APPLICATION OF BORON-DOPED DIAMOND ELECTRODES FOR WASTEWATER TREATMENT

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Key Words: Boron-doped diamond, electro-Fenton, photoelectro-Fenton, electro-oxidation

ABSTRACT

Boron-doped diamond (BDD) thin film is a new electrode material that has received great attention recently because it possesses several technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability, even in strong acidic media, and an extremely wide potential window in aqueous and non-aqueous electrolytes. Due to these properties, diamond electrodes are promising anodes for electrochemical treatment of wastewater containing organic pollutants. The objective of this review is to summarise and discuss the recent results available in the literature concerning the application of diamond electrodes to environmentally-oriented electrochemistry. A mechanism of the electrochemical incineration and a kinetic model for organics oxidation on BDD is also presented. Moreover, fundamentals and applications to wastewater treatment of the powerful electro-oxidation method using an undivided cell with BDD anode and the cathodic electrogeneration of hydrogen peroxide by electro-Fenton or photoelectro-Fenton processes are discussed. In these processes, organics are effectively destroyed by the large amounts of hydroxyl radical (•OH) produced on the BDD surface by water oxidation and by Fenton’s reaction between added Fe2+ and H2O2 electrogenerated at the cathode. The presence of Cu2+ as co-catalyst with UVA irradiation enhances the degradation of organics, making the photoelectro-Fenton with BDD anode viable for industrial application.

INTRODUCTION

As many industries produce wastewater containing toxic organic pollutants, there has been a notable increase in both research and the number of businesses concerned with the treatment of such industrial effluents and, nowadays, many new technologies are available, including biological, physical and chemical processes. In this field, oxidative electrochemical technologies, providing versatility, energy efficiency, amenability to automation and environmental compatibility have reached a promising stage of development and can now be effectively used for the destruction of toxic or biorefractory organics [1].

The overall performance of the electrochemical processes is determined by the complex interplay of parameters that may be optimized to obtain an effective and economical incineration of pollutants. The principal factors determining the electrolysis performance are electrode potential and current density, mass transport regime, cell design, electrolysis medium and, above all, electrode materials. The ideal electrode material for the degradation of organic pollutants should be totally stable in the electrolysis medium, cheap and exhibit high activity towards organic oxidation and low activity towards secondary reactions (e.g. oxygen evolution). Consequently, many anodic materials have been tested to find the optimum one. According to the
model proposed in previous works [2-4] anode materials can be divided into two extreme classes as follows: (i) Active anodes, which have low oxygen evolution overpotential and consequently are good electrocatalysts for the oxygen evolution reaction and only favour partial and selective oxidation (i.e. conversion), include carbon and graphite, platinum-based anodes, iridium-based oxides and ruthenium-based oxides. And (ii) Non-active anodes have high oxygen evolution overpotential and consequently are poor electrocatalysts for the oxygen evolution reaction but enable the complete and non-selective oxidation of organics to CO$_2$ by electrogenerated hydroxyl radicals, such as antimony-doped tin dioxide, lead dioxide and boron-doped diamond (BDD).

Among the non-active anodes, BDD exhibits several technologically important properties that distinguish it from conventional electrodes, such as: (1) An extremely wide potential window in aqueous and non-aqueous electrolytes: in the case of high-quality diamond, hydrogen evolution commences at about ~1.25 V vs. SHE and oxygen evolution at +2.3 V vs. SHE, then the potential window may exceed 3 V [5]; (2) Corrosion stability in very aggressive media: the morphology of diamond electrodes is stable during long-term cycling from hydrogen to oxygen evolution even in acidic fluoride media [6]; (3) An inert surface with low adsorption properties and a strong tendency to resist deactivation: the voltammetric response towards ferri/ferrocyanide is remarkably stable for up to two weeks of continuous potential cycling [7]; and (4) Very low double-layer capacitance and background current: the diamond-electrolyte interface is ideally polarisable and the current between -1000 and +1000 mV vs. SCE is < 50 μA cm$^{-2}$. The double-layer capacitance is up to one order of magnitude lower than that of glassy carbon [8].

Due to these properties, conducting diamond seems to be a promising electrode material and so, in the last decades, it has been widely studied with the goal of developing applications in the electrochemical oxidation of organics for wastewater treatment [9,10]. In fact, during electrolysis in the potential region of water discharge, BDD anodes involve the production of weakly adsorbed hydroxyl radicals that unselectively and mineralise organic pollutants with high current efficiency [11].

In the last years, several indirect electro-oxidation methods based on the cathodic electrugeneration of hydrogen peroxide like electro-Fenton (EF) and photoelectro-Fenton (PEF) are being developed for the remediation of acidic wastewaters containing toxic and non-biodegradable organic pollutants. They are environmentally friendly techniques since the main oxidant of organics is the in situ electrogenerated hydroxyl radical, which is a very strong oxidizing species due to its high standard potential ($E^0 = 2.80$ V vs. SHE). This radical is able to non-selectively react with most organic pollutants yielding dehydrogenated or hydroxylated products up to total mineralization.

When an undivided electrolytic cell is used, the EF method involves the production of hydroxyl radical in the bulk solution from the catalytic Fenton’s reaction between Fe$^{2+}$ with electrogenerated H$_2$O$_2$, simultaneously to the generation of radical $\bullet$OH from water oxidation at the surface of the anode.

This method thus profits the oxidation ability of both anode and cathode reactions and then, it is expected to be more efficient to destroy organics than direct anodic oxidation (AO). Its oxidation power depends on the electrodes and metallic ions (Fe$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, etc.) used as catalyst. The effectiveness of EF can be enhanced under irradiation of the solution with UVA light in the PEF treatment, which can be even more efficient using sunlight as energy source in the solar PEF (SPEF) process.

The aim of this review is to elucidate the basic principles of electro-oxidation of organics with BDD anode and to discuss the recent progress dealing with the application of diamond electrodes in the electrochemical treatment of wastewater containing organic pollutants. A kinetic model for the prediction of the evolution of COD (chemical oxygen demand) during organics incineration on BDD is also presented. Finally, fundamentals and applications of the AO on BDD, as well as of the EF or PEF processes using the same anode with an undivided cell, will also be discussed herein. The influence of applied current density and metallic ions used as catalyst (Fe$^{2+}$ and/or Cu$^{2+}$) in the EF and PEF processes is also explored.

**MECHANISM OF THE ELECTROCHEMICAL INCINERATION**

In electrochemical incineration (EI) reactions oxygen is transferred from water to the organic pollutant using electrical energy. This is the so-called electrochemical oxygen transfer reaction (EOTR). A typical example of EOTR is the anodic Ei of phenol (Eq. 1).

$$C_6H_5OH + 11H_2O \rightarrow 6CO_2 + 28H^+ + 28e^- \quad (1)$$

In this reaction water is the source of oxygen atoms for the complete oxidation of phenol to CO$_2$ at the anode of the electrolytic cell. The liberated protons in this reaction are discharged at the cathode to dihydrogen (Eq. 2).

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

According to the generally accepted mechanism of the EI, water is firstly discharged at the anode active sites M producing adsorbed hydroxyl radicals (Eq. 3).

$$H_2O + M \rightarrow M(\cdot OH)_{ads} + H^+ + e^- \quad (3)$$

These electrogenerated hydroxyl radicals are involved in the incineration of organic pollutants R (present in an aqueous solution) (Eq. 4)
\[ \text{R}_{\text{aq}} + x \text{M(OH)}_{\text{ads}} \rightarrow x\text{M} + \text{Incineration product} + y\text{H}^+ + ye^- \]  \hspace{1cm} (4)

where \( x \) and \( y \) are the stoichiometric coefficients.

This reaction (Eq. 4) is in competition with the side reaction of the anodic discharge of these radicals to dioxygen (Eq. 5).

\[ \text{M(OH)}_{\text{ads}} \rightarrow \text{M} + \frac{1}{2}\text{O}_2 + \text{H}^+ + e^- \]  \hspace{1cm} (5)

**KINETIC MODEL OF ORGANICS MINERALIZATION ON BDD ANODE**

In this section a kinetic model of electrochemical mineralization of organics (\( R \)) on BDD anodes under electrolysis regime is presented. In this regime, as reported in the previous paragraph, electrogenerated hydroxyl radicals (Eq. 6) are the intermediates for both the main reaction of organics oxidation (Eq. 7) and the side reaction of oxygen evolution (Eq. 8).

\[ \text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD(OH)} + \text{H}^+ + e^- \]  \hspace{1cm} (6)

\[ R + x \text{BDD(OH)} \rightarrow x\text{BDD} + \text{Incineration product} + y\text{H}^+ + ye^- \]  \hspace{1cm} (7)

\[ \text{BDD(OH)}_{\text{ads}} \rightarrow \text{BDD} + \frac{1}{2}\text{O}_2 + \text{H}^+ + e^- \]  \hspace{1cm} (8)

Considering this simplified reaction scheme (Eqs. 6-8) a kinetic model is proposed based on following assumptions:

(i) adsorption of the organic compounds at the electrode surface is negligible;

(ii) all organics have the same diffusion coefficient \( D \);

(iii) the rate of the electrochemical mineralization of organics is a fast reaction and it is controlled by mass transport of organics to the anode surface. The consequence of this last assumption is that the rate of the mineralization reaction is independent on the chemical nature of the organic compound present in the electrolyte. Under these conditions, the limiting current density for the electrochemical mineralization of an organic compound (or a mixture of organics) under given hydrodynamic conditions can be written as:

\[ i_{\text{lim}} = n F k_m C_{\text{org}} \]  \hspace{1cm} (9)

where \( i_{\text{lim}} \) is the limiting current density for organics mineralization (A m\(^{-2}\)), \( n \) is the number of electrons involved in organics mineralization reaction (A m\(^{-2}\)), \( F \) is the Faraday constant (96,487 C \( \text{mol}^{-1} \)), \( k_m \) is the mass transport coefficient (m s\(^{-1}\)) and \( C_{\text{org}} \) is the concentration of organics in solution (mM). For the electrochemical mineralization of a generic organic compound, it is possible to calculate the number of exchanged electrons, from the following electrochemical reaction:

\[ \text{C}_x\text{H}_y\text{O}_z + (2x-z)\text{H}_2\text{O} \rightarrow x\text{CO}_2 + (4x+y-2z)\text{H}^+ + (4x+y-2z)e^- \]  \hspace{1cm} (10)

Replacing the value of \( n = (4x+y-2z) \) in Eq. 9 we obtain:

\[ i_{\text{lim}} = (4x+y-2z) F k_m C_{\text{org}} \]  \hspace{1cm} (11)

From the equation of the chemical mineralization of the organic compound (\( \text{C}_x\text{H}_y\text{O}_z \)),

\[ \text{C}_x\text{H}_y\text{O}_z + \left(\frac{4x+y-2z}{4}\right)\text{O}_2 = x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} \]  \hspace{1cm} (12)

It is possible to obtain the relation between the organics concentration (\( C_{\text{org}} \) in mM) and the COD (in mM):

\[ C_{\text{org}} = \frac{4}{4x+y-2z} \text{COD} \]  \hspace{1cm} (13)

From Eqs. 11 and 12 and at given time \( t \) during electrolysis, we can relate the limiting current density of the electrochemical mineralization of organics with the COD of the electrolyte (Eq. 14):

\[ i_{\text{lim}}(t) = 4F k_m COD(t) \]  \hspace{1cm} (14)

At the beginning of electrolysis, at time \( t = 0 \), the initial limiting current density \( i_{\text{lim},0} \) is given by:

\[ i_{\text{lim},0} = 4F k_m COD_0 \]  \hspace{1cm} (15)

where \( COD_0 \) is the initial COD.

We define a characteristic parameter \( \alpha \) of the electrolysis process (Eq. 16). Working under galvanostatic conditions \( \alpha \) is constant, and it is possible to identify two different operating regimes: at \( \alpha < 1 \) the electrolysis is controlled by the applied current, while at \( \alpha > 1 \) it is controlled by the mass transport control.

\[ \alpha = \frac{i}{i_{\text{lim},0}} \]  \hspace{1cm} (16)

**1. Electrolysis under Current Limited Control (\( \alpha < 1 \))**

In this operating regime (\( i < i_{\text{lim}} \)), the current efficiency is 100% and the rate of COD removal (mol m\(^{-2}\) s\(^{-1}\)) is constant and can be written as:

\[ r = \alpha \frac{i_{\text{lim},0}}{4F} \]  \hspace{1cm} (17)

Using Eq. 17, the rate of COD removal (Eq. 18) can be given by:

\[ r = \alpha k_m COD_0 \]  \hspace{1cm} (18)

It is necessary to consider the mass-balances over the electrochemical cell and the reservoir to describe the temporal evolution of COD in the batch recirculation reactor system given in Fig. 1. Considering that the volume of the electrochemical reactor \( V_E \) (m\(^3\)) is much smaller than the reservoir volume \( V_R \) (m\(^3\)), we can obtain from the mass-balances on COD for the electrochemical cell the following relation:

\[ Q COD_{\text{out}} = Q COD_{\text{in}} - \alpha k_m A COD_0 \]  \hspace{1cm} (19)

where \( Q \) is the flow-rate (m\(^3\) s\(^{-1}\)) through the electrochemical cell, \( COD_{\text{in}} \) and \( COD_{\text{out}} \) are COD (mM) at the inlet and at the outlet of the electrochemical cell, respectively, and \( A \) is the anode area (m\(^2\)). For the
well-mixed reservoir (Fig. 1) the mass balance on COD can be expressed as:

$$Q(\text{COD}_{\text{out}} - \text{COD}_{\text{in}}) = V_R \frac{d\text{COD}}{dt}$$  \hspace{1cm} (20)

Combining Eqs. 19 and 20 and replacing COD\(_{\text{in}}\) by the temporal evolution of COD, we obtain:

$$\frac{d\text{COD}}{dt} = -\alpha \frac{\text{COD}_0 A k_m}{V_R}$$  \hspace{1cm} (21)

Integrating this equation subject to the initial condition COD = COD\(_0\) at t = 0 gives the evolution of COD(t) with time in this operating regime (I < I\(_\text{lim}\)):

$$\text{COD}(t) = \text{COD}_0 \left(1 - \alpha \frac{A k_m t}{V_R} \right)$$  \hspace{1cm} (22)

This behaviour persists until a critical time (t\(_\text{cr}\)), at which the applied current density is equal to the limiting current density, which corresponds to:

$$\text{COD}_{\text{cr}} = \alpha \text{COD}_0$$  \hspace{1cm} (23)

Substituting Eq. 23 in Eq. 22, it is possible to calculate the critical time:

$$t_{\text{cr}} = \frac{1 - \alpha}{\alpha} \frac{V_R}{A k_m}$$  \hspace{1cm} (24)

or in term of critical specific charge (Ah m\(^{-3}\)):

$$Q_{\text{cr}} = i_{\text{lim,0}} \frac{1 - \alpha}{k_m 3600} = \frac{4F \text{COD}_0 (1 - \alpha)}{3600}$$  \hspace{1cm} (25)

### 3. Influence of Organics Concentration and Current Density

A graphical representation of the proposed kinetic model is given in Fig. 2. In order to verify the validity of this model, the AO of various aromatic compounds in acidic solution has been performed varying organics concentration and current density.

#### 3.1 Influence of the nature of organic pollutants

Figure 3 shows both the experimental and predicted values (continuous line) of both ICE and COD evolution with the specific electrical charge passed during the AO of different classes of organic compounds (acetic acid, isopropanol, phenol, 4-chlorophenol, 2-naphtol). This figure demonstrates that the electrochemical treatment is independent on the chemical nature of the organic compound. Furthermore, there is an excellent agreement between the experimental data and predicted values from proposed model.

#### 3.2 Influence of organic concentration

Figure 4a presents both ICE and COD evolution with the specific electrical charge passed during the galvanostatic oxidation (238 A m\(^{-2}\)) of 2-naphtol (2-9 mM) in 1 M H\(_2\)SO\(_4\). As predicted from the model, the critical specific charge Q\(_\text{cr}\) (Eq. 25) increases with increase of the initial organic concentration (COD\(^0\)). Again, there is an excellent agreement between the experimental and predicted values.

#### 3.3 Influence of applied current density

The influence of current density on both ICE and COD evolution with the specific electrical charge...
Fig. 2. Evolution of a) COD and b) ICE in function of time (or specific charge); (A) represents the charge transport control; (B) represents the mass transport control.

Fig. 3. Evolution of COD and ICE (inset) in function of specific charge for different organic compounds: (x) acetic acid, (■) isopropanol, (□) phenol, (△) 4-chlorophenol, (◊) 2-naphtol; i = 238 A m⁻²; T = 25 °C; Electrolyte: 1 M H₂SO₄; The solid line represents model prediction.

passed during the galvanostatic oxidation of a 5 mM 2-naphtol in 1 M H₂SO₄ at different current densities (119-476 A m⁻²) is shown in Fig. 4b. As previously noted, an excellent agreement between the experimental and predicted values is observed.

DEGRADATION OF ORGANICS BY AO ON BDD

As mentioned above, thanks to its unique properties, during electrolysis in the region of water discharge, BDD anode produces a large quantity of •O2H that is weakly adsorbed on its surface, and consequently it has high reactivity for organic oxidation, providing the possibility of efficient application to wastewater treatment. So far, many papers have reported that during electrolysis at BDD electrodes at high potentials, a large number of organic pollutants are completely mineralised by the reaction with electrogenerated •OH radicals [12-34]. Some examples are summarised in Table 1.

Comninellis and co-workers investigated the behaviour of Si/BDD anodes in an acidic solution for the oxidation of a wide range of pollutants, and they observed that complete mineralisation was obtained with all the experimental conditions studied. In particular, they found that the oxidation is controlled by the diffusion of the pollutants towards the electrode surface, where the hydroxyl radicals are produced, and the current efficiency is favoured by a high mass-transport coefficient, high organic concentration and low current density [35-42]. Performing electrolysis in optimised conditions, without diffusion limitation, the current efficiency approaches 100%.

The electrochemical oxidation of different phenolic compounds (phenol, chlorophenols, nitrophenols) and carboxylic acids on BDD anodes was also studied by Canizares et al. [43-50]. They reported that the organic compounds were completely mineralised regardless of the characteristics of the wastewater (initial concentration, pH and supporting media) and operating conditions (temperature and current density) used. They also observed that the organics were ox-
Table 1. Some examples of organic compounds oxidised on diamond electrodes.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Experimental conditions</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acids</td>
<td>$i = 30$ mA cm$^{-2}$; $T = 30$ °C; 1 M H$_2$SO$_4$ pH of 11.</td>
<td>Average current efficiency: 70-90%</td>
<td>[12,13]</td>
</tr>
<tr>
<td>Cyanides</td>
<td>7.7 mM of cyanide, 0.05 M Na$_2$SO$_4$, pH of 11.</td>
<td>Energy consumptions of 20-70 kWh m$^{-3}$ to remove 70-80% of initial cyanides</td>
<td>[14]</td>
</tr>
<tr>
<td>Surfactants</td>
<td>$i = 4-20$ mA cm$^{-2}$; initial TOC = 15 mg L$^{-1}$</td>
<td>Average current efficiency of 6% and 12% for anionic and cationic surfactants</td>
<td>[15,16]</td>
</tr>
<tr>
<td>Carwash wastewater</td>
<td>$i = 15-60$ mA cm$^{-2}$</td>
<td>Initial current efficiency of about 40%</td>
<td>[17]</td>
</tr>
<tr>
<td>Naphthol</td>
<td>$i = 15-60$ mA cm$^{-2}$; 1 M H$_2$SO$_4$</td>
<td>Oxidation favoured by the formation of peroxodisulfuric acid</td>
<td>[19]</td>
</tr>
<tr>
<td>Triazines</td>
<td>$i = 50$ mA cm$^{-2}$; impinging cell</td>
<td>The degradation of triazines follows a pseudo first order kinetic</td>
<td>[20,21]</td>
</tr>
<tr>
<td>Mixture of phenols</td>
<td>$i = 30$ mA cm$^{-2}$; 0.1 M Na$_2$CO$_3$</td>
<td>Model proposed for the degradation of mixture of organics</td>
<td>[22]</td>
</tr>
<tr>
<td>Industrial wastewaters</td>
<td>$i = 7-36$ mA cm$^{-2}$; initial COD 1500-8000 mg L$^{-1}$</td>
<td>Current efficiency of 85-100%</td>
<td>[23]</td>
</tr>
<tr>
<td>Synthetic dyes</td>
<td>Amaranth, Basic Yellow, Reactive Black, Alizarin Red, Methyl Red, Orange II</td>
<td>Complete decolourization of the solutions</td>
<td>[24-29]</td>
</tr>
<tr>
<td>Herbicides</td>
<td>Chloromethylphenoxy herbicide, clotibric acid</td>
<td>Complete TOC removal</td>
<td>[30-33]</td>
</tr>
<tr>
<td>Effluent of a fine chemical plant</td>
<td>COD 6000 mg L$^{-1}$, TOC 1600 mg L$^{-1}$, pH = 6</td>
<td>Energy consumption of about 7 kWh m$^{-3}$ for complete mineralization</td>
<td>[34]</td>
</tr>
</tbody>
</table>

Discharged on both the electrode surface by reaction with hydroxyl radicals and in the bulk of the solution by inorganic oxidants electrogenerated on the BDD anodes, such as hydrogen peroxide, peroxodisulfates, peroxodiphosphates or percarbonates.

Some investigations have also tried to compare the behaviour of BDD with other electrodes, such as SnO$_2$, PbO$_2$, IrO$_2$, for the oxidation of organic pollutants. Chen an co-workers [51] reported that the current efficiency obtained with Ti/BDD in oxidizing acetic acid, maleic acid, phenol, and dyes was 1.6-4.3-fold higher than that obtained with the typical Ti/Sb$_2$O$_5$-SnO$_2$ electrode. Other papers have demonstrated that Si/BDD electrodes are able to achieve faster oxidation and better incineration efficiency than Ti/PbO$_2$ in the treatment of naphthol [18], 4-chlorophenol [35], chloranilic acid [52] and synthetic dyes [53].

**FUNDAMENTALS OF INDIRECT ELECTRO-OXIDATION METHODS WITH H$_2$O$_2$ ELECTROGENERATION**

Hydrogen peroxide is a green chemical that decomposes to O$_2$ and water. It is a hazardous product due to its comburant character, easily being decomposed under the action of metallic ions, UVA light and high temperature [54,55]. For these reasons, the on-site production of H$_2$O$_2$ for environmental applications is desirable for avoiding its dangerous transport and storage. However, the direct treatment of wastewaters with H$_2$O$_2$ is limited by its low oxidation power since it can only attack reduced sulfur compounds, cyanides, chlorine and certain organics like aldehydes, formic acid and some nitro-organic and sulfo-organic compounds.

It is known since 1882 that hydrogen peroxide can be produced from the cathodic reduction of dissolved O$_2$ at high surface area carbon electrodes [55,56]. In the last years the electrogeneration of H$_2$O$_2$ in acid medium has been applied to wastewater remediation by means of indirect electro-oxidation methods. These techniques are based on the continuous supply of H$_2$O$_2$ to the contaminated solution from the two-electron reduction of O$_2$ gas usually at carbon-felt [57-66] and carbon-polytetrafluoroethylene O$_2$-diffusion [65-76] cathodes:

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (30)$$

In an undivided electrolytic cell with a Pt [70] or BDD [67] anode, H$_2$O$_2$ is anodically oxidized to O$_2$ yielding hydroperoxyl radical (HO$_2$.•) as intermediate, a much weaker oxidant than •OH:

$$H_2O_2 \rightarrow HO_2. + H^+ + e^- \quad (31)$$

$$HO_2. \rightarrow O_2 + H^+ + e^- \quad (32)$$

Hydrogen peroxide is then accumulated in the solution up to attain a steady concentration directly proportional to the applied current, just when the rates of reactions become equal. Direct application of this technique to wastewater treatment, so-called AO with electrogenerated H$_2$O$_2$ (AO-H$_2$O$_2$), involves the destruction of organics mainly with Pt(•OH) or BDD(•OH) formed on Pt or BDD, respectively. In the first case using a Pt/O$_2$ cell, pollutants can also react more slowly with H$_2$O$_2$ and HO$_2$.• and in the second
one with a BDD/O₂ cell, they can be oxidized with other weaker oxidants like ozone, peroxodisulfate, peroxodicarbonate or peroxodiphosphate, respectively. Generated H₂O₂ can be utilized by Eq. 35, with hydroperoxyl radical (HO₂•) by Eq. 36 and/or with organic radical intermediates R• by Eq. 37:

Fe³⁺ + e⁻ → Fe²⁺ (34)
Fe³⁺ + H₂O₂ → Fe²⁺ + H⁺ + HO₂• (35)
Fe³⁺ + HO₂• → Fe²⁺ + H⁺ + O₂ (36)
Fe³⁺ + R• → Fe²⁺ + R• (37)

However, a part of •OH produced in the medium is lost by oxidation of Fe²⁺ from Eq. 38 and by decomposition of H₂O₂ from Eq. 39:

Fe²⁺ + •OH → Fe³⁺ + OH⁻ (38)
H₂O₂ + •OH → HO₂• + H₂O (39)

The rate of Fenton’s reaction can also decay by oxidation of Fe²⁺ in the bulk with HO₂• by Eq. 40 and at the anode by Eq. 41 when an undivided cell is used:

Fe²⁺ + HO₂• → Fe³⁺ + HO₂⁻ (40)
Fe²⁺ → Fe³⁺ + e⁻ (41)

The EF method in a BDD/O₂ cell, for example, involves the simultaneous oxidation of pollutants with BDD(•OH) produced by Eq. 33 and by •OH formed by Eq. 41 (Fenton’s reaction), although a slower degradation with weaker oxidants (H₂O₂, HO₂•, O₃, S₂O₈²⁻, etc.) is feasible.

In the PEF process the solution treated under EF conditions is exposed to UVA illumination. The action of this irradiation is complex and can be accounted for by: (i) a greater production of •OH from photorereduction of Fe(OH)²⁺, the predominant Fe³⁺ species in acid medium [77], by Eq. 42 and (ii) the photodecarboxylation of complexes of Fe(III) with generated carboxylic acids, as shown in Eq. 43 for oxalic acid [78]. This acid is generated during the oxidation of most organics and the fast photolysis of Fe(III)-oxalate complexes (Fe(C₂O₄)³⁺, Fe(C₂O₄)₂²⁻ and Fe(C₂O₄)³⁻) favours the decontamination process [68-71].
Fig. 5. (a) TOC abatement vs. specific charge and (b) chloride ion concentration vs. electrolysis time for the treatment of 100 mL of solutions containing 179 mg L\(^{-1}\) clofibric acid and 0.05 M Na\(_2\)SO\(_4\) of pH 3.0 using a BDD/O\(_2\) cell at 100 mA cm\(^{-2}\) and 35.0 °C by: (●) AO with electrogenerated H\(_2\)O\(_2\) (AO-H\(_2\)O\(_2\)-BDD), (○) AO-H\(_2\)O\(_2\)-BDD with UVA irradiation, (■) electro-Fenton (EF-BDD) with 1.0 mM Fe\(_{2+}\), (▲) photoelectro-Fenton (PEF-BDD) with 1.0 mM Fe\(_{2+}\) [76].

mineralization becomes greater since larger proportions of reactive BDD(•OH) and •OH are wasted by non-oxidizing reactions involving for example, the AO of BDD(•OH) to O\(_2\) and recombination of •OH to H\(_2\)O\(_2\). Moreover, a high current accelerates the formation of weaker oxidants like peroxodisulfate and ozone that also reduce the relative proportion of reactive BDD(•OH). The optimum conditions for EF-BDD and PEF-BDD treatments are found at pH 3.0, near the optimal pH of 2.8 for Fenton’s Eq. 33, and operating with 0.5-1.0 mM Fe\(_{2+}\).

The comparative oxidation power of indirect electro-oxidation methods can be better explained from its mineralization current efficiency (MCE, in %), calculated for each treated solution at a given electrolysis time \(t\) (h) from the expression [75]:

\[
MCE = \frac{n F V S \Delta TOC_{exp}}{4.32 \times 10^5 m I t} \tag{44}
\]

where \(n\) is the number of electrons consumed in the mineralization process, \(V\) is the solution volume (L), \(\Delta TOC_{exp}\) is the experimental TOC decay (mg L\(^{-1}\)), \(4.32 \times 10^5\) is a conversion factor (3,600 s h\(^{-1}\) x 12,000 mg of C mol\(^{-1}\)/100), \(m\) is the number of carbon atoms in the pollutant molecule and \(I\) is the applied current (A).

Table 2 summarizes the MCE values thus determined for 4-chlorophenoxyacetic acid (4-CPA), 4-chloro-2-methylphenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) using Pt/O\(_2\) and BDD/O\(_2\) cells under comparable conditions. In the first system a 10 cm\(^2\) Pt sheet of 99.99% purity was used as anode and at 3 h of electrolysis efficiencies of 3-6% for AO-H\(_2\)O\(_2\)-Pt, 14-20% for EF-Pt and 25-29% for PEF-Pt, corresponding to 12-19, 53-66 and 90-96% mineralization, are obtained. The first two methods with Pt do not allow total mineralization and are much less efficient than AO-H\(_2\)O\(_2\)-BDD and EF-BDD, respectively, which decontaminate completely all solutions practically at the same \(t_{TM}\). This confirms the much greater oxidation power of BDD than Pt, producing enough amount of reactive BDD(•OH) to destroy the initial contaminants and their by-products. Overall mineralization can only be attained by PEF-Pt due to the efficient photodecarboxylation of Fe(III)-oxalate complexes as ultimate by-products under the action of UVA light [68-71].

The decay kinetics for the above herbicides was followed by reversed-phase HPLC chromatography showing that they undergo a pseudo-first-order reaction with the different hydroxyl radicals. The last column of Table 3 shows a similar pseudo-first-order rate constant \(k_1\) for the AO-H\(_2\)O\(_2\) methods, independent of the anode used, indicating that the initial chloroaromatics are removed at similar rate by BDD(•OH) and Pt(•OH). A much higher and similar \(k_1\)-value can...
Table 2. Percent of TOC removal and mineralization current efficiency (MCE) determined after 3 h of electrolysis of 100 mL of solutions of chlorophenoxyacetic acid herbicides with a concentration equivalent to 100 mg L\(^{-1}\) TOC at pH 3.0 by indirect electro-oxidation methods at 100 mA. The last column gives the rate constant determined for their pseudo-first-order decay with hydroxyl radical [68-72].

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Method(a)</th>
<th>(T (^\circ C))</th>
<th>TOC removal (%)</th>
<th>MCE</th>
<th>(k_1 (s^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CPA</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td>35</td>
<td>19</td>
<td>5.6</td>
<td>8.2×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td></td>
<td>54</td>
<td>16</td>
<td>9.0×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>EF-Pt</td>
<td></td>
<td>66</td>
<td>20</td>
<td>2.0×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td></td>
<td>75</td>
<td>22</td>
<td>4.5×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td></td>
<td>96</td>
<td>29</td>
<td>2.7×10(^{-3})</td>
</tr>
<tr>
<td>MCPA</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td></td>
<td>19</td>
<td>6.0</td>
<td>9.8×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td></td>
<td>58</td>
<td>18</td>
<td>1.2×10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>EF-Pt</td>
<td></td>
<td>65</td>
<td>20</td>
<td>2.0×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td></td>
<td>76</td>
<td>24</td>
<td>2.3×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td></td>
<td>91</td>
<td>29</td>
<td>2.3×10(^{-3})</td>
</tr>
<tr>
<td>2,4-D</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td>25</td>
<td>13</td>
<td>3.6</td>
<td>1.3×10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td>35</td>
<td>57</td>
<td>16</td>
<td>1.2×10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>EF-Pt</td>
<td>25</td>
<td>57</td>
<td>16</td>
<td>3.0×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td>35</td>
<td>78</td>
<td>22</td>
<td>5.2×10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td>25</td>
<td>90</td>
<td>25</td>
<td>3.8×10(^{-3})</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td>35</td>
<td>12</td>
<td>3.1</td>
<td>2.0×10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td></td>
<td>59</td>
<td>15</td>
<td>1.1×10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>EF-Pt</td>
<td>53</td>
<td>14</td>
<td>1.6×10(^{-4})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td>80</td>
<td>21</td>
<td>4.0×10(^{-3})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td>99</td>
<td>26</td>
<td>2.0×10(^{-3})</td>
<td></td>
</tr>
</tbody>
</table>

\(a\)AO-H\(_2\)O\(_2\)-Pt: anodic oxidation in a Pt/O\(_2\) cell, AO-H\(_2\)O\(_2\)-BDD: anodic oxidation in a BDD/O\(_2\) cell, EF-Pt: electro-Fenton with 1 mM Fe\(^{2+}\) in a Pt/O\(_2\) cell, EF-BDD: electro-Fenton with 1 mM Fe\(^{2+}\) in a BDD/O\(_2\) cell, PEF-Pt: photoelectro-Fenton with 1 mM Fe\(^{2+}\) in a Pt/O\(_2\) cell.

Table 3. Percent of TOC removal and mineralization current efficiency (MCE) after 2 h of treatment and time for total mineralization \(t_{TM}\) and energy cost for total mineralization \(E_{TM}\) of 2.5 L of p-cresol solutions of pH 3.0 by solar photoelectro-Fenton using a flow reactor with a 20 cm\(^2\) BDD anode and a 20 cm\(^2\) O\(_2\)-diffusion cathode, at 30 \(^\circ\)C and liquid flow rate of 180 L h\(^{-1}\) [75].

<table>
<thead>
<tr>
<th>[p-cresol(_0)] (mg L(^{-1}))</th>
<th>[Fe(^{2+})(_0)] (mM)</th>
<th>Current density (mA cm(^{-2}))</th>
<th>TOC removal (%)</th>
<th>MCE</th>
<th>(t_{TM}) (min)</th>
<th>(E_{TM}) (kWh m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>0.25</td>
<td>25</td>
<td>42</td>
<td>119</td>
<td>300</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>25</td>
<td>56</td>
<td>158</td>
<td>240</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>50</td>
<td>75</td>
<td>104</td>
<td>240</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>50</td>
<td>87</td>
<td>118</td>
<td>180</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>100</td>
<td>89</td>
<td>60</td>
<td>180</td>
<td>51</td>
</tr>
<tr>
<td>256</td>
<td>1.0</td>
<td>50</td>
<td>55</td>
<td>148</td>
<td>330</td>
<td>27</td>
</tr>
<tr>
<td>512</td>
<td>1.0</td>
<td>50</td>
<td>36</td>
<td>195</td>
<td>450</td>
<td>37</td>
</tr>
<tr>
<td>1024</td>
<td>1.0</td>
<td>50</td>
<td>34</td>
<td>373</td>
<td>(-)</td>
<td>(-)</td>
</tr>
</tbody>
</table>

\(\text{Not determined}\)

be seen for EF-Pt, EF-BDD and PEF-Pt, thus confirming that in these treatments the herbicides react much more rapidly with \(\cdot\)OH. The greater oxidation ability of indirect methods using a BDD/O\(_2\) cell in comparison to a Pt/O\(_2\) is then due to the faster mineralization of final by-products with reactive BDD(\(\cdot\)OH).

GC-MS and HPLC analyses of chlorophenoxyacetic acid solutions electrolyzed in a BDD/O\(_2\) cell revealed the formation of primary phenol intermediates such as 4-chlorophenol for 4-CPA, 4-chloro-o-cresol for MCPA, 2,4-dichlorophenol for 2,4-D and 2,4,5-trichlorophenol for 2,4,5-T [72]. These species react rapidly with the same oxidant since they were uniquely detected while starting herbicides are destroyed. HPLC analysis of generated carboxylic acids revealed the large persistence of the ultimate oxalic acid in AO-H\(_2\)O\(_2\)-BDD or its Fe(III) complexes in EF-BDD, since these species can only be converted to CO\(_2\) by BDD(\(\cdot\)OH). This explains the long \(t_{TM}\) for chloroaromatic pollutants in EF-BDD. In contrast, the
Fig. 6. Dependence of TOC on specific charge for the mineralization of 100 mL of a 220 mg L\(^{-1}\) indigo carmine solution in 0.05 M Na\(_2\)SO\(_4\) of pH 3.0 at 33 mA cm\(^{-2}\) and 35.0 °C using a Pt/O\(_2\) or BDD/O\(_2\) cell [74]. (○) EF-Pt with 1.0 mM Fe\(^{2+}\), (■) PEF-Pt with 1.0 mM Fe\(^{2+}\), (◆) EF-BDD with 1.0 mM Fe\(^{2+}\), (▲) PEF-Pt with 1.0 mM Fe\(^{2+}\) + 0.25 mM Cu\(^{2+}\).

Fig. 7. Evolution of the concentration of: (a) oxalic acid and (b) oxamic acid during the degradation of a 220 mg L\(^{-1}\) indigo carmine solution under the conditions given in Fig. 6.

The much quicker mineralization found for PEF-BDD (Fig. 5a) is related to the fast photolysis of Fe(III)-oxalate complexes [76].

The high oxidation power of the EF-BDD method has been confirmed in the comparative treatment of acidic aqueous solutions containing up to 0.9 g L\(^{-1}\) of the dye indigo carmine by EF and PEF using BDD/O\(_2\) and Pt/O\(_2\) cells [74]. As illustrates by Fig. 6 for 220 mg L\(^{-1}\) of the dye at pH 3.0, the use of EF-Pt with 1.0 mM Fe\(^{2+}\) leads to a fast degradation up to attain 46% mineralization at \(Q = 3\) Ah L\(^{-1}\) (3 h), but at longer time decontamination becomes so slow that TOC is only reduced by 49% at \(Q = 9\) Ah L\(^{-1}\) (9 h). Surprisingly, the PEF-Pt method only yields a partial mineralization of 84% at the end of electrolysis, as expected if some Fe(III) complexes different to those oxalic acid can not be photodecomposed by UVA light. A quicker TOC destruction takes place in EF-BDD with 1.0 mM Fe\(^{2+}\), where 91% of TOC is removed at 9 h and complete mineralization is reached at \(t_{TM} = 13\) h. That means that all complexes of Fe(III) with final carboxylic acids are efficiently oxidized with BDD(\(^{\bullet}\)OH). Figure 6 shows that overall destruction of all by-products is also feasible by PEF-Pt if 1.0 mM Fe\(^{2+}\) and 0.25 mM Cu\(^{2+}\) are combined as co-catalysts. For all procedures tested, a higher mineralization rate was found with increasing current density and initial dye content. The initial nitrogen of indigo carmine was mainly released as ammonium ion, along with a small fraction of nitrate ion.

The indigo carmine decay always followed a pseudo-zero-order reaction. GC-MS and HPLC analyses of electrolyzed solutions evidenced its conversion into isatin-5-sulfonic acid, indigo and isatin, which are degraded to oxalic and oxamic acids. The different oxidation power of the EF and PEF treatments of the dye can be satisfactorily explained from the evolution of the Fe(III) and/or Cu(II) complexes of these final by-products, as can be seen in Figs. 7a and 7b. Thus, Fe(III)-oxalate and Fe(III)-oxamate remain stable in EF-Pt because they can not be oxidized either with Pt(\(^{\bullet}\)OH) or with \(^{\bullet}\)OH, but the latter complexes can be photolyzed under the action of UVA light in PEF-Pt. The opposite behaviour can be observed for EF-BDD where both complexes can be completely removed with BDD(\(^{\bullet}\)OH). When Cu\(^{2+}\) is used as co-catalyst in PEF-Pt, Cu(II)-oxalate and Cu(II)-oxamate are competitively produced and efficiently destroyed by Pt(\(^{\bullet}\)OH) and/or \(^{\bullet}\)OH. This evidences the positive catalytic action of combining Fe\(^{2+}\), Cu\(^{2+}\) and UVA light for the treatment of wastewaters with aromatic pollutants containing nitrogen if oxamic acid is formed as by-product.

The studies carried out for the mineralization of aromatic compounds with a BDD/O\(_2\) cell have clearly demonstrated the fastest removal of all pollutants by PEF-BDD. Recently, the alternative use of sunlight in this method has been assessed using a flow plant with a filter-press electrochemical cell coupled to a solar photoreactor [67,75]. This system treated 2.5 L of a contaminated solution operating in batch and under steady conditions. The liquid circulated continuously through the BDD/O\(_2\) cell containing electrodes of 20
of Table 3 shows that ETM decreases strongly as less cm² area and the solar photoreactor, which was a polycarbonate box (irradiated volume 600 mL) with a mirror at the bottom and inclined 30° from the horizontal to collect better the direct sun rays.

Figure 8a presents the TOC-time plots obtained for the degradation of 128 mg L⁻¹ of o-cresol, m-cresol or p-cresol (corresponding to 100 mg L⁻¹ TOC), 0.25 mM Fe²⁺ and 0.05 M Na₂SO₄ of pH 3.0 in the flow plant by EF-BDD and SPEF-BDD at 50 mA cm⁻² [75]. A fast destruction of the o-cresol solution for 120 min of EF-BDD with 50% TOC reduction can be observed, but at longer time its mineralization becomes so slow that at 180 min only 54% decontamination is attained due to the hard oxidation of final Fe(III)-oxalate complexes with BDD(•OH) and/or •OH. In contrast, the same o-cresol solution, as well as the m-cresol and p-cresol solutions, are much more rapidly degraded by SPEF-BDD, being completely decontaminated at t_TM =180 min (Q = 1.20 Ah L⁻¹) due to the quick and efficient photodecarboxylation of Fe(III)-oxalate complexes by the incident UVA light supplied by solar irradiation.

Figure 8b evidences a gradual rise in degradation rate of the p-cresol solution with increasing current density of 25, 50 and 100 mA cm⁻², yielding total mineralization at decreasing t_TM of 240, 180 and 160 min, respectively, corresponding to increasing Q of 0.80, 1.20 and 1.41 Ah L⁻¹. Accordingly, Table 3 shows a higher percent of TOC removal at 2 h of electrolysis, along with the concomitant fall in efficiency, for these experiments. This corroborates the greater production of more amounts of BDD(•OH) and •OH when current density rises, but with an acceleration of their non-oxidizing reactions in larger extent. Results of Table 3 also reveal an enhancement of the mineralization as the contaminant content rises up to 1 g L⁻¹, as expected if the waste reactions of the above oxidants are gradually less significant. A MCE value as high as ca. 400% is found after 2 h treatment of the most concentrated solution, indicating the high efficiency of sunlight to photolyze final Fe(III)-oxalate complexes. In addition, p-cresol solutions are more rapidly destroyed with 1.0 mM Fe²⁺ than with 0.25 mM Fe²⁺ by the quicker photolysis of great amounts of such complexes.

The energy cost for total mineralization (ETM, in kWh m⁻²) of p-cresol solutions at time t_TM (h) in the flow plant was determined as follows:

\[
ETM = \frac{V I t_{TM}}{V_s}
\]

where V is the average cell voltage (V). An inspection of Table 3 shows that ETM decreases strongly as less current density is applied due to the drop in cell voltage and the gradual increase in MCE. This parameter falls with rising Fe²⁺ content from 0.25 to 1.0 mM due to the faster photodecarboxylation of Fe(III)-oxalate complexes, but increases with rising initial pollutant concentration because longer t_TM is needed for greater contents of p-cresol. The lowest ETM value of 6.6 kWh m⁻² is found when treating a 128 mg L⁻¹ p-cresol solution with 1.0 mM Fe²⁺ at 25 mA cm⁻². These results confirm the high efficiency and low energy cost required for the degradation of cresols by SPEF-BDD, making this technique viable for industrial application.

CONCLUSIONS

This paper summarizes recent researches carried out on electrochemical oxidation of organic pollutants for wastewater treatment using diamond electrodes and indirect electro-oxidation methods with a BDD/O₂ cell. During electrolysis in the potential region of water discharge, BDD anodes involve the production of weakly adsorbed hydroxyl radicals that unselectively and completely mineralise organic pollutants with high current efficiency.

The oxidation rate on BDD is independent on the chemical nature of organic pollutants but depends only on the operating conditions. In particular higher
current efficiency, near 100%, were obtained at high organic concentration and low current density.

A theoretical kinetic model of organic mineralization on boron-doped diamond anodes has been presented for the prediction of the evolution of chemical oxygen demand and current efficiency during organic oxidation. The experimental verification of the model at several levels (fluence of the nature of the organic pollutants, organic concentration and applied current density) shows excellent agreement with theory in all investigated cases.

In AO with electrogenerated H₂O₂, organics are effectively destroyed by BDD(•OH). The EF-BDD treatment removes more rapidly the aromatic pollutants because they mainly react with •OH formed from Fenton’s reaction. However, complexes of Fe(III) with final carboxylic acids like oxalic and oxamic can only be slowly oxidized with BDD(•OH). The PEF-BDD method is more efficient due to the parallel and quicker photodecarboxylation of final Fe(III)-oxalate complexes by UVA light. When oxamic acid is produced, its Fe(III) complexes can not be photolyzed and the use of Cu²⁺ as co-catalyst enhances the mineralization process since Cu(II)-oxamate complexes are quickly removed with hydroxyl radicals. SPEF can be a viable technique for the treatment of industrial wastewaters due to its high efficiency and low operational cost.

REFERENCES


Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.