Electrochemical Treatment of Landfill Leachates Using a Boron–Doped Diamond Anode

3 AUTHORS, INCLUDING:

Inmaculada Ortiz
Universidad de Cantabria
290 PUBLICATIONS   **5,474** CITATIONS

Article

Electrochemical Treatment of Landfill Leachates Using a Boron-Doped Diamond Anode

Adelaida Cabeza, Ana M. Urtiaga, and Inmaculada Ortiz

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

APPLIED CHEMISTRY

Electrochemical Treatment of Landfill Leachates Using a Boron-Doped Diamond Anode

Adelaida Cabeza, Ana M. Urtiaga, and Inmaculada Ortiz*

Departamento Ingeniería Química y Química Inorgánica, ETSII Y T, Universidad de Cantabria 39005 Santander, Spain

The objective of this work is, first, to analyze the viability of the electrochemical oxidation process by means of a boron-doped diamond electrode to treat leachates from a municipal landfill site, because a high loading of ammonium and chemical oxygen demand (COD) and poor biodegradability are the main characteristics of the leachates. The second objective of this work is to study the influence of operating conditions (i.e., applied current density, initial COD and ammonium loading, and chloride concentration) on the oxidation. Almost-complete removal of both pollutants was experimentally achieved. The kinetics of the COD disappearance was successfully predicted using a model that was based on mass-transfer control of the electrochemical process. Finally, a mathematical model that is able to describe the kinetics of ammonium removal has been reported, depending on the applied current density, the chloride concentration, and the mass-transfer coefficient of the electrochemical cell.

1. Introduction

Recently, there has been increased interest in the use of electrochemical oxidation processes for the treatment of polluted wastewaters. This technology is considered to be a promising alternative, because of its easy operation and effectiveness for the destruction of pollutants, especially refractory organic compounds. According to the literature, the electrochemical oxidation process has been tested for remediation of different types of wastewaters such as tannery wastewaters,[1−3] effluents coming from the anaerobic digestion of dairy manures,[4] wastewaters from a power plant,[5] domestic wastewater,[6] and phenolic aqueous wastes.[7] In the case of landfill leachate, electrochemical degradation techniques using different types of anodes (i.e., TiO_2/RuO_2,[6,8] PbO_2/SnO_2,[4] Ti/Pt,[9] SPR,[10] and PbO_2/Ti[11,12]) have also proved to be capable of removing both the organic and the ammonium loading, achieving high removal efficiencies. The effects of several operating factors on the electro-oxidation of leachates have been investigated, including pretreatment, anode materials, pH, current density, and chloride concentration, as well as added electrolytes.[13] However, the gap between those works and application of the technology needs reliable mathematical models that are able to predict the kinetic behavior of the oxidation process.

Recently, an innovative material called boron-doped diamond (BDD) has begun to be studied as an anode for the electrochemical remediation of wastewaters that contain organic pollutants.[14] Previous works developed a theoretical model that permits the prediction of the evolution of chemical oxygen demand (COD) with time during the electrochemical oxidation of organic pollutants using BDD anodes.[15] Thus far, there are no previous references, other than those performed in the context of the present work,[16] that concern the electrochemical treatment

of landfill leachates using BDD electrodes, because of the novelty of this material. Main advantages of this material are its high chemical inertness and extended lifetime.[17] In addition to these advantages, this type of electrode permits one to produce OH• radicals directly from water electrolysis, because of the high overpotential for oxygen production, which leads to an excellent COD removal efficiency.[18] However, the oxidation of ammonium with BDD electrodes has not been reported yet. Another reported characteristic of BDD electrodes is the very efficient generation of secondary oxidants (i.e., chorine, peroxodisulfate, and peroxodiphosphate), because it has been tested in the oxidation of waters that contain azoic dyes[19] and polyhydroxybenzenes,[20] and also in water disinfection.[21]

The objective of this work is, first, to analyze the viability of the electrochemical oxidation process by means of a BDD electrode to treat leachates from a municipal landfill site, given that a high loading of ammonium and poor degradability are the main characteristics of the leachates. The second objective is to analyze the influence of operating conditions on the remediation kinetics of COD and ammonium, while developing a reliable mathematical model that can be used for design purposes of this type of technology.

2. Fundamentals

Electrochemical oxidation of the pollutants contained in the landfill leachates can be fullfiled through two different approaches: direct anodic oxidation and indirect oxidation.[13] In direct oxidation, pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron-transfer reaction.[22] This process can occur in either one stage or multiple stages, and it proceeds until the final oxidation product is generated (usually carbon dioxide (CO_2)). At the same time, the decomposition of water molecules can lead to the appearance of hydroxyl radicals.[23]

* To whom correspondence should be addressed. Tel.: 34 942 201585. Fax: 34 942 201591. E-mail address: ortizi@unican.es.

The simplified overall chemical reaction involved during the direct anodic oxidation of organic molecules, based on C, H, and O, can be expressed using the following equation:

$$C_xH_yO_z + 2(x - z)H_2O \rightarrow xCO_2 + (4x + y - 2z)H^+ +$$
$$(4x + y - 2z)e^- \quad (1)$$
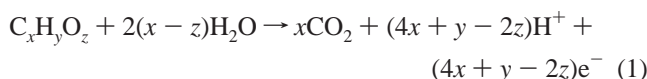
The current density value that implies null accumulation of oxidable substances at the surface of the anode is called the limiting current density. If this limiting current density is exceeded, it would induce a decrease in the current efficiency on the electrolysis of these substances. The excess of applied current density may lead to a transfer of charges by the water molecules, which are oxidized to O_2 on the anode and reduced to H_2 on the cathode. For this reason, several works on the anodic oxidation of organic compounds by means of a BDD anode[15,24,25] have taken into account the value of the limiting current density for COD. It can be calculated by the expression

$$j_{lim} = 4Fk_m COD \quad (2)$$

where j_{lim} is the limiting current density (expressed in units of A/m^2), F the Faraday constant (given in units of C/mol), k_m the mass-transport coefficient in the electrochemical cell (given in terms of meters per second (m/s)), and COD the chemical oxygen demand (expressed in terms of the number of moles of oxygen per cubic meter (mol O_2/m^3)). The number 4 is the number of exchanged electrons in the oxidation of organic molecules, based on C, H, and O, relative to 1 mol of O_2, as is demonstrated by comparing eqs 1 and 3:

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad (3)$$
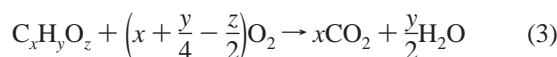
Pollutant removal may be also due to indirect oxidation, utilizing secondary oxidants formed by anodic oxidation of some species originally existing or added to the leachate. For instance, if the Cl^- anion is a major compound of the landfill leachate, chlorine is formed during the electrochemical process. The anodic reaction is followed by the diffusion of molecular chlorine (Cl_2) to the bulk and hydrolytic disproportionation to form hydrochlorous acid and hypochlorite ions, depending on the pH.[10] Hypochlorite ions generated in these reactions are strong oxidants that can not only oxidize aqueous organic compounds, but it is also proposed to be responsible for the oxidation of NH_4^+ through a series of reactions similar to "breakpoint reactions".[26] Several studies have noted the efficiency of COD and ammonium oxidation through the in situ production of hypochlorite.[12,27] As the chloride concentration increased, the removal efficiencies for both COD and ammonium improved. Because higher chlorine/hypochlorite production efficiency could be obtained at a higher chloride concentrations, the increase in chloride concentration enhanced the effect of indirect oxidation.

3. Materials and Methods

3.1. Apparatus. The experiments were conducted in a single-compartment electrochemical cell that was manufactured by Adamant (DiaCell 106). Boron-doped diamond (BDD) on silicon was used as the anode and stainless steel (316 L) was used as the cathode. Both electrodes were circular, with a surface area of 70 cm^2 each and an electrode gap of 5 mm. The electric power required during the electro-oxidation experiments was provided by a laboratory power supply (Agilent 6654A) that had a maximum output of 9 A, 60 V. The leachate was stored
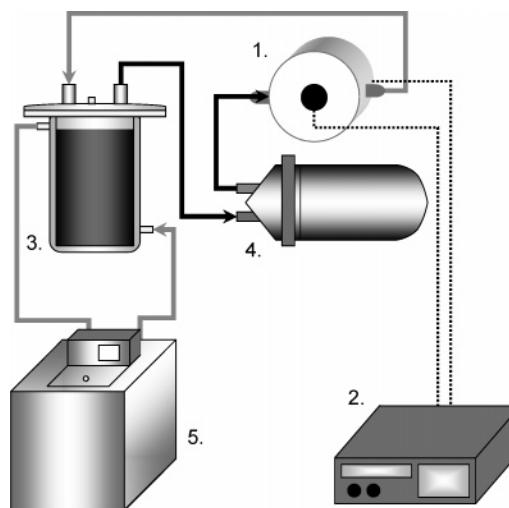
Figure 1. Schematic diagram of the experimental apparatus. Figure legend: 1, electrochemical cell; 2, power supply; 3, leachate feed tank; 4, pump; and 5, refrigeration bath.

Table 1. Landfill Leachates Characterization

parameter	raw leachate	pretreated leachate
pH	8.35	7.51
conductivity (mS/cm)	12.77	14.36
total suspended solids, TSS (mg/L)	317	1450
total organic carbon, TOC (mg/L)	2780	949
chemical oxygen demand, COD (mg O_2/L)	4430	1130
biological oxygen demand, BOD$_5$ (mg O_2/L)	640	120
BOD$_5$/COD	0.14	0.11
[N−NH$_4^+$] (mg/L)	1930	859
anion concentrations		
fluoride (mg/L)	16	38.5
chloride (mg/L)	3230	1560
nitrite (mg/L)		
nitrate (mg/L)		
phosphate (mg/L)	55	
sulfate (mg/L)	39	172

in a glass tank and circulated through the electrolytic cell by a magnetic pump. Continuous pumping of the solution caused the temperature to increase; therefore, a refrigeration fluid was circulated to maintain a constant leachate temperature (see Figure 1).

3.2. Leachate Characteristics. Leachates from municipal landfills are considered to be wastewaters that are generated as a consequence of rainwater percolation through wastes, the decomposition of organic waste, and the inherent water content of wastes themselves. As a result of those factors, a dark-gray foul-smelling effluent with a high concentration of pollutants is generated.

Leachates were collected from July 2005 to November 2005 from the municipal landfill site of Meruelo in Cantabria, Spain. Experiments were conducted with raw leachates, as well as with biologically and physicochemically pretreated leachates. The physicochemical characteristics of either of the two types of leachates are summarized in Table 1. The BOD$_5$/COD ratio (where BOD is the biological oxygen demand) can be considered to be an index of biodegrability of the landfill leachate. The low BOD$_5$/COD ratio of the raw leachate (0.14) is attributed to the predominant fraction of high-molecular-weight compounds, which results in the poor biodegradability. The high concentrations of COD (1134 mg/L) and ammomium (859 mg/L) that persisted in the leachate after the biological and the physicochemical treatments confirmed the difficulties that are

Table 2. Initial Compositions and Current Densities Used in the Experiments

expt	j (A/m^2)	COD (mg/L)	$[N-NH_4^+]$ (mg/L)	$[Cl^-]$ (mg/L)
		Preliminary Experiments		
1	900	3800	1710	2760
2	600	3280	2020	3030
3	600	1730	1110	2160
4	300	1810	943	2060
5	300	853	487	1790
6	150	773	487	1900
		Influence of Chloride Concentration		
7	300	1010	756	1420
8	300	1020	738	3670
9	300	1120	696	6350
10	300	1060	732	8570

involved in treating this type of aqueous solution. The other major component present in the leachate was the concentration of Cl^- anions. Hence, the latter might favor the formation of chlorine/hypochlorite during the electrochemical process and, consequently, the indirect oxidation effect. Moreover, the high value of the electrical conductivity suggests that the landfill leachate used in this study heavily consists of a saline effluent, and, consequently, it permits electrochemical oxidation treatment without the addition of more electrolytes.

3.3. Analytical Determinations. Leachates were characterized by means of the following procedures.

The pH was mesured with a Combo Gro'Check pH meter (Hanna Instruments), and the conductivity was measured with a Crison CM 35 conductivity meter. The total suspended solids (TSS) retained by a glass fiber and dried at 103−105 °C were determined gravimetrically.

The COD was determined by closed reflux and colorimetric methods; the ammonium nitrogen concentration was obtained by distillation (Buchi model UK-355) and titration, both according to the Standard Methods for the Examination of Water and Wastewater.[28] The BOD was measured by incubation for 5 days at 20 °C. The total organic carbon (TOC) was determined by measuring the CO_2 formed from the complete oxidation of the sample, with a nondispersive infrared (NDIR) detector (TOC 1200 Euroglas). Ion chromatography (Dionex 120 IC, with an IonPac AS9-HC Column) was used to determine the concentration of inorganic anions.

3.4. Experimental Setup. The electro-oxidation experiments were performed while working at a constant current density, ranging from 150 A/m^2 to 900 A/m^2. The flow rate was adjusted to 11 L/min, to facilitate turbulence, because a hydraulic flow that is too weak limits the kinetics of the reactions on the electrode surfaces and could lead to poor evacuation of gases.

The experiments were conducted at a constant leachate temperature of 20 °C. In all cases, the leachate was previously filtered to avoid the input of large particles or solid elements in the electrochemical compartments, which could block hydraulic canals. A volume of $V = 1$ L of leachate was treated in each experiment. During the experiments, leachate samples were periodically collected from the feed tank.

Experiments were performed working with raw leachate or with a biologically and physicochemically pretreated leachate. Table 2 reports the initial characteristics of the feed batches used in this investigation, as well as the current density applied in their electrochemical oxidation.

First, a set of preliminary experiments was conducted with raw leachate (experiments 1−6), to analyze the viability of the electrochemical oxidation process. Three ranges of contaminant loading that were obtained after dilution of the leachate were studied. To avoid the influence of the Cl^- anion, NaCl was
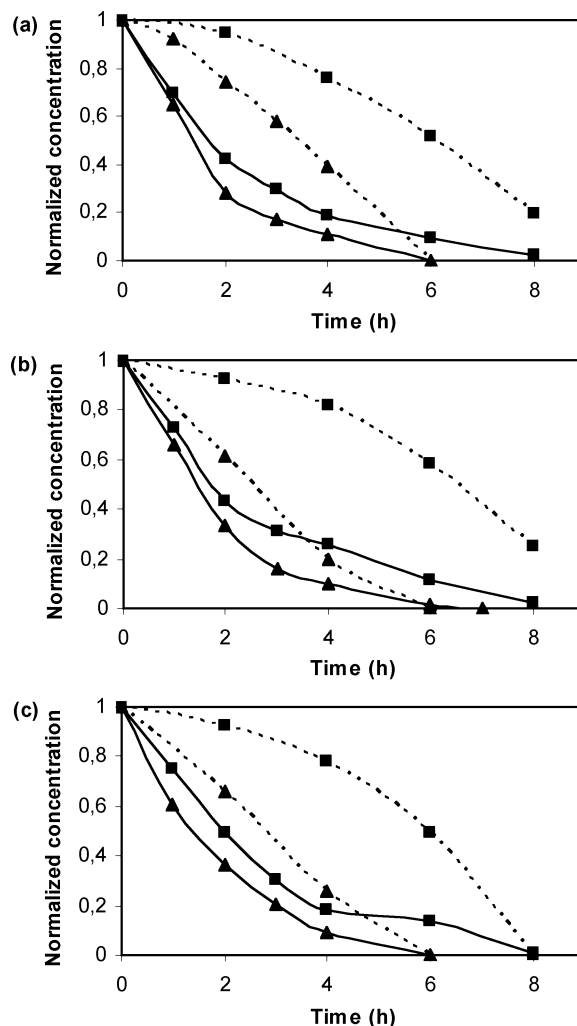
Figure 2. Normalized chemical oxygen demand (COD) and NH_4^+ concentration profiles during the electrochemical treatment of preliminary experiments. Initial conditions are given in Table 2 (experiments 1−6). Legend: (a) (▲) data for experiment 1 and (■) data for experiment 2; (b) (▲) data for experiment 3 and (■) data for experiment 4; and (c) (▲) data for experiment 5 and (■) data for experiment 6. Continuous lines represent COD/COD_0 and dotted lines represen $(N-NH_4^+)/(N-NH_4^+)_0$.

added to diluted batches, to obtain approximately the same chlorine concentration as the original chloride concentration of the raw leachate. In this set of experiments, different current density values were applied, depending on the initial concentration of pollutants.

Second, a different set of experiments was conducted using the biologically and physicochemically treated leachate (experiments 7−10). In this set of experiments, the influence of the initial chloride concentration, which was varied in the range of 1420−8570 mg/L, on the oxidation of COD and ammonium was studied. All these experiments were conducted at a constant current density of 300 A/m^2.

4. Results and Discussion

4.1. Kinetics of COD and Ammonium Removal. To determine the viability of the electrochemical treatment, the evolution of COD and ammonium concentration during the process was followed. Figure 2a−c shows the normalized COD (COD/COD_0) and ammonium $(N-NH_4^+)/(N-NH_4^+)_0)$ concentration profiles during the electrochemical treatment of experiments 1−6. These figures show the influence of the applied current density working at three different ranges of initial

(a)

(b)
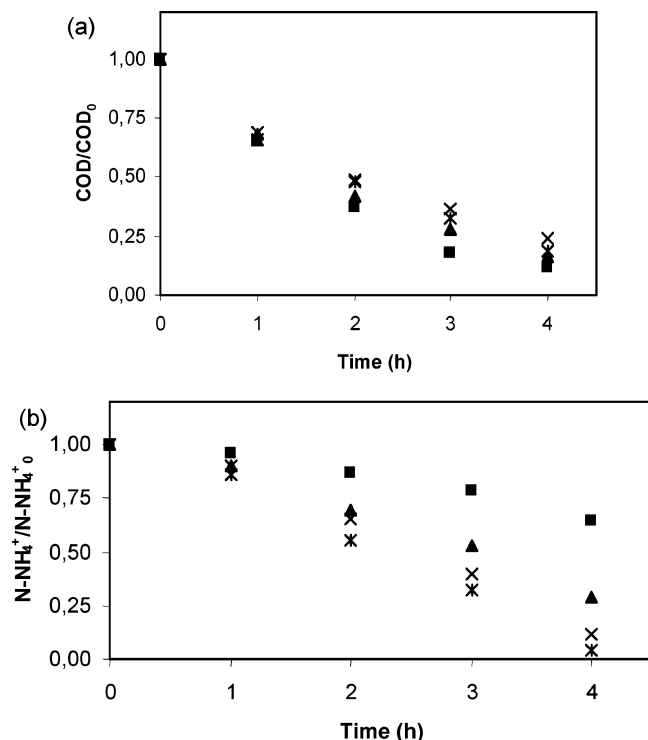
Figure 3. (a) COD dimensionless concentration and (b) ammonium dimensionless concentration during the electrochemical treatment in experiments 7−10. Conditions were as follows: COD_0, ~1000 mg/L; $[N-NH_4^+]_0$, ~ 700 mg/L, and j = 300 A/m². Figure legend: (■) data for experiment 7, $[Cl^-]$ = 1420 mg/L; (▲) data for experiment 8, $[Cl^-]$ = 3670 mg/L; (×) data for experiment 9, $[Cl^-]$ = 6350 mg/L; and (∗) data for experiment 10, $[Cl^-]$ = 8570 mg/L.

contaminants loading (COD_0 = 3500, 1800, and 850 mg/L and $[N-NH_4^+]_0$ = 2000, 1000, and 500 mg/L).

In all cases, the COD and ammonium were completely removed after 6−8 h. As is observed by a comparison of the COD and ammonium profiles during the electro-oxidation runs, ammonium removal occurs at a slower rate than that of COD. However, when COD is almost completely removed, the ammonium removal accelerates. Note that, as explained in the Introduction, one of the principal advantages of the BDD anode is its excellent efficiency for COD removal.[18] Similarly, Cossu et al.,[9] using a Ti/Pt electrode, reported that the removal rate of ammonium was lower than that of COD at the initial stage of electro-oxidation, when direct oxidation was dominant, and then $N-NH_4^+$ was substantially removed in the subsequent electrochemical oxidation stage when indirect oxidation became prevalent. In contrast, Chiang et al.[12] and Li et al.,[29] while working with Ti/PbO_2 electrodes, reported that the ammonium oxidation was dominant in the competition with COD. As reported by Deng and Englehardt,[13] the rule of competition between the removal of COD and the removal of ammonium seems to be that the removal of $N-NH_4^+$ is favored when indirect oxidation is dominant, whereas the removal rate of COD takes priority under direct anodic oxidation.

As shown in Figure 2a−c, it can be observed that the influence of the applied current density is much more significant in the case of ammonium degradation than in the case of COD removal. Furthermore, it is observed that COD degradation profiles show an exponential rate, which is consistent with the results presented by Chiang et al.[30] and Cossu et al.[9] However, significant differences on the trend of ammonium removal are observed, depending on the applied current density. Linear
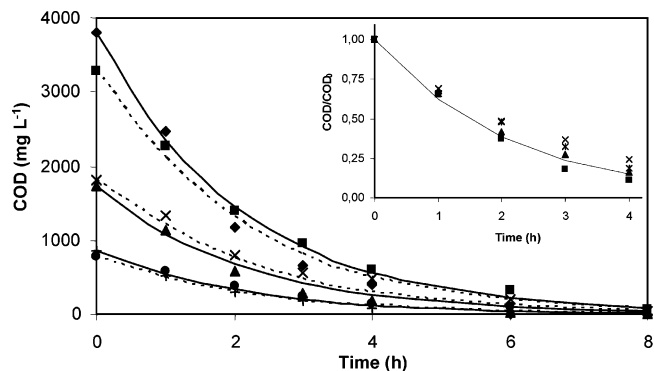
Figure 4. Experimental data of COD for experiments 1−6; initial conditions are given in Table 2. Figure legend: (◆) data for experiment 1, (■) data for experiment 2, (▲) data for experiment 3, (×) data for experiment 4, (●) data for experiment 5, and (+) data for experiment 6. Inset shows the dimensionless COD concentration data of experiments 7−10 ((■) data for experiment 7, (▲) data for experiment 8, (×) data for experiment 9, and (∗) data for experiment 10). All lines correspond to simulated data obtained using the mathematical model described in Table 3.

profiles (zeroth-order kinetics) are observed when working with high values of the applied current density, whereas curved evolutions with an initial delay are observed when working at lower values of the applied current density. The initial delay can be attributed to the fact that, at the beginning of the experiment, the oxidation of the organic compounds was occurring preferentially. The complex behavior of the ammonium degradation is supported with the results reported by other authors. Szpyrkovicz and co-workers,[2,3] Chiang et al.,[12] Panizza and Cerisola,[31] and Moraes and Bertazzoli[8] presented exponential-like decaying ammonia concentration curves using Ti/Pt−Ir and $Ti/TiRuO_2$ anodes, whereas Ihara et al.[4] and Vanlangendonck et al.[5] obtained zeroth-order ammonium oxidation kinetics when working with dimensionally stable anodes (DSAs).

These preliminary experiments highlighted the fact that the influence of the applied current density was more significant on ammoniun degradation than on COD removal. Hence, in this case, it is possible to conclude that the effect of the electrochemical oxidation by means of secondary oxidants has a more important role on the electrochemical oxidation of ammonium. According to the literature, chloride concentration is of great importance in the formation of the hypochlorite ion; a higher chloride concentration helps both the formation reaction of ClO^- and indirectly ammonia oxidation.[5] Therefore, a second set of experiments was planned (experiments 7−10), using biologically and physicochemically treated leachates as a feed phase and varying the initial concentration of chloride (1420 mg/L < $[Cl^-]$ < 8570 mg/L) to analyze the influence of this variable on the oxidation behavior. These experiments were conducted at a constant current density of 300 A/m², which is a value that was similar to that of the limiting current density calculated for the initial COD concentration, thus allowing a high value of the instantaneous current efficiency for COD removal.[2]

COD dimensionless profiles of this set of experiments are shown in Figure 3a. It is observed that the variation of the chloride concentration in the range of 1420 mg/L < $[Cl^-]$ < 8570 mg/L has only a slight effect on the kinetics of COD removal. These results are consistent with those obtained by Cossu et al.,[9] who also observed negligible influence of the chloride concentration on the COD oxidation rate in the range of 1600 mg/L < $[Cl^-]$ < 3600 mg/L. Moreover, increasing the chloride concentration values can cause the

Table 3. Equations Describing the Evolution of the Chemical Oxygen Demand (COD) during Electrochemical Oxidation at the Boron-Doped Diamond (BDD) Anode[a]

process	COD (mol O$_2$/m^3)[b]	equation number
$j_{appl} < j_{lim}$, current control	$COD(t) = COD_0[1 - (\alpha A k_m/V)t]$	(4)
Change in the kinetic regimes during the electrochemical treatment	$j_{appl} < j_{lim} \rightarrow COD(t) = COD_0[1 - (\alpha A k_m/V)t]$	(5)
	$j_{appl} > j_{lim} \rightarrow COD(t) = \alpha COD_0 \exp[-(A k_m/V)t + (1 - \alpha)/\alpha]$	(6)
$j_{appl} > j_{lim}$, mass-transport control	$COD(t) = COD_0 \exp[-(A k_m/V)t]$	(7)

[a] Data taken from ref 15. [b] $\alpha = j_{appl}/(4Fk_m COD_0)$.

Table 4. Regression Parameters Obtained by Fitting the Experimental Data to eq 10

expt	[Cl$^-$] (mg/L)	K (h^{-1})	R^2
7	1420	0.260	0.994
8	3670	0.339	0.998
9	6350	0.393	0.996
10	8570	0.413	0.996

opposite effect. As noted by Pignatello et al.,[32] Cl$^-$ anions may act as scavengers of hydroxyl radicals, which are a very strong oxidant that is also formed through the anodic oxidation of water. Moreover, the BDD anode can lead to the formation of higher oxidation states of chlorine, i.e., chlorite, chlorate,[10] and perchlorate. These anions are not as efficient as hypochlorite, in regard to their use as oxidants of organics, or ammonium.

Figure 3b shows the evolution with time of the dimensionless ammonium concentration in experiments 7–10. The results demonstrated that, as the chloride concentration increased, the kinetics of ammonium were improved. It is observed that kinetic curves show an initial region where the ammonium concentration scarcely decreases. The delay at the beginning of the ammonium oxidation curves was also observed in the preliminary group of experiments (see the results given in Figure 2) when low values of applied current density were used.

4.2. Kinetic Modeling. 4.2.1. Kinetics of COD Removal. A kinetic modeling that predicts the evolution of COD with time during the electrochemical oxidation of organic pollutants on BDD electrodes has been developed[15] and tested in previous works.[24,31,33–36] The basic assumptions of the model are that direct oxidation is responsible for the electrooxidation of the organic matter and that the rate of the electrochemical degradation with electrogenerated OH$^{\bullet}$ radicals and/or direct electron transfer is a fast reaction, so the process is controlled by mass transport of the pollutants toward the anode.

In the description of the model,[15] two types of operating regimes are defined, depending on the value of the applied current density, j_{appl}:

(i) If $j_{appl} < j_{lim}$, the electrolysis is under current control and the COD decreases linearly with time.

(ii) If $j_{appl} > j_{lim}$, the electrolysis is under mass-transport control and the COD evolution follows an exponential trend.

The equations that predict COD evolution curves during the electrochemical oxidation are shown in Table 3. The model permits calculation of the COD concentration during the electrochemical treatment, based on the initial value of COD, the area of the electrodes (A), the volume of leachate in the feed tank (V), the applied current density (j_{appl}), and the value of the mass transport coefficient (k_m).

The values of the instantaneous limiting current density for COD have been calculated for the preliminary experiments (experiments 1–6). If the COD was considered to be the main component to be oxidized electrochemically, experiments 2 and 4 would have been performed under mass-transport
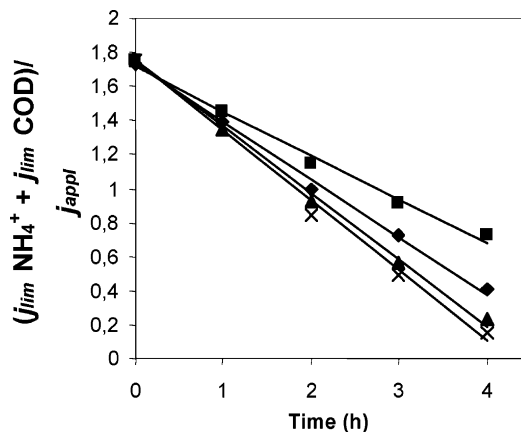

Figure 5. Experimental values of the term $(j_{lim,NH_4^+} + j_{lim,COD})/j_{appl}$ (from eq 10), as a function of time: (■) data for experiment 7, (◆) data for experiment 8, (▲) data for experiment 9, and (×) data for experiment 10.

control; however, a change in the kinetic regime from current control to mass-transport control had occurred during the first hour of the electrochemical treatment in the other experiments. That is consistent with the exponential shape of the COD oxidation curves. The value of the mass-transport coefficient was estimated by comparing the experimental results with simulated values using the minimum weighted standard deviation as criterion. Aspen Custom Modeler, which is a general-purpose process systems simulator, was used to solve the kinetic equations. The estimated value of the mass-transport coefficient was $k_m = 1.89 \times 10^{-5}$ m/s, which is very similar to the value of the mass-transport coefficient that was given by the manufacturer of the cell ($k_m = 2 \times 10^{-5}$ m/s). The model was tested for the first set of experiments. Figure 4 shows a comparison of the experimental and simulated data obtained with the reported model and the parameters. Simulated profiles are represented by the solid and dotted lines. The electrochemical oxidation of COD has been successfully predicted by the model, with standard deviations between the experimental and simulated results ranging from 3.4% to 7.5%. In addition, the model has been tested against the second set of experiments. As shown in Figure 4, the model reported in Table 3 predicts the behavior of COD oxidation satisfactorily well, with standard deviations in the range of 3.8%–13.2%.

4.2.2. Kinetics of Ammonium Oxidation. Based on the kinetic results reported in the previous section, the influence of chloride concentration, the applied current density, and the initial ammonium concentration must be taken into account to develop a mathematical model for the description of the kinetics of ammonium oxidation. Also, according to Figure 2a–c and the comparison of Figures 3a and 3b, it is observed that ammonium oxidation accelerates when most of the COD has been degraded. Thus, the influence of the COD concentration must be also considered in this case.
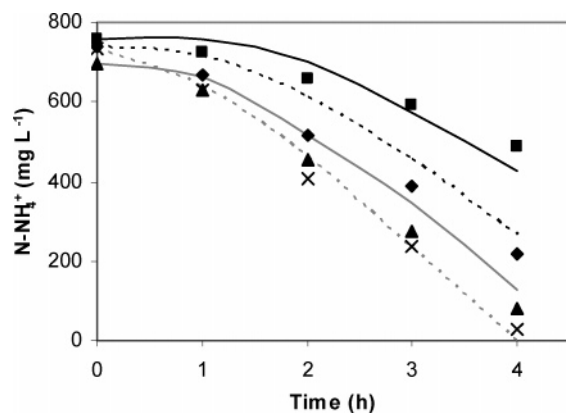
Figure 6. $N-NH_4^+$ concentration versus time during the electrochemical treatment: (■) data for experiment 7, $[Cl^-] = 1420$ mg/L; (◆) data for experiment 8, $[Cl^-] = 3670$ mg/L; (▲) data for experiment 9, $[Cl^-] = 6350$ mg/L; and (×) data for experiment 10, $[Cl^-] = 8570$ mg/L. Solid lines represent simulated data obtained by the empirical model described by eq 12, and dotted lines represent simulated data obtained by the empirical model described by eq 14.
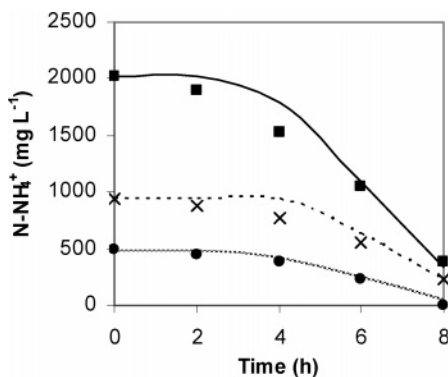

Figure 7. Experimental and predicted ammonia nitrogen concentrations during the electrochemical treatment: (■) data for experiment 2, $[N-NH_4^+]_0 \approx 2000$ mg/L, $j = 600$ A/m²; (×) data for experiment 4, $[N-NH_4^+]_0 \approx 1000$ mg/L, $j = 300$ A/m²; and (●) data for experiment 6, $[N-NH_4^+]_0 \approx 500$ mg/L, $j = 150$ A/m². Solid lines represent simulated data obtained by the empirical model described by eq 12, and dotted lines represent simulated data obtained by the empirical model described by eq 14.

The kinetics of this oxidation has been defined as the ratio $(j_{lim,NH_4^+} + j_{lim,COD})/j_{appl}$, where $j_{lim,COD}$ is the value of the instantaneous limiting current density for COD (as given in eq 2), j_{appl} the value of the applied current density, and j_{lim,NH_4^+} the value of the instantaneous limiting current density for NH_4^+, which can be calculated using an expression that is analogous to eq 2:where the number 3 is the number of electrons

$$j_{lim} = 3Fk_mNH_4^+ \qquad (8)$$

exchanged during the oxidation of 1 mol of ammonium, as determined by eq 9:[26]

$$2NH_4^+ + 6OH^- \rightarrow N_2 + 6H_2O + 2H^+ + 6e^- \qquad (9)$$
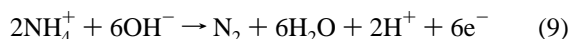
The term $(j_{lim,NH_4^+} + j_{lim,COD})/j_{appl}$ varies with the electrolysis time. Moreover, because the chloride concentration was demonstrated to have a significant effect on the kinetics of ammonium removal, the dependence on this variable must be also considered.
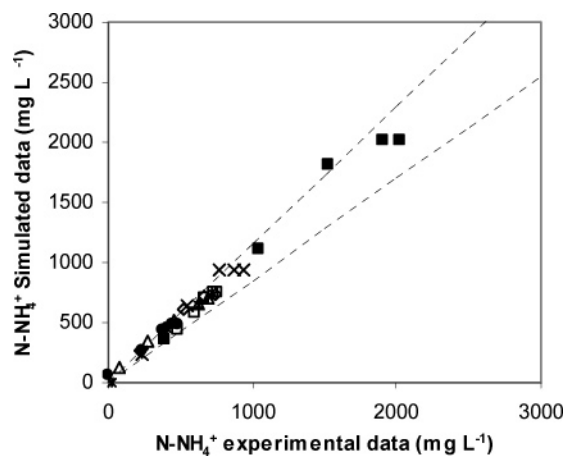
Figure 8. Parity graph: (■) data for experiment 2, (×) data for experiment 4, (●) data for experiment 6, (□) data for experiment 7, (◇) data for experiment 8, (△) data for experiment 9, and (∗) data for experiment 10.

A simple equation that considers a zeroth-order evolution with time and an implicit dependence on the Cl^- anion is defined next:

$$\frac{j_{lim,NH_4^+} + j_{lim,COD}}{j_{appl}} = \left(\frac{j_{lim,NH_4^+} + j_{lim,COD}}{j_{appl}}\right)_0 - K(Cl^-)t \qquad (10)$$

This expression considers the oxidation of both COD and ammonium globally. Applying an analogous definition of the operating regimes established by the mathematical model that describes COD oxidation, a zeroth-order kinetic would imply that the joint oxidation of COD and ammonium might be performed under current control.

By substituting the expressions of the instantaneous limiting current densities for COD and ammonium oxidation (eqs 2 and 8) into eq 10, the evolution with time of the ammonium concentration can be derived:

$$[NH_4^+] = [NH_4^+]_0 + \frac{4}{3}(COD_0 - COD) - \left(\frac{j_{appl}}{3Fk_m}\right)K(Cl^-)t \quad (11)$$

Finally, substituting the dependence of COD with time t, according to the mathematical model developed by Comninellis and co-workers,[15] eq 12 is obtained:

$$[NH_4^+] = [NH_4^+]_0 + \frac{4}{3}COD_0\left\{1 - \exp\left[\left(-\frac{k_mA}{V}\right)t\right]\right\} - \left(\frac{j_{appl}}{3Fk_m}\right)K(Cl^-)t \quad (12)$$

Equation 12 can be used to predict the kinetic evolution of the ammonium concentration in the landfill leachate during the electro-oxidation treatment, as a function of the operation variable j_{appl} and the parameter K, which is dependent on the chloride concentration.

From the experimental data of the COD and ammonium concentration with time, and using eqs 2 and 8, the instantaneous limiting current densities of ammonium and COD were calculated, and, therefore, eq 10 was tested against the experimental data obtained in the second set of experiments (see Figure 5). It was observed that the value of the term $(j_{lim,NH_4^+} + j_{lim,COD})/j_{appl}$ is >1 during the first 2−3 h of the electrochemical treatment; thus, according to the definition of limiting current

density, the value of applied current density was not sufficient to perform the direct oxidation of both COD and ammonium. Hence, it is assumed that, initially, the applied current is primarily applied to the direct oxidation of COD and the ammonium begins to degrade only when a significant amount of the COD is removed. Increasing values of the slope, relative to the increase in the chloride concentration, are observed in Figure 5.

The values of the slope (K) obtained from the linear fitting, together with correlation coefficients, are depicted in Table 4. The empirical equation obtained via a linear fitting of the data in Table 4 is

$$K = 2.12 \times 10^{-5}[Cl^-] + 0.245 \ (h^{-1}) \qquad (R^2 = 0.937) \quad (13)$$

The comparison between the experimental ammonium concentration profiles and the ammonium concentration predicted by eq 13 is shown in Figure 6, where concentrations are expressed in terms of ammonia nitrogen. The constraints in the use of eq 13 are related to the initial delay in the degradation of ammonium when the COD value is still high. In such a case, the following restriction is imposed:

$$\text{if} \quad \frac{4}{3}COD_0\left\{1 - \exp\left[\left(-\frac{k_mA}{V}\right)t\right]\right\} > \left(\frac{j_{appl}}{3Fk_m}\right)K(Cl^-)t$$

$$\text{then} \quad [NH_4^+] = [NH_4^+]_0 \qquad (14)$$

The model satisfactorily predicts the electrochemical oxidation process, with the standard deviations between the experimental and simulated results ranging from 4.2% to 9.5%.

In addition, this mathematical model was applied to predict the ammonium concentration during the electrochemical oxidation of leachates that were treated in the preliminary experiments. Experimental and simulated results are compared in Figure 7. Although the operating conditions were different from the conditions of the second set of experiments, satisfactory results have been obtained. Standard deviations are 7.5%, 10.7%, and 9.1% for experiments 2, 4, and 6, respectively. In this case, to predict the ammonium concentration correctly, the experimental chloride concentration during the electrochemical treatment must be known, because the concentration of Cl^- anions and, consequently, the value of K decreased with the experimental time.

Finally, a parity graph of ammonium concentration is shown in Figure 8, including all data of the preliminary experiments 2, 4, and 6 and kinetic experiments 7−10. Good agreement between the experimental and simulated data is observed, because >83% of the simulated ammonium concentration results fall within the experimental N−NH$_4^+$ concentration range of ±15%.

5. Conclusions

In this work, the viability of the electrochemical oxidation process, using a boron-doped diamond (BDD) anode, to treat raw leachates and biologically and physicochemically treated leachates from a municipal landfill site has been analyzed. Although ammonium removal was slower than that of the chemical oxygen demand (COD), complete removal of both COD and ammonium was obtained after 6−8 h. Moreover, the influence of applied current density was studied, and its influence was much more significant in the case of the ammonium degradation than in the case of COD removal. In addition to this, the influence of chloride concentration on the removal rate of ammonium was studied. The results demonstrated that, as the chloride concentration increased, the kinetics of the ammonium were improved. The kinetics of the COD disappearance was described using a model that was based on mass-transfer control of the electrochemical process. COD values were successfully predicted by the model, with standard deviations ranging from 3.4% to 7.5%. The model also led to the estimation of the mass-transport coefficient: $k_m = 1.89 \times 10^{-5}$ m/s. Finally, a mathematical model that predicts the evolution of the ammonium concentration during the electrochemical treatment was developed. This model incorporates the influence of the chloride concentration. The model successfully predicted the oxidation of ammonium, with standard deviations ranging from 4.2% to 9.5%.

Nomenclature

A = area (m^2)

BDD = boron-doped diamond

BOD$_5$ = biological oxygen demand (mg O$_2$/L)

COD = chemical oxygen demand (mg O$_2$/L)

COD$_0$ = initial chemical oxygen demand (mg O$_2$/L)

F = Faraday constant (C/mol)

j_{appl} = applied current density (A/m^2)

j_{lim} = limiting current density (A/m^2)

$j_{lim,COD}$ = limiting current density for COD concentration (A/m^2)

j_{lim,NH_4^+} = limiting current density for ammonium concentration (A/m^2)

$K(Cl^-)$ = zeroth-order kinetic constant, defined in eq 10 (h^{-1})

k_m = mass-transport coefficient (m/s)

$[NH_4^+]$ = ammonium concentration (mg/L)

$[NH_4^+]_0$ = initial ammonium concentration (mg/L)

$[N-NH_4^+]$ = ammonium nitrogen concentration (mg/L)

$[N-NH_4^+]_0$ = initial ammonium nitrogen concentration (mg/L)

t = time

TOC = total organic carbon (mg/L)

TSS = total suspended solids (mg/L)

V = treated volume (m^3)

Acknowledgment

Literature Cited

(1) Szpyrkowicz, L.; Kaul, S. N.; Neti, R. N.; Satyanarayan, S. Influence on the anode material on electrochemical oxidation for the treatment of tannery wastewater. *Water Res.* **2005**, *39*, 1601−1613.

(2) Szpyrkowicz, L.; Kelsall, G.; Kaul, S. N.; De Faveri, M.; Satyanarayan, S. Performance of electrochemical reactor for treatment of tannery wastewaters. *Chem. Eng. Sci.* **2001**, *56*, 1579−1586.

(3) Szpyrkowicz, L.; Naunczyk, J.; Zilio-Grandi, F. Electrochemical treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir electrodes. *Water Res.* **1995**, 517−524.

(4) Ihara, I.; Umetsu, K.; Kanamura, K.; Watanabe, T. Electrochemical oxidation of the effluent from anaerobic digestion of dairy manure. *Bioresour. Technol.* **2005**, *97*, 1360−1364.

(5) Vanlangendonck, Y.; Corbisier, D.; Van Lierde, A. Influence of operating conditions on the ammonia electro-oxidation rate in wastewaters from power plants (ELONITA technique). *Water Res.* **2005**, *39*, 3028−3034.

(6) Vlyssides, A. G.; Karlis, P. K. Electrochemical treatment in relation to pH of domestic wastewater using Ti/Pt electrodes. *J. Hazard. Mater.* **2002**, 215−226.

(7) Nars, B.; Abdellatif, G.; Cañizares, P.; Sáez, C.; Lobato, J.; Rodrigo, M. A. Electrochemical oxisdation of hydroquinone, resorcinol and catechol on boron-doped diamond anodes. *Environ. Sci. Technol.* **2005**, *39*, 7234−7239.

(8) Moraes, P. B.; Bertazzoli, R. Electrodegradation of landfill leachate in a flow electrochemical reactor. *Chemosphere* **2005**, *58*, 41−46.

(9) Cossu, R.; Polcaro, A. M.; Lavagnolo, M. C.; Mascia, M., Palmas, S.; Renoldi, F. Electrochemical treatment of landfill leachate: Oxidation at Ti/PbO$_2$ and Ti/SnO$_2$ anodes. *Environ. Sci. Technol.* **1998**, *32*, 3570−3573.

(10) Vlyssides, A. G.; Karlis, P. K. Treatment of leachate from a domestic solid waste sanitary landfill by an electrolysis system. *Environ. Technol.* **2001**, *22*, 1467−1476.

(11) Chiang, L. C.; Chang, J. E. Electrochemical treatability of refractory pollutants in landfill leachate. *Hazard. Waste Hazard. Mater.* **1995**, *12* (1), 71−82.

(12) Chiang, L.; Wen, T. Indirect Oxidation effect in electrochemical oxidation treatment of landfill leachate. *Water Res.* **1995**, *29* (2), 671−678.

(13) Deng, Y.; Englehardt, J. D. Electrochemical oxidation for landfill leachate treatment. *Waste Manage.* **2006**, in press. (Available via the Internet at www.elsevier.com/locate/react, DOI: 10.1016/j.wasman.2006.02.004.)

(14) Kraft, A.; Stadelmann, M.; Blaschke, M. Anodic oxidation with doped diamons electrodes: a new advanced oxidation process. *J. Hazard. Mater.* **2003**, *B103*, 247−261.

(15) Panizza, M.; Michaud, P. A.; Cerisola, G.; Comninellis, Ch. Anodic oxidation of 2-naftol at boron-doped diamond electrodes. *J. Electroanal. Chem.* **2001**, *507*, 206−214.

(16) Cabeza, A.; Primo, O.; Urtiaga, A.; Ortiz, I. Definition of a clean process for the treatment of landfill leachates. Integration of Electrooxidation and Ion Exchange Technologies. *Sep. Sci. Technol.*, in press.

(17) Tröster, I.; Fryda, M.; Herrmann, D.; Schäfer, L, Hännni, W.; Perret, A.; Blaschke, M.; Kraft, A.; Stadelmann M. Electrochemical advanced oxidation process for water treatment using Diachem electrodes. *Water Sci. Technol.* **2002**, *49* (4), 207−212.

(18) Tröster, I.; Schäfer, L.; Fryda, M.; Matthée, T. Electrochemical advanced oxidation process using Diachem electrodes. *Diamond Relat. Mater.* **2004**, *11*, 640−645.

(19) Chen, G. Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.* **2004**, *38*, 11−41.

(20) Cañizares, P.; Saez, C.; Lobato, J.; Rodrigo, M. A. Electrochemical oxidation of polyhydroxibenzenes on boron-doped diamond anodes. *Ind. Eng. Chem. Res.* **2004**, *43*, 6629−6637.

(21) Furuta, T.; Tanaka, H.; Nishiki, Y.; Pupunat, L.; Haenni, W.; Rychen, Ph. Legionella inactivation with diamond electrodes. *Diamond Relat. Mater.* **2004**, *13*, 2016−2019.

(22) Cañizares, P.; Garcia-Gomez, J.; Lobato, J.; Rodrigo, M. A. Modelling of Wastewater Electro-oxidation Processes Part I. General Descrption and Application to Inactive Electrodes. *Ind. Eng. Chem. Res.* **2004**, *43*, 1915−1922.

(23) Marselli, B.; Garcia-Gomez, J.; Michaud, P. A.; Rodrigo, M. A.; Comninellis, Ch. Electrogeneration of Hydroxyl radicals on Boron-Doped Diamond Electrodes. *J. Electrochem. Soc.* **2003**, *150*, D79.

(24) Cañizares, P.; Saez, C.; Lobato, J.; Rodrigo, M. A. Electrochemical treatment of 2,4-dinitrophenol aqueous wastes using boron-doped diamond anodes. *Electrochim. Acta* **2004**, *49*, 4641−4650.

(25) Iniesta, J.; Michaud, P. A.; Panizza, M.; Cerisola, G.; Aldaz, A.; Comninellis, Ch. Electrochemical oxidation of phenol at boron-doped diamond electrode. *Electrochim. Acta* **2001**, *46*, 3573−3578.

(26) White, G. C. *The Handbook of Chlorination*, 2nd Edition; Van Nostrand Reinhold: New York, 1986.

(27) Wang, P.; Lau, I. W. C.; Fang, H. H. P. Electrochemical oxidation of leachate pretreated in an upflow anaerobic sludge blanket reactor. *Environ. Technol.* **2001**, *22*, 373−381.

(28) *Standard Methods for the Examination of Water and Wastewater*, 17th Edition; American Public Health Association (APHA):Washington, DC, 1986.

(29) Li, X. M.; Wang, M.; Jiao, Z. K.; Chen, Z. Y. Study on electrolytic oxidation for landfill leachate treatment. *China Water Wastewater Res.* **2001**, *17* (8), 14−17.

(30) Chiang, L. C.; Chang, J. E. Electrochemical oxidation combined with physical-chemical pretreatment processes for the treatment of refractory landfill leachate. *Environ. Eng. Sci.* **2001**, *18* (6), 369−379.

(31) Panizza, M.; Cerisola, G. Electrochemical Oxidation as a final Treatment of Synthetic Tannery wastewater. *Environ. Sci. Technol.* **2004**, *38*, 5470−5475.

(32) Pignatello, J. J.; Oliveros, E.; MacKay, A. Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1−84.

(33) Panizza, M.; Michaud, P. A.; Cerisola, G.; Comninellis, Ch. Electrochemical treatment of wastewater containing organic pollutants on boron-doped diamond electrodes: prediction of specific energy consumption and required electrode area. *Electrochem. Commun.* **2001**, *3*, 336−339.

(34) Rodrigo, M. A.; Michaud, P. A.; Duo, I.; Panizza, M.; Cerisola, G.; Comninellis, Ch. Oxidation of 4-chlorophenol at boron-doped-diamond electrode for wastewater treatment. *J. Electrochem. Soc.* **2001**, *148* (5), D60−D64.

(35) Montilla, F.; Michaud, P. A.; Morallón, E.; Vázquez, J. L.; Comninellis, Ch. Electrochemical oxidation of benzoic acid at boron-doped diamond electrodes. *Electrochim. Acta* **2002**, *47*, 3509−3513.

(36) Morão, A.; Lopes, A.; Pessoa de Amorim, M. T.; Gonçalves, I. C. Degradation of mixtures of phenols using boron-doped diamond electrodes for wastewater treatment. *Electrochim. Acta* **2004**, *49*, 1587−1595.