Electrochemical incineration of dimethyl phthalate by anodic oxidation with boron-doped diamond electrode

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Abstract

The anodic oxidation of aqueous solutions containing dimethyl phthalate (DMP) up to 125 mg/L with sodium sulfate (Na2SO4) as supporting electrolyte within the pH range 2.0–10.0 was studied using a one-compartment batch reactor employing a boron-doped diamond (BDD) as anode. Electrolyses were carried out at constant current density (1.5–4.5 mA/cm2). Complete mineralization was always achieved owing to the great concentration of hydroxyl radical (·OH) generated at the BDD surface. The effects of pH, apparent current density and initial DMP concentration on the degradation rate of DMP, the specific charge required for its total mineralization and mineralization current efficiency were investigated systematically. The mineralization rate of DMP was found to be pH-independent and to increase with increasing applied current density. Results indicated that this electrochemical process was subjected, at least partially, to the mass transfer of organics onto the BDD surface. Kinetic analysis of the temporal change of DMP concentration during electrolysis determined by High Performance Liquid Chromatography (HPLC) revealed that DMP decay under all tested conditions followed a pseudo first-order reaction. Aromatic intermediates and generated carboxylic acids were identified by Gas Chromatography-Mass Spectrometry (GC-MS) and a general pathway for the electrochemical incineration of DMP on BDD was proposed.

Key words: dimethyl phthalate; anodic oxidation; boron-doped diamond; mineralization

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Introduction

Dimethyl phthalate (DMP) is mainly used as an additive in plastic manufacture to improve the flexibility and softness of plastic resin (Giam et al., 1978) and is also used in the production of cosmetics, lubricants, carpeting, decorative cloths and other products (Baikova et al., 1999). The large production and utilization cause a significant environmental diffusion of this compound. DMP has been detected in diverse environmental samples including surface water, wastewater, sewage sludge and sediments (Fromme et al., 2002), as well as landfill leachate (Marttinen et al., 2003). Known for endocrine-disrupting activity, DMP interferes with the reproductive system and normal development for animals and human. Meanwhile, DMP may also promote chromosome injuries in human leucocytes and is suspected to be responsible for functional disturbances in the nervous system and liver of animals (Jobling et al., 1995; Zacharewski et al., 1998; Gray et al., 1999). Since DMP is difficult to be biologically and photo-chemically degraded (Stales et al., 1997), it is necessary to look for an effective novel treatment process for this pollutant.

In recent years, effective electrochemical treatments for the destruction of biorefractory organics in water are being developed. One of the most commonly applied technique is anodic oxidation, where the destruction of contaminants are achieved by adsorbed hydroxyl radical (·OH) electro-generated at the anode surface from oxidation either of water in acid and neutral media or hydroxide ion at pH ≥ 10 (Reactions (1) and (2)) (Marselli et al., 2003; Torres et al., 2003).

\[ \text{H}_2\text{O} \rightarrow \cdot\text{OH}_{\text{ads}} + \text{H}^+ + \text{e}^- \] (1)

\[ \text{OH}^- \rightarrow \cdot\text{OH}_{\text{ads}} + \text{e}^- \] (2)

When conventional anodes such as Pt, PbO2, SnO2, doped PbO2 and IrO2 are utilized in anodic oxidation, most aromatics in acid and alkaline media usually cannot be fully mineralized, which is largely due to the generation of difficulty oxidizable carboxylic acids (Rodgers et al., 1999; Bonfatti et al., 2000; Torres et al., 2003; Brillas et al., 2004). Besides, for PbO2 and SnO2, the release of toxic ions is also a potential danger and most of these electrodes have a short service-life.

The recent use of a boron-doped diamond (BDD) thin film anode has shown that it has much larger O2 over-voltage than the above anodes, giving a much higher...
concentration of adsorbed -OH and a quicker oxidation of pollutants. Along with its good chemical and electrochemical stability even in strong aggressive media and long service life, BDD is promising anode for incineration of aqueous organic pollutants. Indeed, this technique has proven its high efficiency in mineralizing many toxic and biorefractory compounds such as phenol (Iniesta et al., 2001), 4-chlorophenols (Rodrigo et al., 2001), 2-naphthol (Panizza et al., 2001), 4-nitrophenol (Cañizares et al., 2004), 4,6-dinitro-o-cresol (Flox et al., 2005), benzene (Olivera et al., 2007), benzoic acid (Montilla et al., 2002), carboxylic acids (formic, oxalic and maleic) (Cañizares et al., 2003), paracetamol (Brillas et al., 2005), diuron (Polcaro et al., 2004), chloromethylphenoxy herbicides (Boye et al., 2006), Orange II (Chen and Chen, 2006), azoic dyes (Cañizares et al., 2006), and sulfur-containing compounds (homocysteine, glutathione, 2-mercapto ethane-sulfonic acid and cephalixin) (Chailapakul et al., 2001).

This article reports a detailed study on the anodic oxidation with BDD of aqueous solution containing DMP at low salt content of 0.05 mol/L sodium sulfate (Na2SO4). Higher DMP concentration than those found in sewage treatment plant (STP) and natural effluents was chosen to evaluate better the oxidation ability of the BDD anode. The influences of pH (2.0–10.0), applied current density and initial DMP concentration on the degradation rate, consumed specific charge, and mineralization current efficiency were examined. Aromatic and carboxylic acid intermediates were identified by Gas Chromatography-Mass Spectrometry (GC-MS) and a general mechanism for the mineralization of DMP in Na2SO4 was proposed.

1 Materials and methods

1.1 Chemicals

Dimethyl phthalate was reagent grade from Beijing Chemical Co., China. Acetonitrile, dichloromethane (CH2Cl2) and methyl tert-butyl ether (MTBE) were chromatographically pure from Fisher Scientific, USA. N,O-bistrimethylsilyl trifluoroacetamide/trimethylchlorosilane (BSTFA/TMCS) (V/V, 99/1) purchased from Supelco, USA, was employed as trimethylsilylation reagent for GC-MS analysis. All solutions were prepared with deionized water. The solution pH was adjusted by a diluted sulfuric acid or sodium hydroxide.

1.2 Apparatus and analysis procedures

Mineralization of dimethyl phthalate was monitored by the abatement of their total organic carbon (TOC) determined using a Pheonix 8000 TOC analyzer (Tekmar-Dohrmann Co., USA). Prior to injection into the TOC analyzer, the samples were filtrated with a 0.45-μm Millipore filter. The decay of dimethyl phthalate concentration was determined using L-2000 High Performance Liquid Chromatography (HPLC) (Hitachi Co., Japan). Samples of 20 μL were injected into the chromatograph and a 50/50 (V/V) acetonitrile/water mixture passed at a flow rate of 1.0 mL/min as mobile phase. The separation was performed using an ODS-2, 5 μm (150 mm × 4.6 mm) column (Thermo Electro Co., USA) at 25°C. The photodiode array detector was set at 274 nm, corresponding to the maximum absorption wavelength of DMP.

The electro-oxidation products of DMP were detected by GC-MS (Agilent 7890GC-5975MSD) equipped with a HP-5MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness). Samples for GC-MS analysis were prepared by either of the following two procedures. Procedure No. 1: the aqueous samples were freeze-dried first, and then the solid residue was dissolved in 2.5 mL CH2Cl2, followed by being trimethylsilylated with 0.2 mL BSTFA/TMCS for 60 min at 60°C. Finally the samples were dehydrated using milled Na2SO4 and concentrated to 0.5 mL for GC-MS analysis. Procedure No. 2: after freeze-drying, the solid residue was dissolved in 2.5 mL MTBE, followed by esterification with 2.5 mL 1/9 (V/V) sulfuric acid/methanol for 120 min at 50°C. Then, 7 mL of 150 g/L Na2SO4 aqueous solution was added into the sample vials. After vigorous shake, the sample vials were allowed to settle for a few minutes. The lower phase (acidic aqueous methanol) was removed from the vials and discarded. Afterwards, 1 mL of saturated sodium hydrocarbonate (NaHCO3) aqueous solution was added into the vials to neutralize the remaining solution, and the mixture was vibrated intensely and settled for several seconds. At last, the upper ether phase was transferred to new sample vials for GC-MS analysis. Correspondingly, the GC oven temperature program for samples prepared by procedure No. 1 was: 35°C hold 2 min, rate 4°C/min to 80°C, hold for 8 min, rate 3°C/min to 180°C, hold for 2 min, rate 8°C/min to 280°C, hold for 10 min. The GC program for samples pretreated by procedure No. 2 was: 80°C hold 8 min, rate 4°C/min to 180°C, hold for 2 min, rate 10°C/min to 280°C, hold for 10 min. The injector temperature was 280°C and helium was employed as carrier gas. The NIST05 library was used to identify products.

1.3 Electrolytic system

Anodic oxidation of dimethyl phthalate solution was carried out in a one-compartment reactor (35 mm × 35 mm × 70 mm) operated in batch mode. A BDD thin film deposited on single crystal p-type Si (100) wafer (CSEM, Switzerland) was used as the anode and its effective working area was 9.2 cm². The Pt wire, 72 mm in length with a 1.5 mm diameter, was used as a counter electrode. Saturated calomel electrode (SCE) was used as a reference electrode. The current density was controlled using a galvanostat (EG&G model 263A, Princeton Applied Research, USA).

2 Results and discussion

2.1 Effect of initial pH

In order to determine whether BDD electrodes could have good performance in oxidizing DMP in a wide pH range, a series of electrolyses were carried out with 50 mg/L DMP solutions (corresponding to 30.9 mg/L of TOC) in
0.05 mol/L Na₂SO₄ of different initial pH values at 1.5 mA/cm² to test their comparative degradation. Figure 1 depicts the variation of solution TOC with applied specific charge (the electrical charge applied to per unit volume of the reaction solution; designated as \( Q \) (mA·h)/L) for such trials. A similar and rapid TOC abatement can be observed in all cases, attaining overall mineralization (>95% of TOC decay) at 180 min after consumption of 993 (mA·h)/L. These results indicate that dimethyl phthalate and its byproducts are destroyed at similar rates in pH range 2.0–10.0 by anodic oxidation with BDD. This behavior can be explained by the generation of similar concentration of \( \cdot \)OH from Reaction (1) or (2), being truly high enough for complete destruction of DMP as well as its oxidation products, irrespective of acidic, neutral or alkaline reaction media. This is very important to the practical application of BDD for wastewater treatment, because actual effluents may have different pH values. The wide effective pH range implies that pH adjustment before treatment with this technique is not necessary in most cases.

2.2 Effect of current density

Current density is a very important parameter in electrochemical engineering. In order to study the effect of apparent current density (\( j_{\text{app}} \)) on DMP degradation with BDD, depollutions of 50 mg/L DMP solutions in 0.05 mol/L Na₂SO₄ at initial pH 2.0 were performed at 1.5, 3.0, 4.5 mA/cm², respectively. The TOC-Q plots obtained are illustrated in Fig. 2. It is found that the residual TOC increased as \( j_{\text{app}} \) increased at a given specific charge, and more specific charge was consumed for total mineralization, which varied from 993 (mA·h)/L at 1.5 mA/cm² to 2311 (mA·h)/L at 4.5 mA/cm². Nevertheless, increasing \( j_{\text{app}} \) actually resulted in a faster TOC removal and the time required for overall decontamination dropped from 180 min at 1.5 mA/cm² to 140 min at 4.5 mA/cm². This increase in TOC removal rate caused by increasing \( j_{\text{app}} \) can be easily deduced from the results given in Table 1, where after 90-min treatment, for example, TOC removal percentage was raised gradually from 54.3% to 78.3% between 1.5 and 4.5 mA/cm². This behavior can be explained as follows. The more rapid TOC abatement with time when increasing \( j_{\text{app}} \) was related to the concomitant greater production of \( \cdot \)OH on BDD surface from Reaction (1), as a result, the oxidation of all organics were accelerated. Whereas the enhancement in \( Q \) consumption for complete depollution indicated that a smaller proportion of generated \( \cdot \)OH was used to oxidize pollutants because a quicker waste of \( \cdot \)OH was caused by other competitive and non-oxidizing reactions, for example, its decomposition to O₂ and its recombination to give H₂O₂ owing to the fact that the concentration of produced \( \cdot \)OH was excessively high for the degradation of the organic molecules transferred onto the BDD surface. From these findings, it can be

![Fig. 1](image1.png)  
**Fig. 1** Effect of initial pH on TOC (total organic carbon) abatement versus \( Q \) (specific charge) for the treatment of 50 mg/L DMP (dimethyl phthalate) in 0.05 mol/L Na₂SO₄ at 1.5 mA/cm² by anodic oxidation with BDD (boron doped diamond).

![Fig. 2](image2.png)  
**Fig. 2** Effect of current density on TOC abatement versus specific charge for the treatment of 50 mg/L DMP in 0.05 mol/L Na₂SO₄ at initial pH 2.0 by anodic oxidation with BDD.

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>( j_{\text{app}} ) (mA/cm²)</th>
<th>After 90 min treatment</th>
<th>After 180 min treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TOC removal (%)</td>
<td>MCE (%)</td>
</tr>
<tr>
<td>25</td>
<td>3.0</td>
<td>77.5</td>
<td>8.46</td>
</tr>
<tr>
<td>50</td>
<td>1.5</td>
<td>54.3</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>73.8</td>
<td>27.6</td>
</tr>
<tr>
<td>75</td>
<td>4.5</td>
<td>78.3</td>
<td>18.1</td>
</tr>
<tr>
<td>100</td>
<td>3.0</td>
<td>57.8</td>
<td>35.7</td>
</tr>
<tr>
<td>125</td>
<td>3.0</td>
<td>51.7</td>
<td>40.6</td>
</tr>
</tbody>
</table>

\( C_0 \): Initial DMP concentration; \( j_{\text{app}} \): applied current density. --: solution completely mineralized at short time.
inferred that the degradation process under the above conditions was limited, at least partially, by the mass transfer control.

2.3 Effect of initial DMP concentration

Figure 3 shows the TOC-Q plots obtained for the electrochemical incineration of 25, 50, 75, 100 and 125 mg/L DMP solutions. All solutions were completely mineralized, requiring the consumption of a specific charge of about 1324 (mA·h)/L (120 min), 1655 (mA·h)/L (150 min), 2482 (mA·h)/L (225 min), 3530 (mA·h)/L (320 min) and 5075 (mA·h)/L (460 min) for 25, 50, 75, 100 and 125 mg/L of initial compound. The increase in Q with increasing initial concentration can be simply explained by the existence of more pollutants in the effluent. In fact, the TOC removal rate became faster when enlarging DMP concentration, which can be analyzed well from the percentages of TOC removal after 90 min and 180 min of electrolysis collected in Table 1. It appears that a smaller percentage of TOC was removed as the initial concentration rose, but if taking their respective starting concentration into account, the amount of removed TOC actually turned out to be larger at higher DMP concentration. This gradual enhancement in oxidizing power of BDD anode can be interpreted by the reaction of more -OH with greater amount of DMP and its byproducts transported to BDD surface.

2.4 Current efficiency for mineralization process

The above findings allow concluding that the mineralization of dimethyl phthalate by anodic oxidation with BDD involves its conversion into CO₂, without the release of any other inorganic ions due to its own chemical composition. This overall reaction can be expressed as follows:

\[ C_{10}H_{10}O_4 + 16H_2O \rightarrow 10CO_2 + 42H^+ + 42e^- \]  

(3)

Reaction (3) indicates that the overall destruction of each mole DMP requires the consumption of 42 F charge. Taking Reaction (3) into account, the mineralization current efficiency (MCE) for the treated solutions at a given time t was then calculated by the following Eq. (4):

\[ \text{MCE} = \frac{\Delta \text{TOC}_\text{exp}}{\Delta \text{TOC}_\text{theor}} \times 100\% \]  

(4)

where, \( \Delta \text{TOC}_\text{exp} \) is the experimental solution TOC removal at time t and \( \Delta \text{TOC}_\text{theor} \) is the theoretically calculated TOC decay considering that the applied electrical charge, equaled to current \( \times \) time, is only consumed in the mineralization process of dimethyl phthalate.

Figure 4 illustrates the current efficiencies determined from Eq. (4) for the trials described in Figs. 2 and 3. Several selected MCE values are listed in Table 1. Similar MCE variation trends can be observed in Fig. 4. The current efficiencies were first enhanced at the early treatment stages, and then underwent a continuous decay after passing their maximum values during the remaining periods of electrolysis. The mineralization of DMP was a stepwise process, which forms many intermediates before being converted into CO₂. At the beginning, the effective current was mainly employed to decompose DMP into intermediates, leaving little current for further degradation of those intermediates into CO₂; thereby the current efficiency measured by mineralization degree was low. As DMP was gradually converted into intermediates, the part of current used for further oxidizing intermediates into CO₂ became larger correspondingly, hence leading to an increase in MCE. However, with the continuous

![Fig. 3 Effect of DMP initial concentration (C₀) on TOC abatement versus specific charge for DMP treatment at initial pH 2.0, 3.0 mA/cm² in 0.05 mol/L Na₂SO₄ by anodic oxidation with BDD.](image-url)

![Fig. 4 Dependence of calculated MCE on specific charge for the experimental results reported in Figs. 2 and 3.](image-url)
TOC removal the pollutants concentration in the solution declined, resulting in that a smaller amount of pollutants transported onto BDD surface to react with -OH and in turn favored the waste of this radical by its parallel non-oxidizing reactions, which is accounted for the subsequent decrease in MCE.

Figure 4b shows that MCE generally decreased with decreasing DMP concentration with a few exceptions. For example, as shown in Table 1, MCE values of 43.1%, 40.6%, 35.7%, 27.6% and 8.46% were obtained for 125, 100, 75, 50 and 25 mg/L of this compound after 90 min of treatment at 3.0 mA/cm². This trend could be related again with a slower degradation of organics at lower concentration thus facilitating an enhancement of non-oxidizing reactions of generated -OH. The data in Table 1 also exhibits that MCE values after 90-min treatment of 50 mg/L DMP declined from 36.9% to 18.1% as \( j_{\text{app}} \) increased from 1.5 to 4.5 mA/cm². This trend could be related again with a slower degradation of organics at lower concentration thus facilitating an enhancement of non-oxidizing reactions of generated -OH. The data in Table 1 also exhibits that MCE values after 90-min treatment of 100 mg/L DMP declined from 28.1% to 1.5% as \( j_{\text{app}} \) increased from 2.5 to 6.0 mA/cm². Figure 4a roughly shows this tendency of a drop in MCE at higher \( j_{\text{app}} \). Although the increase in current density led to a faster TOC removal because of the generation of more -OH at the BDD surface, a larger proportion of this radical was rapidly consumed to produce \( \text{O}_2 \) and other weak oxidants making less efficient reaction with organics.

2.5 Kinetics of DMP decay

The concentration decay of DMP was detected by HPLC, where it displayed a well-defined peak with a retention time of 5.3 min. Kinetic analysis of these results only gave good linear plots when they were fitted to a pseudo first-order reaction with regression coefficients > 0.99. These correlations are presented in the inset of Fig. 5. Figure 5a shows a rapid degradation of DMP on BDD in 0.05 mol/L \( \text{Na}_2\text{SO}_4 \) at 3.0 mA/cm² and initial pH 2.0. DMP disappeared from the medium at approximately 65, 80, 90, 100, and 110 min, which were lower than 120, 150, 225, 320, and 460 min required for their total depollution for 25, 50, 75, 100 and 125 mg/L, respectively. A similar phenomenon could be found in the treatment of 50 mg/L DMP at different current densities in 0.05 mol/L \( \text{Na}_2\text{SO}_4 \) at pH 2.0 (Fig. 5b). DMP disappeared within about 90, 80, and 75 min at 1.5, 3.0, and 4.5 mA/cm², while its overall mineralization was achieved after 180, 150 and 140 min of electrolysis. It can then be inferred that DMP was comparatively more oxidizable than those persistent byproducts which were accumulated in the media at first and then were gradually degraded after DMP was mainly removed.

The kinetic analysis as pseudo first-order reactions indicated that the rate constant (\( k \)) was increased from 0.0493 to 0.0573 min⁻¹ when enlarging the initial concentration from 25 to 50 mg/L. A rather similar \( k \) value was obtained for 75, 100 and 125 mg/L, corresponding to an average of \( 0.0415 \pm 0.0019 \) min⁻¹. Though it dropped as compared with the \( k \) value obtained for 25 mg/L, the rate constant obtained for 75, 100 and 125 mg/L was only reduced by 16% when the initial DMP content increased three, four and even five times. This behavior suggested that increasing amount of -OH reacted with greater DMP at higher DMP concentrations on the BDD anode. The degradation rate of DMP was obviously enhanced as \( j_{\text{app}} \) rose from 1.5 to 3.0 mA/cm², and the corresponding first-order kinetic analysis also demonstrated an increasing \( k \) value from 0.0396 to 0.0573 min⁻¹. Nevertheless, when further raising current density upto 4.5 mA/cm² the DMP decay rate was almost similar with that at 3.0 mA/cm², attaining a similar \( k \) of 0.0549 min⁻¹. The results allow us to conclude that the increase in \( j_{\text{app}} \) is not necessary for the increase in the rate constant of DMP degradation. Even if an increase occurred in the rate constant when increasing \( j_{\text{app}} \), the obtained \( k \) did not vary proportionally with the applied \( j_{\text{app}} \), for example, \( k \) was merely increased by 45% as \( j_{\text{app}} \) increased twofold. This phenomenon could be related to the fact (already stated above) that although greater production of -OH was expected on the BDD surface when supplying higher \( j_{\text{app}} \), a smaller proportion of this oxidant became efficient to react with organics, suggesting a gradual greater generation of other poor oxidants such as \( \text{O}_2 \) and \( \text{H}_2\text{O}_2 \).

![Fig. 5](image-url) DMP concentration decay with electrolysis time for the treatment of DMP of initial pH 2.0 in 0.05 mol/L \( \text{Na}_2\text{SO}_4 \) at 3.0 mA/cm² (a) and the treatment of 50 mg/L DMP in 0.05 mol/L \( \text{Na}_2\text{SO}_4 \) at initial pH 2.0 (b) by anodic oxidation with BDD. The inset panel presents the kinetic analysis assuming a pseudo first-order reaction for DMP.
<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Product</th>
<th>Retention time (min)</th>
<th>Product</th>
</tr>
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<tbody>
<tr>
<td>18.398&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1,1,2-Ethylenetricarboxylic acid</td>
<td>37.566&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Maleic acid</td>
</tr>
<tr>
<td>21.710&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Oxalic acid</td>
<td>38.705&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Methyl-propanedioic acid</td>
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<tr>
<td>23.896&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1,1,2-Ethanetricarboxylic acid</td>
<td>39.168&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Dimethyl phthalate</td>
</tr>
<tr>
<td>26.294&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1,1,2,2-Ethanetetracarboxylic acid</td>
<td>40.536&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2,2-Dihydroxy- propanedioic acid</td>
</tr>
<tr>
<td>32.428&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Propanedioic acid</td>
<td>41.726&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>33.103&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>45.216&lt;sup&gt;a&lt;/sup&gt;</td>
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</tr>
<tr>
<td>34.001&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4-Hydroxy-1,2-benzenedicarboxylic acid</td>
<td>46.120&lt;sup&gt;a&lt;/sup&gt;</td>
<td>DL-Tartaric acid</td>
</tr>
</tbody>
</table>

<sup>a</sup> Main intermediates produced in electro-oxidation of 50 mg/L DMP; <sup>b</sup> main intermediates produced in electro-oxidation of 125 mg/L DMP.
2.6 Identification of intermediates and proposed mineralization pathway of DMP

To identify the aromatics and carboxylic acids generated as byproducts during the electrochemical oxidation of DMP with the BDD anode, 50 mg/L DMP of initial pH 2.0 in 0.05 mol/L Na2SO4 was electrolyzed at 1.5 mA/cm² for 60 min. Before injection into GC-MS, collected sample was prepared according to procedure No. 1. Besides, 125 mg/L DMP in 0.05 mol/L Na2SO4 that underwent 60 min electrolysis at initial pH 2.0 and 1.5 mA/cm² was also tried to be analyzed by GC-MS to obtain more information about the ring-opening process of DMP. Correspondingly, procedure No. 2 was the pretreatment method for this sample. The main intermediates produced in electro-oxidation of 50 and 125 mg/L DMP are summarized in Table 2. The detected aromatic and aliphatic intermediates were mainly alcohols and organic acids. Based on the identified intermediates, a general reaction sequence for the electrochemical incineration of DMP on BDD anode is proposed in Fig. 6. This process was initiated with demethylation to give o-phthalic acid, which was in accordance with the results reported by Horikoshi et al. (2004). o-Phthalic acid could then undergo a possible attack of -OH on its C(4)-position yielding 4-hydroxy-1,2-benzenedicarboxylic acid. After that, the aromatic ring was broken down generating in parallel 1,1,2,2-ethanetetracarboxylic acid and 1,1,2-ethylenetricarboxylic acid. 1,1,2,2-Ethanetetracarboxylic acid was further degraded to 1,1,2-ethylenetricarboxylic acid, which was subsequently oxidized into oxalic acid, in turn via succinic acid, propanedioic acid and 2,2-dihydroxyl-propanedioic acid. 1,1,2-Ethylenetricarboxylic acid was decomposed into maleic acid that was oxidized into oxalic acid via DL-tartaric acid. Finally, oxalic acid was converted into CO2 and H2O.

3 Conclusions

The present study demonstrated that anodic oxidation with BDD was very effective for the complete mineralization of dimethyl phthalate up to 125 mg/L in pH range 2.0–10.0 due to the efficient production of oxidant ·OH by Reaction (1) or (2). The removal of solution TOC was practically pH-independent and became faster with increasing \( j_{app} \), although with the consumption of more specific charge, which is due to the higher production of ·OH and concomitant higher conversion ratio of this radical into other weaker oxidants such as O2 and H2O2. Enlarging DMP initial concentration also enhanced the oxidizing power of this anode, because more ·OH was able to react with greater amount of pollutants, decelerating other non-oxidizing reactions with this oxidant. The above behavior indicated that this process was subjected, at least partially, to the mass transfer of organics onto the BDD surface. The increases in mineralization current efficiency with decreasing \( j_{app} \) and increasing initial DMP concentration also supported this mass-transfer-control assumption. The DMP decay followed a pseudo first-order kinetics. The rate constant did not decrease proportionally with the increase in DMP initial concentration and even showed a boost when raising the concentration from 25 to 50 mg/L. An unproportionate rise in the rate constant was gained when \( j_{app} \) rose from 1.5 to 3.0 mA/cm² and the constant remained almost similar when \( j_{app} \) further rose from 3.0 to 4.5 mA/cm². The GC-MS analysis allowed the identification of aromatic and carboxylic acid intermediates. The mineralization process started with the formation of o-phthalic acid, and oxalic acid was produced as ultimate organic product.

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References


