Degradation of humic acid from water by advanced electrochemical oxidation method
I. Vlaicu, A. Pop, F. Manea and C. Radovan

ABSTRACT

In this study, the electrooxidation treatment method using boron-doped diamond (BDD) electrodes was investigated for the degradation of humic acid (HA) following absorbance at 254 nm (A_{254}), color (A_{436}) and total organic carbon (TOC) analysis. Also, a surrogate SUVA_{254} parameter was used to evaluate the aromatic carbon content. Prior to the application of the electrooxidation for HA degradation the electrochemical behavior of BDD electrode in HA containing 0.1M Na_{2}SO_{4} supporting electrolyte was studied by cyclic voltammetry (CV), and the working conditions of bulk electrolysis corresponding to water decomposition potential range were selected. The influence of the applied current density, pH, HA initial concentration on the performance of BDD electrode was investigated in relation with the specific electrical consumption. Applying electrooxidation using BDD electrodes for the real surface water treatment led to the mineralization efficiency of 65% after 150 minutes.

Key words | BDD electrodes, electrochemical efficiency, electrooxidation, humic acid degradation, removal efficiency, SUVA_{254}

INTRODUCTION

Humic acids (HAs) are water-soluble compounds with high molecular weight, refractory and characterized as yellow to black in color (Portjanskaja et al. 2006). Humic acid represents a fraction of humic substances that is insoluble in water under acidic conditions at pH < 2 and soluble at higher pH values (Uyguner & Bekbolet 2005a). Water quality can be adversely affected by the HAs. They may contribute to undesirable water color, complexing with metals and yielding metal concentration exceeding normal solubility (Uyguner & Bekbolet 2005a). Also, they may form complexes with pesticides and heavy metals and lead to plugging and fouling problems on membranes (Selcuk & Bekbolet 2008). From the drinking water treatment perspective, HAs are important due to their role as precursors to the formation of harmful disinfection by-products (DBP). Hence, in drinking water supplies or process water it is desirable to remove or minimize the HAs concentration.

Many different treatment methods are suitable for water treatment technology to remove HA from water, such as: coagulation, sorption, biofiltration, membrane process and advanced oxidation processes (Eggins et al. 1997; Qiao et al. 2003; Uyguner & Bekbolet 2005b; Uyguner et al. 2007; Wong et al. 2007; Selcuk & Bekbolet 2008; Mariquit et al. 2008; Stepiak et al. 2009). The choice of the treatment method is based on the technical-economical considerations as well as ease of control and reliability.

Recently, the so-called advanced oxidation processes (AOPs) have received attention because they can provide an efficient degradation of organics from water (Eggins et al. 1997; Qiao et al. 2003; Uyguner & Bekbolet 2005b; Brillas et al. 2006; Uyguner et al. 2007; Brillas et al. 2008; Mariquit et al. 2008; Martinez-Huitle & Brillas 2009). These environmentally friendly methods are based on the generation of hydroxyl radicals (OH), which represent a non-selective...
strong oxidant able to mineralize organics to CO₂ and H₂O. The application of advanced oxidation techniques are considered effective tools for the elimination of HA from natural waters, because can completely mineralize it.

Electrochemical oxidation is a very promising advanced method for organics degradation (Chiang et al. 2000; Motheo & Pindeho 2000; Alfaro et al. 2006; Brillas et al. 2006, 2008; Liao et al. 2008; Martinez-Huitle & Brillas 2009). The key of the electrooxidation performance is represented by the electrode materials, a major factor responsible for the electrooxidation mechanism. Based on the type of generation of hydroxyl radicals, Comninellis (Comninellis 1994) classified the electrode materials as so-called “active” and “non-active” electrodes in relation with the implication of the electrode surface in the interaction with hydroxyl ions. Boron-doped diamond (BDD) is a “non-active” electrode, which interacts very weakly with OH, allowing direct reaction with organics (Martinez-Huitle & Brillas 2009). In the last years, electrochemical oxidation by boron-doped diamond (BDD) electrodes has attracted great attention for decontamination of the water polluted with organics (Carter & Farrell 2008; Ochiai et al. 2010). This process is interesting for the treatment of natural waters and dilute wastewaters, and it is in competition with the process of chemical oxidation using strong oxidants (Kapalka et al. 2010). The wide potential window of BDD electrode makes it possible to generate different highly active oxidants, with the possibility of very effective anodic hydroxyl radical production and improvement in the current efficiency. Also, its physical properties, i.e. hardness, low environmental impact, high hole mobility etc. and stable surface made this anode material suitable for electrochemical degradation of organics (Alfaro et al. 2006; Ochiai et al. 2010).

The electrochemical combustion of HA using BDD electrodes was reported by Liao (Liao et al. 2008) with a different approach in relation with the assessment of humic acid concentration and mineralization performance. In the present investigation, the degradation and mineralization of humic acid in 0.1M Na₂SO₄ supporting electrolyte is achieved by the electrochemical process using commercial BDD/Nb electrodes. The performance of the degradation and mineralization of humic acid was determined in relation with the bulk electrolysis under galvanostatic regime operated at optimal working conditions, which were established for a synthetic solution with known concentration of humic acid.

To establish the range of applied current density, the electrochemical behavior of BDD electrode in the presence of humic acid was investigated by cyclic voltammetry. Also, HA degradation and mineralization rates were monitored and the apparent rate constants were determined. A practical application of the electrolysis using BDD electrode was achieved for real surface water from Bega river to degrade and mineralize HA.

**METHODS**

**Electrochemical characterization of BDD electrode**

The electrochemical behaviour of the disc BDD electrode with the surface areas of 0.07068 cm² (Windsor Scientific Ltd, UK) in the presence of humic acid was studied by cyclic voltammetry (CV). Subsequently, an electrochemical pre-treatment by three repetitive cycling between 0.05 V to 2 V vs. SCE in 0.1M Na₂SO₄ supporting electrolyte was performed. All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode and BDD working electrode.

**Bulk electrolysis experiments and analytical procedures**

The degradation experiments were carried out by batch process using an undivided cell of 1 dm³ volume, for different humic acid concentrations in 0.1M Na₂SO₄ supporting electrolyte. The initial parameters for humic acid in solution are gathered in Table 1.

Table 1: The initial parameters of humic acid

<table>
<thead>
<tr>
<th>HA concentration (mg dm⁻³)</th>
<th>TOC (mg dm⁻³)</th>
<th>A₂₅₄</th>
<th>A₄₃₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.4</td>
<td>7.72</td>
<td>0.361</td>
<td>0.079</td>
</tr>
<tr>
<td>24.2</td>
<td>17.01</td>
<td>0.773</td>
<td>0.175</td>
</tr>
<tr>
<td>44.0</td>
<td>29.84</td>
<td>0.467*</td>
<td>0.102*</td>
</tr>
</tbody>
</table>

*1:3 dilutions.
The BDD/Nb electrodes (100 mm × 50 mm × 1 mm) with 280 cm² geometric area provided by CONDIAS, Germany were used as anodes, and stainless steel plates (100 mm × 50 mm × 1 mm) were employed as cathodes under vertical arrangement. A regulated DC power supply (HY3003, MASTECH) was used under galvanostatic regime at 100 A m⁻², 50 A m⁻² and respective, 25 A m⁻² current densities.

After each 30 minutes, samples were drawn from the cell and HA degradation was monitored in terms of A₂₅₄ and A₄₃₆ based on the literature data (Uyguner & Bekbolet 2005b) characterized by UV-VIS spectroscopy. Also, TOC parameter was used to check HA mineralization. In addition, specific UV absorbance (SUVA₂₅₄, m⁻¹ mg⁻¹ dm³) defined as A₂₅₄ per milligram of total organic carbon has been used as surrogate of the disinfection-by-products precursors, as well as a good evaluation of aromatic carbon content. Also, SUVA₂₅₄ can be used to assess the hydrophilic or hydrophobic character of humic acid. SUVA₂₅₄ > 4 indicates mainly hydrophobic and SUVA₂₅₄ < 3 represents hydrophilic materials (Uyguner & Bekbolet 2005a; Wong et al. 2007). UV-VIS spectrometric measurements were performed on a Varian 100 Carry using 1 cm quartz cell, and TOC content of the samples was analyzed at a Shimadzu TOC analyzer. Measurements of pH were done by an Inolab WTW pH meter.

The removal efficiency of HA (η, %) was determined as the percentage of removed HA reported at the initial HA concentration, and the electrochemical efficiency for HA oxidation was determined based on Equation (1) (Wang et al. 2006):

\[ E_{HA} = \frac{(HA_0 - HA)}{Q \cdot S} \times V \text{ (mg/C cm}^2\text{)} \] (1)

where \((HA_0 - HA)\) is the change in the humic acid concentration determined by A₂₅₄ and colour A₄₃₆ during experiments for a charge consumption of \(Q\) corresponding to various electrolysis time, \(V\) is the sample volume (700 cm³) and \(S\) is the area of the electrode surface (cm²).

The electrochemical efficiency for HA mineralization defined as an overall efficiency for complete oxidation to CO₂ was determined based on Equation (2) modified as (1') taking into consideration the change in TOC measurements during experiments, determining \((TOC_0 - TOC)\).

\[ E_{TOC} = \frac{(TOC_0 - TOC)}{Q \cdot S} \times (V \text{ mg/C cm}^2) \] (1')

The mineralization current efficiency (MCE, %), defined also as current output for direct faradayc complete oxidation, for each electrolyzed solution was calculated based on Equation (2) (Guinea et al. 2009):

\[ MCE = \frac{nFVs \cdot A(TOC)_{exp}}{4.32 \times 10^7 \text{ mIt}} \times 100\% \] (2)

where \(n\) is the number of electrons consumed in the mineralization process of HA, \(F\) is the Faraday constant (= 96 487 C mol⁻¹), \(V_s\) is the solution volume (dm³), \(A(TOC)_{exp}\) is the experimental TOC decay (mg dm⁻³), 4.32107 is a conversion factor for units homogenization (= 5 600 s h⁻¹ × 12 000 mg of carbon mol⁻¹), \(m\) is the number of carbon atoms in humic acid, \(I\) is the applied current (A), and \(t\) is time (h). The number of electrons consumed is determined based on the overall mineralization reaction of humic acid to CO₂ (\(C_9H_9NO_6 + 14 H_2O = 9CO_2 + NO_2 + 37 H^+ + 37e^-\)).

The specific energy consumption, \(W_{sp}\), was calculated with the relation (3):

\[ W_{sp} = Q_{sp} \cdot U \text{ (kWh dm}^{-3}\text{)} \] (3)

where \(Q_{sp}\) represents the specific charge consumption of C corresponding to 1 dm³ and \(U\) is the cell voltage (V).

Also, the energy consumption for the removal of 1 kg organic carbon (expressed by TOC) was calculated according to:

\[ W_{sp} = \frac{U \cdot I \cdot t}{m} \] (4)

where \(U\) is the potential (V), \(I\) is the applied current (A), \(t\) is the electrolysis time (hour), and \(m\) represent the quantity of TOC removed in the electrolysis process (kg). Sodium sulphate were analytical grade from Merck, and Fluka humic acid solutions were freshly prepared with double-distilled water at different concentrations and filtered through 0.2 μm Millipore filters.
RESULTS AND DISCUSSION

Electrochemical characterization

The electrochemical behavior of the BDD electrode in 0.1 M Na₂SO₄ was studied by cyclic voltammetry (CV) to explore the electrochemical characteristics of humic acid in relation with the oxidation process on BDD electrode to clarify the relationship between experimental variables and the electrode response. Figure 1 shows the three scans of cyclic voltammograms for BDD electrode recorded in supporting electrolyte and in the presence of 2 mg dm⁻³ humic acid, and the potential of oxygen evolution is about +1.5 V/SCE, much lower than the value reported in the literature (2.3 V/SCE) (Liao et al. 2008). In the presence of humic acid the anodic current increased starting from the potential value of about +1.0 V/SCE, but no limiting current for the oxidation of humic acid was noticed. This result informed that humic acid oxidation occurred by the direct electron transfer process at the electrode surface under water stability potential. However, decreasing anodic current corresponding to direct humic acid oxidation for the second and the third scans informed that the electrode fouling occurred under the water stability potential. Thus, CVs results suggest that in order to avoid the electrode fouling during electrooxidation, the operating conditions for the further bulk electrolysis experiments to be conducted under water decomposition range of oxygen evolution.

Bulk electrolysis

The anodic oxidation of HA on BDD/Nb electrodes in 0.1M Na₂SO₄ supporting electrolyte has been performed under bulk electrolysis conditions and galvanostatic regime, without agitation, at the oxygen evolution potential range to achieve the destruction of HA under the action of hydroxyl radical formed as intermediate from water oxidation to O₂. The performance of the electrooxidation process for humic acid degradation is assessed versus the influence of working parameters, i.e., current densities values, initial concentration of humic acid and pH values in order to optimize it for real applications.

Influence of current density

Under all current density conditions applied for the electrooxidation process, the degradation of humic acid occurred under the action of hydroxyl radical generated, physisorbed or remained near the BDD surface (Martinez-Huitle & Brillas 2009). Also, in sulfate media, besides hydroxyl radicals other weaker oxidants can be generated, e.g., S₂O₈²⁻, H₂O₂ and O₃ (Panizza & Cerisola 2005). These active intermediates can further oxidize the humic acid. However, the values of the current density were chosen based on the economical considerations given by the lower specific energy consumption.

Solutions of 25 mg dm⁻³ HA at pH 6.2 were degraded by applying various current density of 25, 50 and respective, 100 A m⁻². In each series, the HA degradation efficiency was followed, in terms of A₂₅₄, A₄₃₆ and TOC. Also, the electrochemical efficiency determined taking into account the charge consumption based on Equation (1), and the results obtained are presented in Figure 2.

In general, an increase in current density improves the electrooxidation efficiency evolution versus time. For humic acid expressed as A₂₅₄, A₄₃₆, the current density of 100 A m⁻² lead to better efficiencies especially at the beginning of the electrolysis process. After about 100 minutes electrolysis time, by applying 100 and 50 A m⁻² current densities, no increase of HA removal efficiency was reached. The tendency of HA removal efficiency during electro-
Figure 2 | Influence of applied current density 1–100 A m⁻²; 2–50 A m⁻²; 3–25 A m⁻² on the trends of the humic acid removal efficiency and electrochemical efficiency evolution in time using BDD electrodes in electrooxidation process in 0.1 M Na₂SO₄ at the initial concentration of 25 mg dm⁻³ HA, characterized by (a,a') UV 254 nm (A₂54), (b,b') Color 436 nm (A₄36) and (c,c') TOC.
oxidation process by applying 25 A m$^{-2}$ current density are different, the efficiency increasing with electrolysis time (Figure 2a and b). Also, an increasing in mineralization efficiency with electrolysis time was evidenced for all studied current densities conditions (Figure 2c). A different behavior for the assessment of the electrooxidation performance for HA degradation and mineralization was found based on the electrochemical efficiency determination, which takes into account the charge consumed during the electrooxidation process. The relationship between specific energy consumption and electrolysis time for the used current densities is shown in Figure 3. For the same electrolysis time, at higher current density the consumed charge and implicit, specific energy consumption increased. For all process parameters that characterize the electrochemical performance for HA degradation and mineralization, applying the current density of 50 A m$^{-2}$ allowing to reach the best results from technical-economical point of view at the electrolysis time of
The humic acid removal efficiency and electrochemical efficiency evolution in time using BDD electrodes in electrooxidation process at the current density of 100 A m$^{-2}$ for the initial concentration of HA: 1–44.0 mg dm$^{-3}$; 2–24.2 mg dm$^{-3}$; 3–11.4 mg dm$^{-3}$ in 0.1 M Na$_2$SO$_4$, characterized by (a,a$'$) UV 254 nm ($\eta$A$_{254}$), (b,b$'$) Color 436 nm ($\eta$A$_{436}$) and (c,c$'$) TOC.

**Figure 5**
60 minutes. This result is supported by the mineralization current efficiencies in relation with the specific energy consumption shown in Figure 3a and b, and the kinetics results gathered in Table 2.

For the electrooxidation processes the pseudo first-order equations were chosen to determine the apparent rate constants ($k_{app}$ and $k'_{app}$), which were calculated based on the relations of $\ln(C_0/C_t) = k_{app}(t)$, and respective, $\ln(C_0/C_t) = k'_{app}(Q)$, in which Q represents the electrical charge passed during electrooxidation of HA. The effective mineralization rate was assessed as the ratio between the apparent rate constants calculated for TOC analysis and the apparent rate constant calculated for UV254 analysis ($k_{app,TOC}/k_{app,UV}$ and $k'_{app,TOC}/k'_{app,UV}$). The value of this ratio close to 1 indicate that the effective mineralization rate was achieved for all applied current density.

**Influence of pH**

The controlled experiments were exemplified under an applied current density of 100 A m$^{-2}$ at a 12.5 mg dm$^{-3}$ HA concentration to investigate the effect of pH value, i.e., 3.5, 4.0, and 6.2, during the electrolysis process (Figure 4). The performance of the electrooxidation process was slightly improved under more alkaline versus acidic conditions for each process control parameters to characterize HA degradation and mineralization. The results regarding pH influence on HA degradation expressed as $A_{254}$ and $A_{436}$ were not shown here, being similarly with mineralization results (Figure 5). The influence of the pH mainly acts on the level of the oxidation mechanism under water decomposition region via the action of hydroxyl radicals physisorbed on BDD surface (Lissens et al. 2003). Alkaline media may favor the generation of hydroxyl radical and the electrooxidation performance is improved. Also, the electroactive species in alkaline medium is more easily oxidized than that of acid medium (protonated form) (Martinez-Huitle & Brillas 2009). Even if about 70% TOC removal was achieved at pH 6.2, the mineralization current efficiency is low (below 1%), which represents the current output for direct faraday complete oxidation, because of parasite reactions that occur at this applied current density, beside the mineralization reaction of HA, e.g., electrochemical generation of hydroxyl species by hydrogen peroxide reduction at the cathode surface (Martinez-Huitle & Brillas 2009), aspect supported by the pH increasing during the electrooxidation process for all working conditions tested.

**Influence of HA concentration**

The HA concentration influence on electrooxidation process efficiency was studied under the initial pH of 6.2 and the mass transport control at applied current density of 100 A m$^{-2}$ to assure the conditions appropriate for the generation of sufficient quantities of hydroxyl radicals able to attack HA without the electrode fouling. The HA initial concentrations were 44.0, 24.2 and 11.4 mg dm$^{-3}$ (Figure 5). For all studied HA concentrations applying the electrooxidation led to good results regarding the efficiencies of HA degradation and mineralization for all control parameters studied.

The apparent constant rates for all the parameters that characterize humic acid analytically monitored in this study expressed versus time ($k_{app}$), and versus charge passed during electrolysis ($k'_{app}$), were calculated based on the first order equations and they are gathered in Table 3.

### Table 2 | Current density influence on the apparent rate constants versus time and electrical charge consumed

<table>
<thead>
<tr>
<th>Parameter used for HA determination</th>
<th>Current density (A m$^{-2}$)</th>
<th>Apparent rate constant $k_{app}$ (min$^{-1}$) ($\times 10^3$)</th>
<th>Apparent rate constant $k'_{app}$ (C$^{-1}$) ($\times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UV$_{254}$</strong></td>
<td>100</td>
<td>9.1</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9.7</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>4.0</td>
<td>9.6</td>
</tr>
<tr>
<td><strong>TOC</strong></td>
<td>100</td>
<td>8.6</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.5</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>4.0</td>
<td>9.5</td>
</tr>
</tbody>
</table>
For 44.0 mg·dm$^{-3}$ initial HA concentrations the values of $k_{app,TOC}$/$k_{app,UV}$ and $k'_{app,TOC}$/$k'_{app,UV}$ different by 1 indicated that not very effective mineralization was reached. At lower HA concentrations, e.g., 11.4 and 24.2 mg·dm$^{-3}$, the effective mineralization was achieved under this applied current density.

Also, under mass transport control regime of water decomposition, besides the parasitic reactions that occur with the electrooxidation process, the low values of mineralization current efficiencies indicated the formation of an important number of intermediates (Kapalka et al. 2010). This aspect is supported by the evolution of the surrogate parameter SUVA$_{254}$, which decreased from 4.9 m$^{-1}$ mg$^{-1}$ dm$^3$ to 2.4 m$^{-1}$ mg$^{-1}$ dm$^3$ during the electrooxidation process. This indicates a decrease of the hydrophobic character and an increase of the hydrophilic character of the oxidized products resulted during electrolysis.

In according with the literature (Motheo & Pindeho 2000; Liao et al. 2008), all these findings showed that HA mineralization on BDD electrodes is not an instantaneous process and HA mineralization is preceded by cromophor groups destruction and followed by ring opening.

### Real surface water electrolysis

The practical application of the electrooxidation using BDD electrodes under optimized conditions above-determined of pH 6.2 and the current density of 50 A·m$^{-2}$ was achieved for a real surface water from Bega river. The characteristics of the real water before and during the electrooxidation process are presented in Tables 4 and 5.

The structural changes of the humic acid during treatment process monitored by SUVA$_{254}$ informed about the enhancement the hydrophilic character of water sample, which was similarly with the results presented above, which informed about the presence of the intermediates. The color removal efficiency after 60 minutes electrolysis time was about 100%. However, after 150 minutes of electrolysis about 73% of UV$_{254}$ and 65% of TOC was removed.

An important factor in the electrochemical treatment of organic polluted water is the specific energy consumption necessary to achieve the desired results. The specific energy consumption for the removal of 65% of TOC from the natural water after 150 minutes electrolysis time reached the value of $4 \times 10^3$ kW·h·kg$^{-1}$·TOC, which is comparable with those

### Table 3

<table>
<thead>
<tr>
<th>Type of HA determination</th>
<th>HA concentration/mg·dm$^{-3}$</th>
<th>Apparent rate constant $k_{app}$ (min$^{-1}$) ($\times 10^3$)</th>
<th>Apparent rate constant $k_{app}'$ (C$^{-1}$) ($\times 10^5$)</th>
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</thead>
<tbody>
<tr>
<td>UV$_{254}$</td>
<td>11.4</td>
<td>7.6</td>
<td>4.5</td>
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<td></td>
<td>24.2</td>
<td>9.1</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>44.0</td>
<td>14.8</td>
<td>8.9</td>
</tr>
<tr>
<td>TOC</td>
<td>11.4</td>
<td>7.2</td>
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<tr>
<td></td>
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### Table 4

<table>
<thead>
<tr>
<th>Q (Ah)</th>
<th>t (min)</th>
<th>pH</th>
<th>TOC (mg·dm$^{-3}$)</th>
<th>TOC removal efficiency (%)</th>
<th>A$_{254}$</th>
<th>UV$_{254}$ process efficiency (%)</th>
<th>SUVA$_{254}$ (m$^{-1}$·mg$^{-1}$·dm$^3$)</th>
<th>A$_{436}$</th>
<th>UV$_{436}$ process efficiency (%)</th>
<th>W$_{sp}$ (kW·g$^{-1}$·TOC)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>6.20</td>
<td>10.65</td>
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<td>0</td>
<td>4.003</td>
<td>0.108</td>
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<tr>
<td>0.7</td>
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<td>3.601</td>
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<td>60</td>
<td>8.87</td>
<td>4.69</td>
<td>55.96</td>
<td>0.160</td>
<td>61.74</td>
<td>3.403</td>
<td>–</td>
<td>100</td>
<td>1.67</td>
</tr>
<tr>
<td>2.1</td>
<td>90</td>
<td>9.01</td>
<td>4.39</td>
<td>58.78</td>
<td>0.130</td>
<td>68.70</td>
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<tr>
<td>2.8</td>
<td>120</td>
<td>8.99</td>
<td>4.75</td>
<td>62.44</td>
<td>0.116</td>
<td>71.88</td>
<td>2.438</td>
<td>–</td>
<td>100</td>
<td>3.23</td>
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<tr>
<td>3.5</td>
<td>150</td>
<td>8.97</td>
<td>3.73</td>
<td>64.98</td>
<td>0.112</td>
<td>72.80</td>
<td>2.997</td>
<td>–</td>
<td>100</td>
<td>4.05</td>
</tr>
</tbody>
</table>
reported in the literature (Martinez-Huitle & Brillas 2009). A significant increase of the specific energy consumption with electrolysis time was found. After 90 minutes of electrolysis higher increasing specific energy consumption and no significant improvement of HA degradation and mineralization efficiency was noticed, and no longer is electrolysis application justified.

CONCLUSIONS

The assessment of the performances of BDD electrodes in humic acid electrooxidation process was accomplished based on the HA removal and electrochemical efficiencies, mineralization current efficiency and energy consumption. This study demonstrated good performance of BDD electrode to degrade and mineralize HA from aqueous solution. The electrochemical behavior of BDD electrode in the presence of humic acid studied by cyclic voltammetry indicated the operation conditions under water decomposition potential range with hydroxyl radicals generation. The optimum working conditions to operate the electrooxidation process using BDD electrode for HA degradation and mineralization, i.e., applied current density, pH, HA concentration range were established. In comparison with the results reported in the literature (Liao et al. 2008), better results regarding kinetics aspects and operating conditions in direct relation with the effect of lower current density used in this study, were achieved. Based on the kinetics results and on the SUVA254 surrogate parameter that assess quantitatively humic acid, which were achieved during the electrooxidation application for a real surface water treatment an incomplete mineralization occurred and the oxidation intermediated were formed. However, the color removal efficiency after 60 minutes electrolysis time was about 100%, and after 150 minutes of electrolysis about 75% of A254 and 65% of TOC was removed.

### REFERENCES


### Table 5

<table>
<thead>
<tr>
<th>Type of HA determination</th>
<th>Apparent rate constant kapp (min⁻¹ × 10²)</th>
<th>Apparent rate constant kapp’ (C⁻¹ × 10⁵)</th>
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</thead>
<tbody>
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<td>UV254</td>
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<td>TOC</td>
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<td>7.8</td>
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