	11.05	4.39	0
2-Chlorophenol	49.50	4.46	14.69	2.96	23.95	8.80
2,4-Dichlorophenol	61.91	60.25	59.90	41.75	29.51	5.59
Hydroquinone	8.70	16.30	19.14	16.80	23.44	32.37
4-Chlorophenol	0.00	4.01	2.25	2.91	0.00	0.00

Many studies have demonstrated that electrochemical oxidation can occur either by direct or indirect processes. The promoted mechanisms for a given electrolysis are expected to mainly depend on the characteristics of the anodic material, the state of oxygen on the electrode surface and the overpotential for oxygen evolution [44]. These parameters are important in understanding the electrochemical reaction activity, and they affect the efficiency of the oxidation processes. The BDD electrode is usually defined as a "non-active" anode, for which the interaction between the physically absorbed radical $HO^{\bullet}$ and the electrode surface is weak. When oxygen vacancy exists in film, oxygen transition may occur from the physically adsorbed "active oxygen" to the crystal lattice of the films, forming higher oxides called chemisorbed "active oxygen" (MO) [45]. The existence of M(radical $HO^{\bullet}$) favors the electrochemical combustion of organic compounds with CO_2 as the final product, whereas MO favors electrochemical conversion, which produces more intermediates. The results obtained in this work indicate that using electrodes with

a higher graphite carbon content and the enhanced combination of physically absorbed "active oxygen" (M(radical HO$^{\bullet}$)) and chemisorbed "active oxygen" (MO) on the BDD electrode surface leads to a decrease in the electrocatalytic activity towards the total destruction of organics and favors the electrochemical conversion of organic compounds. Therefore, higher concentrations of intermediates are observed. In addition, the dechlorination of pollutants, which is the first step in the depletion, becomes less effective for electrodes with a higher sp^2 content. These results are in agreement with those obtained in a previous study in which diamond anodes with lower sp^3/sp^2 ratios (compared to those used in this work) were used to remove enrofloxacin [20]. The authors in this study observed that, by increasing the sp^3/sp^2 ratio from 45 to 105, the efficiency of the mineralization of this pharmaceutical species increased from 5 to almost 15 mg TOC $(Ah)^{-1}$. More recently, using diamond anodes with an sp^3/sp^2 range closer to those used in the present work produced results for the oxidation of Rhodamine B [21] that also agree with the present study. Thus, complete mineralization of Rhodamine B using a diamond electrode with an sp^3/sp^2 ratio of 329 required 60% of the electric charge necessary for a diamond anode with a ratio of 165.

Once the influence of the sp^3/sp^2 ratio on the removal of organic pollutants is clarified, it is important to focus on the electrolyte. In this work, a chloride medium was selected as the supporting electrolyte because, even though it is clearly not suitable for environmental applications (because of the well-known formation of chlorates and perchlorates), the oxidation of chloride is well characterized and, therefore, gives valuable information about the oxidation mechanisms with diamond coatings. Figure 3 shows the changes in the concentration of ClO_x compounds obtained during the electrolysis test with electrodes containing the lowest (sp^3/sp^2 = 165) and highest (sp^3/sp^2 = 323) diamond contents.

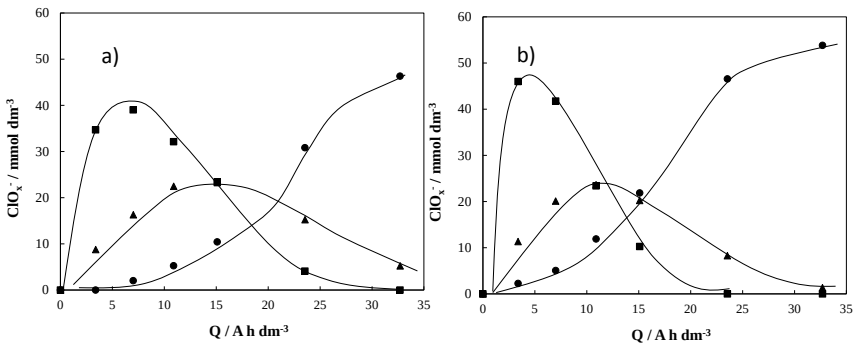

Figure 3. Evolution of ClO_x compounds with an applied charge (Q) during the electrolysis of 100 mg dm^{-3} 2,4-D in chloride media at 100 mA cm^{-2} with sp^3/sp^2= a) 165 and b) 323. (■) Hypochlorite; (▲) Chlorate; (●) Perchlorate.

As observed, chlorides are oxidized to gaseous chlorine/hypochlorite, and the oxidation does not stop at this point as in electrolysis with conventional DSA or Pt electrodes but continues to chlorate and perchlorate. This means that a large fraction of the electric charge applied is spent oxidizing chlorides and ClO_x compounds and not in the oxidation of organics, reducing the efficiency of the treatment. This behavior is very similar in the two electrolysis experiments shown, despite the very different sp^3/sp^2 ratios, and chloride is completely depleted during the experiments. However, electrolysis using the diamond coating with a higher sp^3 content (part b) is faster, and the hypochlorite and chlorate peaks are obtained at 4 and 11 kAh m^{-3}, respectively; the same intermediate peaks are obtained at 8 and 15 kAh m^{-3} using an electrode with a sp^3/sp^2 ratio of 165. To further discuss the influence of diamond/graphite carbon on the oxidation of chlorinated species, Figure 4 compares the production of perchlorate in the six tests. Clearly, the rate of production and the maximum concentration of perchlorate attained depend on the sp^3/sp^2 ratio and increase with the diamond content. Perchlorate should clearly be avoided in any

remediation technology and was only used in the present study to increase the knowledge of the production of oxidants that occurs simultaneously with the depletion of the pesticide. This information is important and reveals that the production of strong oxidants in the reaction media is promoted by diamond anodes with higher sp^3 contents.

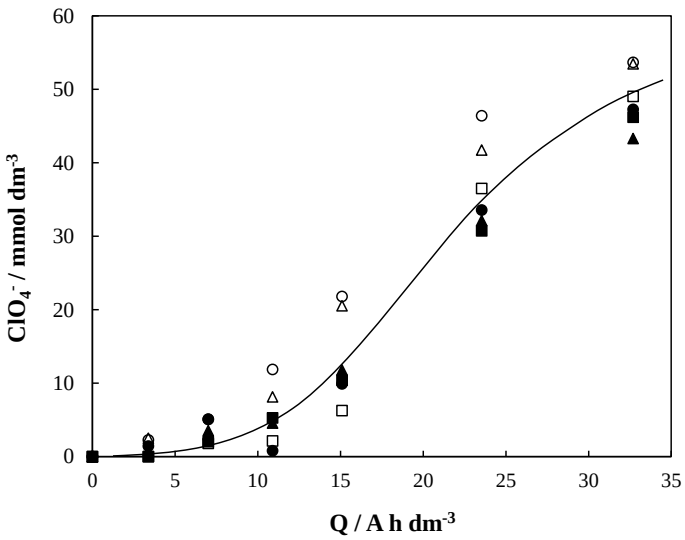

Figure 4. Evolution of a) hypochlorite and b) chlorate compounds as a function of the applied charge per unit volume of electrolyzed solution (Q_{ap}) in the electrolysis of 100 mg dm^{-3} 2,4-D in chloride media at 100 mA cm^{-2} using electrodes with sp^3/sp^2 ratios of (■) 165, (▲) 176, (●) 206, (□) 225, (◊) 262 and (○) 323.

Conclusions

From this work, the following conclusions can be drawn:

- Electrolysis with diamond anodes leads to the complete depletion of 2,4-D and to the mineralization of intermediates, regardless of the sp^3/sp^2 ratio of the diamond anode.
- A higher sp^3/sp^2 ratio results in a more rapid and efficient mineralization of 2,4-D. Increases of more than 100% in the efficiency (and thus in cost) can be obtained by altering the sp^3/sp^2 ratio, illustrating the importance of the proper selection of the sp^3/sp^2 ratio.
- The sp^3/sp^2 ratio influences the concentration but not the type of intermediates observed. Higher sp^3/sp^2 ratios lead to the rapid dechlorination of 2,4-D (and other chlorinated intermediates) and to the transient accumulation of hydroquinone in the bulk.
- The rate of production and the maximum concentration of perchlorate attained depend on the sp^3/sp^2 ratio and increase with the diamond content.

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