Advancements of Electrochemical Removal of
o-Methylphenol from Aqueous
Using BDD Anode Compared to Pt One:
Kinetics and Mechanism Determination

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ABSTRACT: *The oxidation of 216 mg/L o-methylphenol was studied in an acidic aqueous solution using Boron-Doped Diamond (BDD) and platinum (Pt) anodes. o-methylphenol was oxidized by hydroxyl radicals generated on the anode used, however, there was a significant distinction betwixt the BDD and Pt anodes in the effectiveness and accomplishment of electrochemical degradation. o-methylphenol was rapidly mineralized at the BDD anode, but its degradation was much slower at the Pt anode with a Total Organic Carbon (TOC) removal of 98% and 65% for BDD and Pt anodes, respectively. Using BDD anode, 3-methylcatechol, methylhydroquinone, and maleic, fumaric, pyruvic, formic, glyoxylic, succinic, oxalic, and acetic acids were detected. But, there was a formation of dark-colored polymeric compounds and precipitates in the solutions electrolyzed by the Pt anode, which was not observed for the BDD cells.*

KEYWORDS: *Electrochemical oxidation, o-methylphenol, BDD anode, Hydroxyl radical, Degradation.*

INTRODUCTION

A multitude of organic compounds is ejected into effluents of various industries. Among them, phenolic compounds, which are toxic and found in wastewater resulting from pulp and paper, petrochemical, polymeric

resin, and pharmaceutical industries, oil refineries, coal mines, etc...[1-6]. *o*-methylphenol is an isomeric phenol with a methyl substituent at the ortho position relative to hydroxyl group. It is widely used, especially in the manufacture of synthetic resins, herbicides, and various aromatic compounds. In addition to being a highly toxic and potential carcinogen, *o*-methyl phenol causes, even at very low concentration, adverse effects on the central nervous system, cardiovascular system, lungs, kidney, and liver resulting in CNS depression [4]. With toxicity and cancerogenic raised, cresols surfactants are even more toxic than the phenol [7]. Thus, the environmental protection agency has classified *o*-methylphenol as a pollutant of group C (possible human carcinogens) [8]. In order to treat these toxic effluents, several papers have reported the disposal of cresols from waters by photocatalysis with TiO_2/UV [4,9,10]. The Fenton's reagent (H_2O_2/Fe^{2+}) only achieves a 42% degradation, this has been explained by the production of acetic and oxalic acids as major by-products that form complexes with Fe^{3+} ions, which are hardly destroyed under these conditions [11]. In this regard, total degradation of these complexes is achievable using the solar photoelectro-Fenton method [12-16]. For example, *Valsania et al.* [17] described the degradation of $7\ 10^{-7}$ mol of *o*-, *m*- and *p*-cresol by reaction with ozone. They have denoted that the mechanism takes place in three stages, the first stage corresponds to the opening of the cycle, followed by the establishment of many intermediates, and the last stage generates stable products mainly oxalic and malonic acids. Moreover, the methyl group undergoes no oxidation during the degradation process of cresols[17]. In contrast, electro-Fenton oxidation of *m*-cresol using Ti/SnO_2–Sb_2O_5–IrO_2 as anode generated two cyclic organic intermediates and several carboxylic acids [18]. *Rajkumar* and *Palanivelu* [19] used a cell involving Ti/TiO_2–RuO_2–IrO_2 as anode and graphite as cathode for the degradation of cresols; they showed that this system gives low efficiency even in an alkaline medium. In this way, to handle organic pollutants many materials were used as anode, such as platinum [20,21], Lead peroxide [9,21-25], IrO_2 [26,27], Ti/MnO_2 [28], Ti/SnO_2 [29] and BDD [25,30-33].

For the first time, the BDD electrode appeared in electrochemistry within the works of *Pleskov et al.* [34]. Since then, many authors are so interested in a big variety of modal compounds eligible for being oxidized with this electrode. Due to its characteristics: being quite stable, having a wide potential window for water discharge, and its minimal toxicity [23,30,31,35,36], the BDD electrode is a promising candidate for its use in the handling of organic wastewater [23,25,30-40]. In the same context, the Pt anode was largely used in electrochemistry for its excellent catalytic properties [20,35], and particularly for the degradation of halogenated aromatic compounds [20,41-43]. The use of these two electrodes in electrooxidation of organics has received great attention, and the oxidation of organics is performed *via* hydroxyl radicals that are engendered on the electrode surface from water discharge (Eq. (1)) [20,44,45].

$$M + H_2O \rightarrow M\left({}^{\bullet}OH\right) + H^+ + e^- \qquad (1)$$
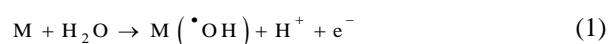
For studying the effect and the optimization of parameters, which influence the electrochemical efficiency of the removal rate of pollutants, two approaches can be used: One Factor-at-a-Time (OFAT) and Design of Experiment (DOE) methodologies. OFAT approach consists of examining one parameter while holding all other parameters constant [46,47]. However, DOE approach implies the interaction between the studied parameters[47]. Although the OFAT approach requires more time and reagents than that of DOE, it remains a very adequate approach for the kinetic study. In this context, many works report the optimization of the parameters of degradation of pollutants by the DOE methodology [46-50]. In the present research, OFAT approach was used to study the degradation of *o*-methylphenol and the degradation of its aqueous solution by the anodic oxidation using BDD and Pt electrodes. A 216 mg/L solution of this pollutant was treated to follow the evolution of aromatic intermediates and carboxylic acids formed during the degradation process. The decay kinetics of *o*-methylphenol and the progress of by-products were followed by chromatographic techniques, allowing the proposal of a reaction pathway for *o*-methylphenol degradation.

EXPERIMENTAL SECTION
Chemicals
Sodium sulfate (Na_2SO_4, ACS reagent, $\geq$99.0%), *p*-hydroxybenzoic acid ((*p*-HBA), $C_7H_6O_3$, Reagent Plus, $\geq$99%), sulfuric acid (H_2SO_4, ACS reagent, 95.0-98.0%), and *o*-methylphenol (C_7H_8O, ReagentPlus, $\geq$99%) were supplied by Sigma-Aldrich.

Electrolysis of o-methylphenol solutions

BDD electrode supported by monocrystalline silicon and p-doped, with a thickness of 2.8 μm, was provided by Neocoat Switzerland.

Oxidation experiments were conducted at galvanostatic mode using BDD or Pt electrodes as anode and stainless steel sheet as a cathode. All electrodes were flat and rectangular with a geometric area of 10 cm² (2.5cm×4cm) and the gap was about 2 cm. The electrolysis of o-methylphenol (216 mg/L) solution was carried out at constant current density equals 60mA cm⁻² in a thermostated cylindrical cell containing a 250 mL solution and stirred magnetically.Electrolysis was done with 7.1 g/L of Na_2SO_4 as electrolyte and at pH=4. The temperature was kept at room temperature (25±2°C). The distance between the two electrodes was 2 cm. The samples were withdrawn during electrolysis at pre-set time intervals to assess the concentration decay of o-methylphenol, as well as the degradation degree of treated solutions.

For the kinetic study, the concentration of o-methylphenol was monitored every 60 min during the electrolysis by withdrawing 1 mL samples of the solution from the reactor. These samples were filtered through a Millipore syringe filter of 0.20 μm and analyzed by High-Performance Liquid Chromatography (HPLC). The kinetic rate constant of the reaction between hydroxyl radicals (•OH) and o-methylphenol was obtained using a competitive kinetic method in the presence p-hydroxybenzoic acid (p-HBA) with a well known absolute rate constant ($k_{abs(p\text{-}HBA)}$ = 1.63 x 10^9 $M^{-1}s^{-1}$) [51]. Thus, an equimolar mixture (0.05 mmol/L) of o-methylphenol and p-HBA was electrolyzed at room temperature and pH=4, using 7.1 g/L of Na_2SO_4 as electrolyte. The evolution of this mixture was monitored by HPLC every 60 min during treatment. The graphic representation of Ln[o-methylphenol]$_0$/[o-methylphenol]$_t$) versus Ln([p-HBA]$_0$/[p-HBA]$_t$) provide a straight line whose slope corresponds to $k_{abs(o\text{-}methylphenol)}/k_{abs(p\text{-}HBA)}$ [51-53].

Analytical techniques

The current density for the electrolysis was kept at the desired level with a Bench Power Supply GPC-3030D.

The solution pH was adjusted with sulfuric acid and the value was detected by Crison 2000 pH-meter.

The Total Organic Carbon content (TOC) was obtained with a Shimadzu VCSH TOC analyzer.

Chemical Oxygen Demand (COD) data were obtained with a Beckman UV/Vis DU 800 spectrophotometer after digestion of samples in a Merck Model TR-300 thermoreactor.

The concentration of o-methylphenol and other aromatic intermediates was followed by High-Performance Liquid Chromatography (HPLC) using a Varian Proster HPLC system with a DAD-spectrophotometer detector at 280 nm. The column was RP-C18 Zorbax (250 mm, 4.6 mm, 5μm) reverse-phase silica gel. The analyses were made by injecting 20 μL aliquots at room temperature. The mobile phase used is water/methanol/acetic acid: 59.5/39.5/1 (v/v/v) at a flow rate of 0.8 mL/min. Aliphatic carboxylic acids were quantified using ODS-C18 column (250 mm, 4.6 mm, 5μm) with a mobile phase of 4 mmol/L H_2SO_4 at a flow rate of 0.2 mL/min. The detection was performed at 210 nm.

RESULTS AND DISCUSSION

### Comparative oxidation of o-methylphenol using BDD and Pt anodes

The electrochemical o-methylphenol degradation using BDD anode had results different than those obtained using Pt anode (Fig. 1a). The total o-methylphenol removal performed by BDD anode was higher than the Pt anode. In fact, the BDD realized the rapid oxidation of the o-methylphenol since its concentration dropped from 216 mg/L to zero after almost six hours of electrolysis. For the Pt anode, the rate of o-methylphenol degradation was much slower. The total o-methylphenol removal was achieved at a time rate of nearly 18h for the Pt anode.

The COD value indicates the amount of oxygen that would be needed when all organic ingredients would be oxidized completely and the oxidation takes place chemically [31,51,54]. The TOC value indicates the total organic carbon of the sample excluding the inorganic carbon such as carbon dioxide dissolved in water. The determination of COD is based on the principle of oxidation by dichromate which is characterized by the acidification of the sample with sulfuric acid and the addition of silver sulfate and mercuric sulfate. This method involves hazardous chemicals and the analysis time is approximately 2 hours. This leads to an increased tendency to replace COD with TOC [51,55]. However, the duration of a TOC analysis is around 10 minutes, however, the information obtained from a TOC analysis is less useful

than that obtained from the COD analysis. Indeed, the TOC test does not differentiate between compounds having the same number of carbon atoms at different stages of oxidation and will therefore produce different oxygen demand results [21,51,55].

The BDD and Pt anodes showed a big difference in the effectiveness of TOC removal (Fig. 1b). The reproducibility of the electrochemical treatments referring to *o*-methylphenol and TOC degradation was valuable for the two anodes. It appears that with the BDD anode much lower electricity consumption was used to accomplish total *o*-methylphenol and TOC removal, by comparing to that used with the Pt anode. With the Pt anode, the TOC remains in the solutions after the elimination of o-methylphenol proves the development of persistent organic intermediates. According to this behavior, it seems that BDD anode exhibited higher performance than Pt anode for the degradation of *o*-methylphenol. These results are confirmed by other similar have been published for other aromatics [9,20,35,41,56].

The efficiency of the BDD anode compared to the Pt anode could be attributed firstly to the production of a quantity of BDD($^\bullet$OH) according to Equation (1) which is higher than that of Pt($^\bullet$OH), and secondly to the release of a considerable amount of O_2 according to Equation (2). This situation minimizes the adsorption of BDD($^\bullet$OH) on the surface of the anode and will be readily available for the oxidation of organic products [41].

$$2\,BDD\left(^\bullet OH\right) \rightarrow 2\,BDD + O_2 + 2H^+ + 2e^- \qquad (2)$$
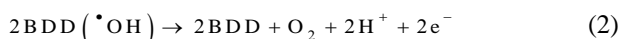
The solution pH also was altered during the electrolysis process (Fig.1c). The pH decreased from the initial value of 4 to below 2.9 while the *o*-methylphenol was being electrochemically oxidized. It was kept at around 2.5 with no sign of an increase in the solutions that were treated by the Pt anode. The pH began to rise after the *o*-methylphenol disappeared from the solution using the BDD anode, and approached 7 when the TOC was completely removed after 8h of electrolysis.

The implication presented in Figure 2 asserts the conclusions obtained in Fig. 1. In fact, the COD abatement as a function of the consumed electrical charges demonstrates that, with BDD electrode, the degradation attains 98% after consumption of electrical charges (Q) of 20 Ah/L at 8 h. In contrast, the usage of Pt anode allows us to obtain only 68%.
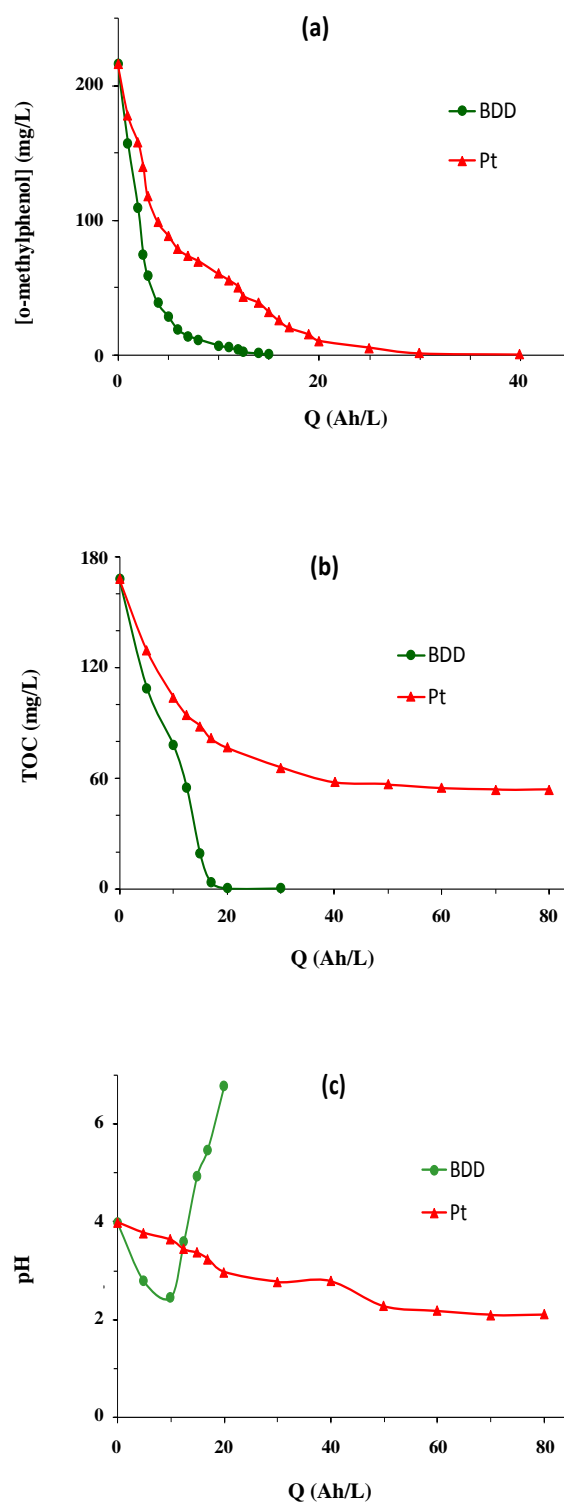

Fig. 1: *Anodic oxidation of 216 mg/L of o-methylphenol on anodes BDD and Pt in 7.1 g/L of Na₂SO₄ at 60 mA/cm² and 25±2°C. (a) Decay of o-methylphenol concentration, (b) TOC removal, and (c) pH variation.*
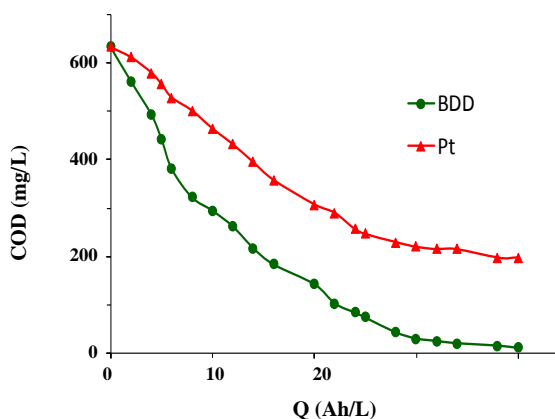
Fig. 2:Chemical oxygen demand removal for the anodic oxidation of 216 mg/L of o-methylphenol on anodes BDD and Pt in 7.1 g/L Na$_2$SO$_4$, at 60 mA/cm^2 and 25±2$^\bullet$C.

Fig. 3:Decay of o-methylphenol on BDD anode in 7.1 g/L of Na$_2$SO$_4$ at 60 mA/cm^2 and 25±2$^\bullet$C. The insert panel shows the kinetic analysis for the corresponding experiments assuming a pseudo-first order reaction.

Kinetics studies of the degradation of o-methylphenol using BDD anode

The kinetic study of the degradation of *o*-methylphenol with BDD($^\bullet$OH) was carried out by following the variation of the concentration of *o*-methylphenol during the reaction. The degradation curve of *o*-methylphenol (Fig. 3) shows an exponential trend, suggesting pseudo-first-order kinetics of the reaction. This is confirmed by the linear variation of Ln(C$_0$/C$_t$) as a function of time (Fig. 3 insert). The degradation of *o*-methylphenol can be represented by:

$$-d\,[0-\mathrm{methylphenol}]\big/dt = \qquad\qquad (3)$$

$$k_{app(o-methylphenol)}\,[o-methylphenol]$$

with, k$_{app}$ = 0.0073 min^{-1}: the apparent rate constant. This value is lower than that obtained by Shokri [57] during the study of the degradation of toluene where the apparent constant rate found is 0.0590 min^{-1}. In this context, Mohadesi et al. [58] showed that the elimination of the COD during the degradation of oil refinery wastewater by the photo-Fenton process follows kinetics of pseudo-first-order.

The oxidation rate of *o*-methylphenolis controlled by the experimental circumstances. In fact, the absolute rate constant of the reaction between *o*-methylphenol and $^\bullet$OH can be determined by the method of competition kinetics with a compound for which the absolute rate constant is known. In order to determine the absolute rate (k$_{abs}$) of *o*-methylphenol, competitive kinetic experiments (Fig. 4) 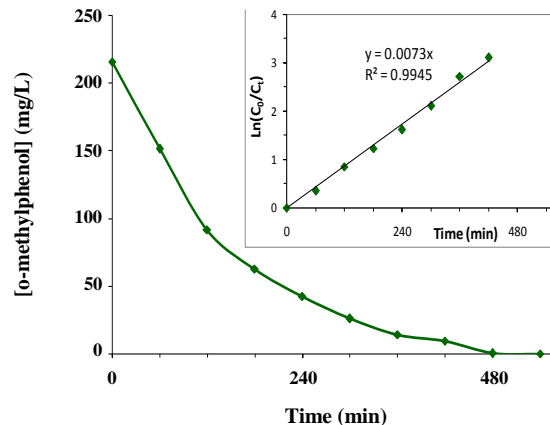were achieved in the presence of equal concentrations of *o*-methylphenoland *p*-hydroxybenzoic acid (k$_{abs(p\text{-HBA})}$ = 1.63 x 10^9 M^{-1}s^{-1}) [51].

$$-d\,[p-HBA]\big/dt = k_{app(p-HBA)}\,[p-HBA] \qquad (4)$$

Supposing that pseudo-first-order kinetics for both *o*-methylphenoland *p*-hydroxybenzoic acid reactions with hydroxyl radicals and no side reactions, apparent rate constants are given by the multiplication between the angular coefficient obtained (2.3044) and *p*-hydroxybenzoic acid absolute constant (1.63 x 10^9 M^{-1} s^{-1}) showed that the value of the *o*-methylphenol absolute constant in pH 4 was equal to 3.75 x 10^9 M^{-1} s^{-1}.

Identification and evolution of intermediates

During the oxidation using the BDD anode, the yellow color of the solution began to fade after 4 hours and disappeared after 8 hours with the total disappearance of *o*-methylphenol. With the usage of Pt anode, in contrast, we notice that the solution turned to dark yellow and brown when the *o*-methylphenol had been completely removed. The color did not fade even after another 24 h of electrolysis. It is generally thought that the yellow color is caused by aromatics compounds [11,59], which are produced by *o*-methylphenol oxidation. The intermediates produced during the oxidation were identified in two stages. The first step included identification of aromatic intermediates. In the second step, the main carboxylic acids formed were identified in separate experiments.

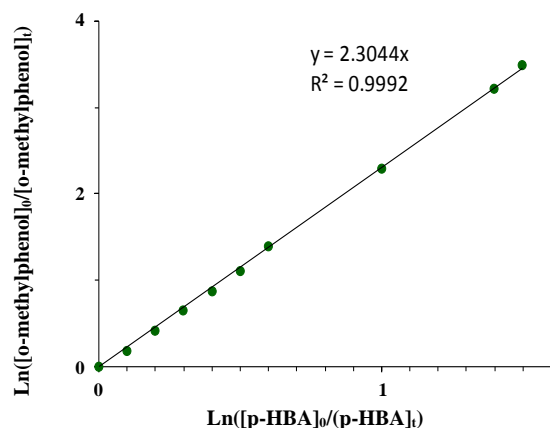During *o*-methylphenolelectrolysis, the main initial reactions were successively additions of ($^\bullet$OH) on the

Fig. 4:Kinetic analysis for the competitive pseudo-first-order reactions of o-methylphenol with hydroxyl radical generated in anodic oxidation with BDD. ([o-cresol]$_0$ = [4-HBA]$_0$ = 0.5 mmol L^{-1}, I = 60 mA/cm^2 and T = 25±2$^\bullet$C).
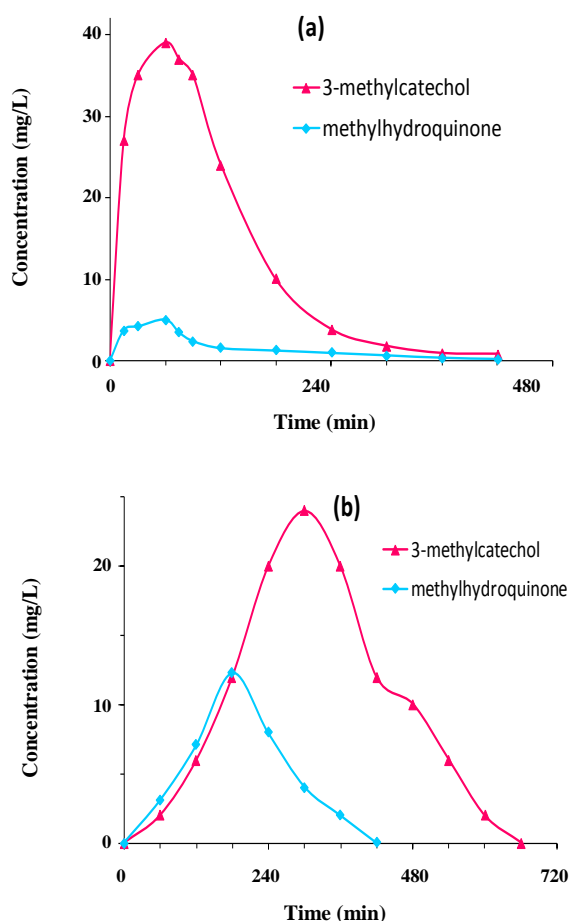

Fig. 5:Evolution of aromatic derivatives formed during anodic oxidation of 216 mg/L of o-methylphenol in 7.1 g/L of Na$_2$SO$_4$ at 25$^\bullet$C, 60 mA/cm^2, and 25±2$^\bullet$C. (a) BDD and (b) Pt.

aromatic ring, leading to the formation of 3-methylcatechol (tr = 6.30 min) and methylhydroquinone (tr = 6.70 min). The same products were detected during the oxidation of cresols by the electro-Fenton process [11].

Fig. 5a illustrates the change in concentration of 3-methylcatechol and methylhydroquinone during the degradation of the *o*-methylphenol. The concentration of these two compounds passes, after 60 minutes of treatment at the BDD anode, by a maximum of 39 and 5 mg/L, respectively. They disappear for a treatment time of 360-420 min (Fig. 5a). Contrary to the preceding case, while using Pt anode, the elimination of 3-methylcatechol and methylhydroquinone is harder and slower than BDD, the disappearance of these products lasts 11 h (Fig. 5b).

The chromatograms of the treated solutions (example in Fig. 6) exposed peaks corresponding to oxalic (tr = 7.52 min), maleic (tr = 9.1 min), pyruvic (tr = 10.6 min), glyoxylic (tr = 11.4 min), formic (tr = 13.9 min), succinic (tr = 14.30 min), acetic (tr = 17 min) and fumaric (tr = 17.4 min) acids. The evolution of carboxylic acids concentration, using BDD and Pt anodes, is illustrated in Fig.7.

Apparently, the majority of these acids are rapidly removed with BDD($^\bullet$OH) more than with Pt($^\bullet$OH). The same behavior has been previously reported [20, 35, 41, 60]. The fumaric, oxalic, and maleic succinic acids are formed from the beginning of the electrolysis with the BDD electrode. A maximum concentration of 12 mg/L is observed for fumaric acid after 60 minutes of reaction and then disappears after 300 minutes. However, succinic acid passes through a maximum (8 mg/L) in 180 minutes of reaction. These acids are formed by the fragmenting of aromatic rings. Maleic, fumaric, succinic, and pyruvic acids, for instance, can be formed by hydroxyls radicals attack to 3-methylcatechol and methylhydroquinone. However, it is noted here that pyruvic acid was undetected using BDD anode, which was not the case when using Pt anode. Formic, acetic, and glyoxylic acids do not begin to form until after 240 min of reaction. The concentration of acetic acid rises rapidly to 5 mg/L at 360 min and drops to nearly 0.5 mg/L at 540 min. The same finding was found for oxalic acid, which attains a maximum content of approximately 10 mg/L at 360 min and drops to 2 mg/L at 540 min. In contrast, at the time of using the Pt anode, acetic acid attains 68 mg/L at 480 min. This indicates that the degradation of this acid is more difficult using Pt($^\bullet$OH) than BDD($^\bullet$OH). Besides, the Figure 6b also shows
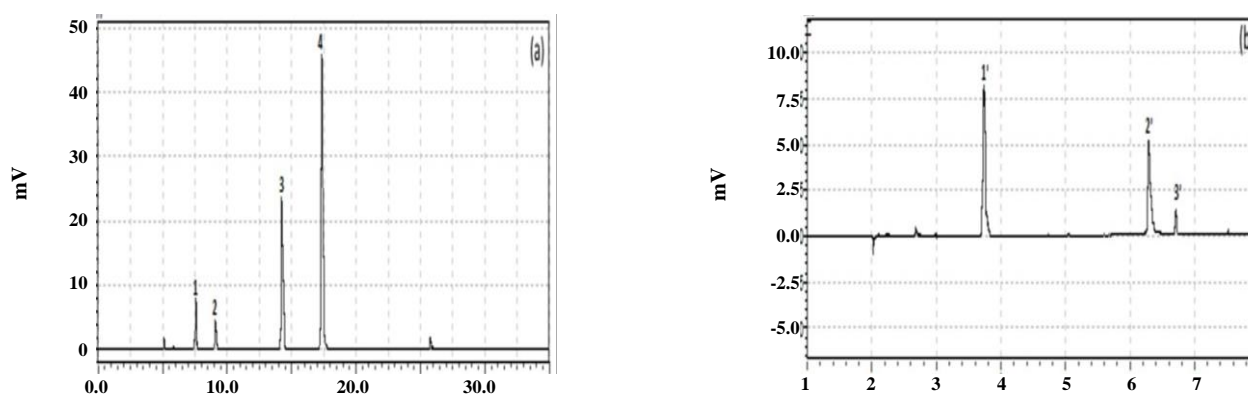
Fig. 6:Ion exclusion HPLC chromatogram (a) and HPLC chromatogram (b) after 120 min of treatment using BDD anode.
1: oxalic acid, 2: maleic acid, 3: succinic acid, 4: fumaric acid, 1': o-methylphenol, 2': 3-methylcatechol, 3': methylhydroquinone.
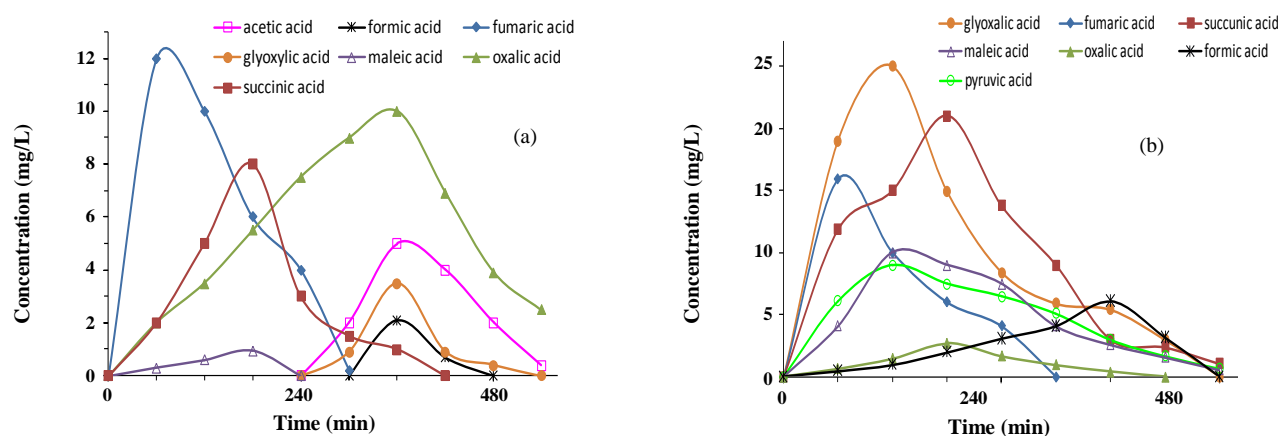

Fig. 7:Evolution of the concentration of carboxylic acids detected during anodic oxidation of 216 mg/L of o-methylphenol solution
in 7.1 g/L of Na₂SO₄ at 25±2°C, 60 mA/cm², and 25°C. (a) BDD and (b) Pt.

thepresence of a low oxalic acid concentration with a maximum of 2.7 mg/L at 180 min of reaction, this can be explained by the fact that oxalic acid was rapidly degraded using the Pt anode than BDD anode.

Reaction sequence for o-methylphenol degradation

Figure8 presents a plausible general pathway for the degradation of *o*-methylphenol by oxidation using BDD electrode. The proposed mechanism takes into account, all products detected during the degradation of*o*-methylphenol in this work. Hydroxyl radical's electrogenerated at the surface of BDD anode react with *o*-methylphenol to produce succinic, glyoxylic, fumaric, and maleic acids. Then, these intermediates undergo a rapid transformation into oxalic and formic acids which are mineralized to CO_2 and H_2O at the end of the process.

CONCLUSIONS

The degradation of *o*-methylphenol at pH 4.0 has been studied by oxidation with BDD and Pt anodes. *o*-methylphenol has been rapidly mineralized at the BDD anode; however, its degradation was considerably slower at Pt anode. The intermediate products of electrochemical *o*-methylphenol degradation, including 3-methylcatechol, methylhydro-quinone, and organic acids, have been subsequently oxidized rapidly by the BDD anode but accumulated in the case of Pt anode. Maleic acid formed from ring cleavage can be oxidized directly to oxalic acid that can be readily mineralized by electrochemical oxidation. However, at the Pt anode, this reaction seems to be more difficult. The accumulation of aromatic intermediates produces stable polymers and complex compounds. In addition, maleic acid undergoes a slow electrochemical degradation process involving the
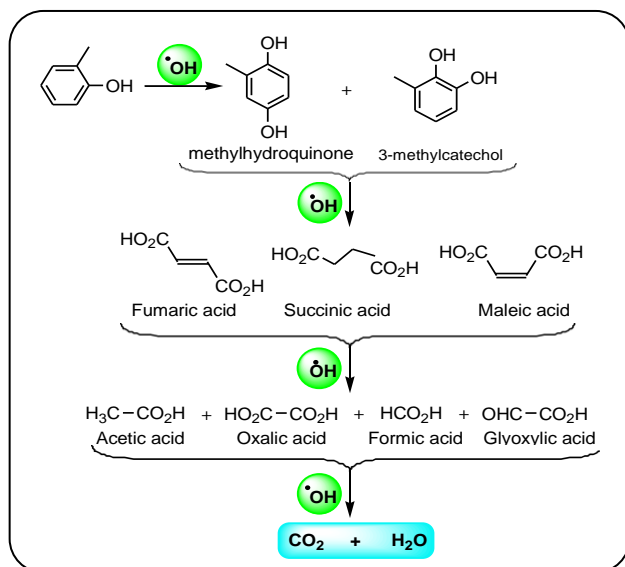
Fig. 8: Proposed reaction pathway for the degradation of o-methylphenol under anodic oxidation process.

formation of a number of intermediate organic acids, including glyoxylic and acetic acids.

Kinetics of the oxidation of *o*-methylphenol by hydroxyl radicals was also investigated and showed that it fitted well with pseudo-first-order. Using competition kinetics method, the absolute rate constant was estimated to be 3.75 x 10^9 M^{-1} s^{-1}.

This study reports for the effective degradation of *o*-methylphenol by an anodic oxidation process, which was shown to be a highly efficient technology for the oxidation of *o*-methylphenol and the degradation of its aqueous solution. The best results were obtained by using the BDD anode compared to Pt anode.

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