

Mineralization of bisphenol A (BPA) by anodic oxidation with boron-doped diamond (BDD) electrode

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Abstract

Anodic oxidation of bisphenol A (BPA), a representative endocrine disrupting chemical, was carried out using boron-doped diamond (BDD) electrode at galvanostatic mode. The electro-oxidation behavior of BPA at BDD electrode was investigated by means of cyclic voltammetric technique. The extent of degradation and mineralization of BPA were monitored by HPLC and total organic carbon (TOC) value, respectively. The results obtained, indicate that the BPA removal at BDD depends on the applied current density (I_{appl}), initial concentration of BPA, pH of electrolyte and supporting medium. Galvanostatic electrolysis at BDD anode cause concomitant generation of hydroxyl radical that leads to the BPA destruction. The kinetics for the BPA degradation follows a pseudo-first order reaction with a higher rate constant $12.8 \times 10^{-5} \text{ s}^{-1}$ for higher I_{appl} value 35.7 mA cm^{-2} , indicating that the oxidation reaction is limited by I_{appl} control. Complete mineralization of BPA was achieved regardless of the variables and accordingly the mineralization current efficiency was calculated from the TOC removal measurements. Considering global oxidation process, the effect of supporting electrolytes has been discussed in terms of the electro generated inorganic oxidants. The better performance of BDD anode was proved on a comparative study with Pt and glassy carbon under similar experimental conditions. A possible reaction mechanism for BPA degradation involving three main aromatic intermediates, identified by GC–MS analysis, was proposed.

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1. Introduction

Bisphenol A (BPA) is, a known endocrine disrupter and an industrial chemical, used in the manufacture of polycarbonate, epoxy resin and numerous plastic articles [1]. These final products are utilized in many food and drink storage containers, polycarbonate baby bottles, tableware, white dental fillings and sealants. Recent studies have shown that the release of BPA into natural environment as well as in surface water is possible during manufacturing process of these final products. Due to a widespread use of these products in recent years, BPA has been detected at considerably high level ranging from 0.14 to $12.0 \mu\text{g dm}^{-3}$ in United States river water [2] and up to

10 mg dm^{-3} in leachates from hazardous waste landfill sites in Japan [3]. With regard to possible effects to humans, researchers have found that even in very low concentration levels of BPA could cause harmful effects such as abnormal physiological changes, reproductive impairments, and testicular and breast cancer [4]. On the contrary, industrial scientists have reported that low level concentration of BPA to human exposure cause no harmful effects [5]. It is also reported [6] that wild lives exposed to low doses may come to puberty earlier. Considering the serious adverse impacts of BPA on human health and environment, it is quite urgent to find an efficient approach for removing such a chemical so as to minimize their contamination.

In the past decade, electro-oxidation technique is proved to be a well established and an efficient technique to destruct the biologically persistent organic pollutants for water and wastewater treatment [7]. It is mainly due to an appropriate choice of anode material that can allow complete removal of total organic carbon (TOC) with high current efficiency. Attempts have been

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made to study the electrochemical removal of BPA using Ti and Pt mesh [8], Pt/Ti [9], SnO₂/Ti [10] and carbon fiber [11] electrodes. But Ti, Pt and Pt/Ti electrodes were not effective to achieve total mineralization of BPA due to electrode deactivation and poor generation of more hydroxyl radicals. In the case of carbon fiber electrode, BPA has been totally removed as polymeric products that form on the electrode surface based on anodic polymerization technique. However, the polymerized film should be considered here to avoid secondary pollution. In recent years, boron-doped diamond (Si/BDD) electrode has been proved as successful anode material to destruct a variety of organic pollutants such as phenol [12], 4 chlorophenol [13] and chloromethylphenoxy herbicides [14]. It has many unique advantages and is largely generating the adsorbed hydroxyl radicals from water decomposition as shown in



To our knowledge, there has not been any work reporting on BPA degradation with BDD anode. Thus, this study explores the potential behavior of BDD to mineralize the BPA in aqueous solutions under galvanostatic control. The effects of applied current density, initial concentration of BPA and electrolyte variable were evaluated. Kinetic analysis was conducted and the mineralization current efficiency (MCE) of BPA was also calculated from the TOC value.

2. Experimental

2.1. Materials

Bisphenol A (BPA) provided by Kanto Chemicals, Japan, was analytical grade granular material and used without further purification. BPA stock solution was prepared with high purity water obtained from a Millipore Milli-Q system and the required concentration of working solution was obtained by diluting this stock solution with deionised water. The concentration of working solution was varied from 10 to 30 mg dm⁻³ based on the BPA concentration in leachates as reported by Yamamoto et al. [3]. The used supporting electrolytes were Na₂SO₄, NaNO₃ and NaCl. The pH value of electrolyte solutions was adjusted with H₂SO₄ or NaOH depending on the desired values. Organic solvents and other chemicals used were either HPLC or analytical grade from Kanto Chemicals, Japan.

2.2. Preparation of BDD electrode

BDD thin film was grown on *p*-Si (111) substrate by microwave plasma-assisted chemical vapour deposition technique (Model AX2115, AsTeX Corp.). The detailed experimental conditions for the BDD film growth have been given in our previous work [15]. After the deposition, the film was sonicated in ethanol for 5 min and deionised the film surface in water prior to use. Ohmic contacts for the electrode with the wire were made using gold and silver paste. The electrode was covered with the masking tape in which the exposed area was 7 cm².

2.3. Electrolytic system

Electrochemical experiments were carried out using a conventional single compartment three-electrode cell in conjunction with a computer-controlled potentiostat/galvanostat HZ-5000 (Hokuto Denko Ltd., Japan). The working solution volume was 250 ml for all experiments. BDD was used as working electrode, Hg/Hg₂Cl₂·KCl (sat.) (SCE) as a reference and Pt as a counter electrode. Both BDD and Pt electrodes were square type plate with effective surface area of 7 and 8 cm², respectively, and the inter electrode gap is 10 mm. Cyclic voltammetry experiment was performed without agitation of the electrolyte. For comparative purpose of anodic oxidation, 7 cm² of Pt and GC each were also employed. In anodic oxidation with Pt, the cathode was 8 cm² GC, while in the case of GC as anode, 8 cm² of Pt was used as cathode. Degradation experiments were conducted at galvanostatic mode in uniform stirring with magnetic stirrer. A thermo-regulated water bath was used to maintain a constant temperature (25 °C). Na₂SO₄ (0.1 M) was used as supporting electrolyte and the initial pH of the electrolyte was adjusted to 6 for general parameter experiments. Anodic polarization of BDD was carried out for 10 min in 0.1 M H₂SO₄ at 100 mA current, prior to every experimental run to remove any kind of deposition and/or impurities from the surface. The cell potential was remained constant during the galvanostatic electrolysis, indicates that electrode activity is not affected.

2.4. Analytical techniques

During the course of reaction, the decay of BPA concentration was measured by HPLC (Model L-2455, Hitachi, Japan) equipped with a multiple wavelength UV detector and Silicagel C₁₈ (150 mm × 4.6 mm) analytical column. It displayed a well-defined peak for BPA at a retention time (*t_r*) of 4.2 min at 276 nm. For these analyses, samples of 20 μl were injected into the chromatograph and a 50:50 (v/v) CH₃CN/3 × 10⁻² M/kg CH₃COOH mixture was passed at a flow rate of 1 ml/min as mobile phase. The evolution and degradation of the peaks for intermediate compounds were followed at the same condition of column. The pH of the solution was measured with a HM-26S pH meter (TOA, Japan). Mineralization of BPA compound was monitored by the abatement of their TOC determined on a Shimadzu VCSN/CPN Model TOC analyzer. The fate of oxidation products were analysed by GC-MS (Shimadzu GC-15A, HP5980II coupled with Jeol JMS-AX500). Chromatographic conditions were as follows: the initial temperature of the column oven was 80 °C for 2 min hold and increased up to 280 °C with a heating rate of 12.5 °C per min. Injection and detector port temperatures were 260 and 280 °C, respectively. The NIST online library search was used for identification of the products.

3. Results and discussion

3.1. Voltammetric study of BPA on BDD

Prior to galvanostatic study, cyclic voltammetric investigation was performed to find out the oxidation behavior of BPA

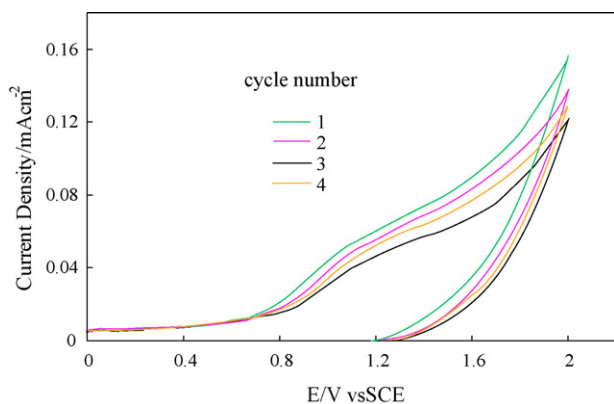


Fig. 1. Cyclic voltammograms for the oxidation of BPA at Si/BDD electrode (BPA, 20 mg dm^{-3} ; electrolyte, $0.1 \text{ M Na}_2\text{SO}_4$; scan rate = 100 mV s^{-1} ; pH 6; T , 25°C).

on BDD surface at a sweep rate of 100 mV s^{-1} and the typical voltammogram is shown in Fig. 1. In the first cycle, the oxidation peak corresponding to BPA appears approximately at 1.2 V vs. SCE. It has been reported that the oxidation peak of BPA at Pt and GC electrode are lower than 0.8 V at neutral pH values [9–11]. The difference in oxidation potential could be attributed to the behavior of the electrode material. In the case of BDD, the anodic current peak decreases in the subsequent cycles. This observation can be explained as a result of fouling phenomenon that the polymeric product deposition on the surface of BDD electrode. The activity of the electrode surface becomes less due to this passivating behavior. However, this fouling layer can be removed by anodic polarization in the potential region of water decomposition ($>2.3 \text{ V}$). This has already been confirmed by some earlier investigations [16–18] where the activity of BDD surface was restored by anodic polarization method. Moreover, in the range of applied current density in the present study, the anodic potential was found to be in the region of water decomposition thus no electrode fouling problem encountered during the galvanostatic electrolysis.

3.2. Anodic oxidation of BPA

Fig. 2a shows the trend of BPA decay as a function of electrolysis time during the anodic oxidation of BPA (20 mg dm^{-3}) with BDD at three different applied current densities (I_{appl}) ranging from 14.28 to 35.7 mA cm^{-2} . As many researchers have already been proved that oxidative degradation of organic pollutants at BDD electrode only takes place in the potential region of water decomposition [13,14], the lower value of applied current was selected so as to attain the anodic potential higher than 2.3 V vs. SCE. It is quite apparent that the complete degradation as well as mineralization of BPA could always be achievable due to the electrochemical decomposition of water molecules on the BDD surface that leads to the concomitant generation of hydroxyl radicals ($\bullet\text{OH}$) according to the reaction (1). As can be seen in Fig. 2a, the rate of BPA degradation is highly dependent on the I_{appl} and becomes faster with increasing current density. For example, nearly 100% degradation could be

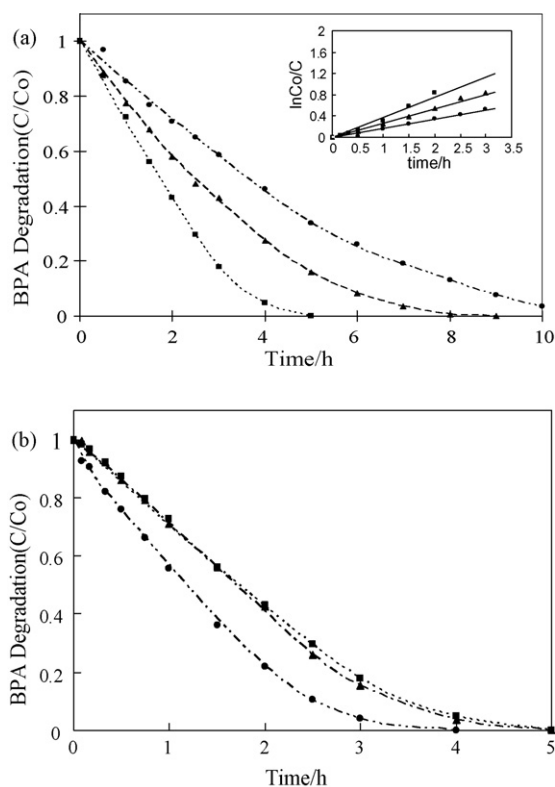


Fig. 2. (a) Effect of I_{appl} on anodic oxidation of BPA with BDD (BPA, 20 mg dm^{-3} ; electrolyte, $0.1 \text{ M Na}_2\text{SO}_4$; pH 6; T , 25°C) (●) 14.28 mA cm^{-2} , (▲) 25 mA cm^{-2} and (■) 35.7 mA cm^{-2} . (Inset) Corresponding kinetic analysis assuming a pseudo-first order reaction for BPA decay. (b) Decay of different initial concentration of BPA by anodic oxidation with BDD at 35.7 mA cm^{-2} (electrolyte, $0.1 \text{ M Na}_2\text{SO}_4$; pH 6; T , 25°C) (●) 10 mg dm^{-3} , (■) 20 mg dm^{-3} and (▲) 30 mg dm^{-3} .

accomplished at higher I_{appl} of 35.7 mA cm^{-2} , after electrolysis time of 4 h, whereas it requires more than 10 h of electrolysis time to achieve the complete degradation at low I_{appl} of 14.28 mA cm^{-2} . This indicates that under constant I_{appl} , the electro generation of $\bullet\text{OH}$ at BDD surface is uniform and it can be greatly enhanced with increasing I_{appl} . Also, it confirms that I_{appl} value is lower than the limiting current density with higher mass transfer rates which always maintain the flux of the pollutant molecules towards the anode. The degradation results of BPA were subjected to the analysis of kinetic equation of different reaction orders and good fittings were found for pseudo-first order reaction. The straight line thus obtained for three different I_{appl} with an initial concentration of 20 mg dm^{-3} , are presented as inset in Fig. 2a. The pseudo-first order rate constants calculated are 5.6×10^{-5} , 9.5×10^{-5} and $12.8 \times 10^{-5} \text{ s}^{-1}$ for 14.28 , 25 and 35.7 mA cm^{-2} , respectively. It could be observed that the rate constants almost linearly increase with increasing I_{appl} , at a constant initial concentration of BPA. These results are consistent with the fact that degradation process is a bimolecular reaction between BPA and $\bullet\text{OH}$ with a constant generation of $\bullet\text{OH}$ which is being approximately proportional to the I_{appl} value.

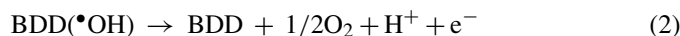
In order to have a concrete conclusion on kinetics of BPA degradation reaction, electrolysis were carried out with three dif-

ferent initial concentration of BPA viz., 10, 20 and 30 mg dm⁻³ at a fixed current density of 35.7 mA cm⁻² and the corresponding results are shown in Fig. 2b. The degradation rate of BPA was found to be decreased and having no proportional variations with increase in the initial concentration. Also, as can be seen in Fig. 2b there is no much difference observed in the degradation rate of BPA when increasing the concentrations from 20 to 30 mg dm⁻³. The decrease in rate of BPA degradation could only lead to the possible fact that the competitive consumption of •OH for oxidizing the intermediate compounds. The earlier study [14] is suggested that the unspecific oxidation of all molecules especially major intermediates with •OH that leads to the side reactions and parallel consumption of •OH. The degradation results of three different initial concentrations with electrolysis time were subjected to kinetic analysis related to simple reaction orders. It was found that BPA decay follows a complex kinetics without following any reaction orders. This is because of the competitive consumption of •OH at the BDD surface by parallel oxidative reactions with intermediate compounds [14].

3.3. Mineralization of BPA and its current efficiency

The mineralization trend of BPA at BDD anode was examined, as a function of electrolysis time, with varying I_{appl} value and initial concentration of BPA. As can be seen in Fig. 3a, the rate of TOC removal is found to be faster, when I_{appl} increased from 14.28 to 35.7 mA cm⁻², since the degradation reaction is

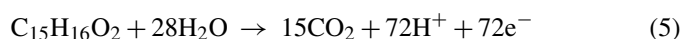
not limited by diffusion of the organic molecules towards the anode. As an example, a complete combustion of BPA from aqueous electrolyte was achieved within the electrolysis time of 14 h ($Q = 14 \text{ A h dm}^{-3}$) at 35.7 mA cm⁻², when it requires about 24 h ($Q = 9.6 \text{ A h dm}^{-3}$) at lower I_{appl} 14.28 mA cm⁻². These results confirm that the •OH generation is accelerated when I_{appl} increases, resulting a rapid destruction of BPA [19]. However, it could also be noted that the specific electrical charge (Q) needed for an equal amount of TOC removal is increased with I_{appl} . This feature can be related to the fact that a part of electro generated •OH is wasted at higher I_{appl} by parallel parasite reaction such as O₂, peroxodisulfate (S₂O₈²⁻) and hydrogen peroxide (H₂O₂) formations as follows:



Thus, increase in the I_{appl} will always lead to the secondary anodic reaction to some extent at the expense of organic molecule degradation, which causes the less efficiency. These facts are in agreement with the earlier study [20]. These intermediated weaker oxidants (S₂O₈²⁻, H₂O₂) have found to be no impact on mineralization of BPA and it will be separately discussed in detail in Section 3.4.

Experiments were performed with three different initial concentrations of BPA viz., 10, 20 and 30 mg dm⁻³, at constant I_{appl} 35.7 mA cm⁻² and the results obtained are shown in Fig. 3b. A considerable decline in TOC removal rate could be observed with increasing initial concentration of BPA. It was found that the rate of TOC removal is only varied up to reaching 80% removal for all initial concentrations. Moreover, it is obvious that a total mineralization requires almost an equal electrolysis period 14 h ($Q = 14 \text{ A h dm}^{-3}$). However, considering the quantity (mg dm⁻³) of TOC removal, the mineralization efficiency increases with increasing the initial concentration. For example, at electrolysis time of 5 h ($Q = 5 \text{ A h dm}^{-3}$), the quantity of TOC removed is 8.6, 12.7 and 17.6 mg dm⁻³ for the initial concentrations of 10, 20 and 30 mg dm⁻³, respectively (data not shown in figure). This is indicative of more pollutants make a possibility of utilizing larger amount of •OH and avoiding O₂ evolution reaction [19].

From the above findings, it can then be concluded that the mineralization of BPA with BDD anode leads to the total destruction of the molecule and the formation of CO₂ as final product. Thus the over all mineralization reaction can be written as follows:



This reaction shows that 72 electrons are involved in incinerating a BPA molecule completely into CO₂. Generally current efficiency is an important issue in electrochemical treatment, due to the relatively high costs of electric power. According to the literature [19], the MCE at a given time for the above TOC removal results of BPA can be comparatively calculated using

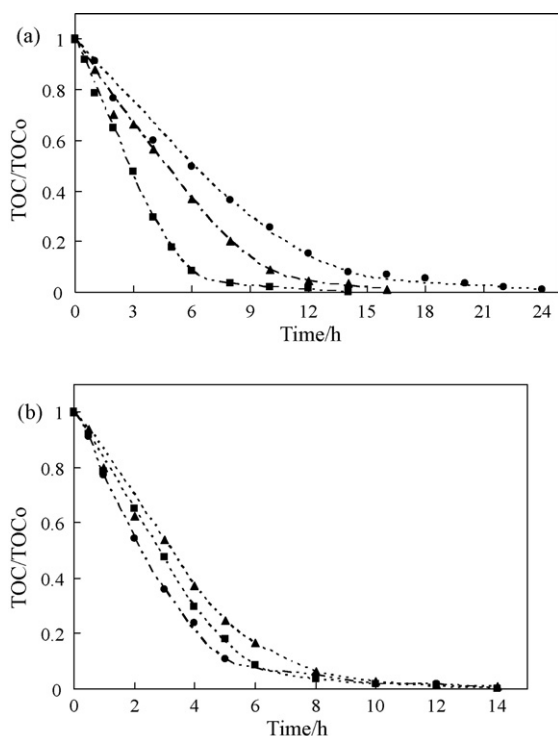


Fig. 3. (a) TOC abatement with reference to electrolysis time at three different I_{appl} for the mineralization of BPA with BDD anode (BPA, 20 mg dm⁻³; electrolyte, 0.1 M Na₂SO₄; pH 6; T, 25 °C) (●) 14.28 mA cm⁻², (▲) 25 mA cm⁻² and (■) 35.7 mA cm⁻². (b) TOC removal for three different initial concentration of BPA at constant I_{appl} 35.7 mA cm⁻² (electrolyte, 0.1 M Na₂SO₄; pH 6; T, 25 °C) (●) 10 mg dm⁻³, (■) 20 mg dm⁻³ and (▲) 30 mg dm⁻³.

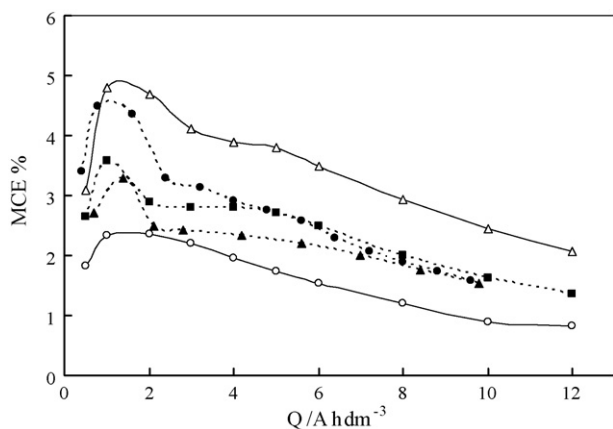


Fig. 4. Dependence of mineralization current efficiency calculated from Eq. (6) on specific electrical charge for the TOC removal results shown in Fig. 3a and b (electrolyte, 0.1 M Na₂SO₄; pH 6; T, 25 °C) [concentration of BPA, 20 mg dm⁻³ for I_{appl} (●) 14.28 mA cm⁻², (▲) 25 mA cm⁻² and (■) 35.7 mA cm⁻²; I_{appl} , 35.7 mA cm⁻² for BPA concentration (○) 10 mg dm⁻³ and (Δ) 30 mg dm⁻³].

the following relation:

$$\text{MCE} = \left[\frac{\Delta(\text{TOC})_{\text{exper}}}{\Delta(\text{TOC})_{\text{theor}}} \right] \times 100 \quad (6)$$

where $\Delta(\text{TOC})_{\text{exper}}$ denotes the experimental solution TOC removal at time t and $\Delta(\text{TOC})_{\text{theor}}$ is the theoretically calculated TOC removal considering that the applied electrical charge (=current \times time) is consumed to yield the reaction (5).

Fig. 4 shows the evolution of the MCE with specific electrical charge passed as a function of I_{appl} and initial concentration of BPA. As can be seen, a sharp increase in MCE value was found irrespective of the experimental conditions during the initial phase of the electrolysis time i.e., up to the Q value of 1 A h dm⁻³. This trend can be attributed to the initial formation of propylene alcohol molecule from BPA molecule breaking reaction. This aliphatic molecule can be mineralized into CO₂ and water in higher rate comparing to aromatic oxidation products. Sires et al. [21] have also observed the similar trend and justified that some oxidation products formed at initial stages, are more rapidly degraded by hydroxyl radicals. In each case, a similar and gradual decrease in MCE could be observed, indicating a continuous fall in oxidizing ability of the process. This behavior can be put down to the fact that progressively decreasing the pollutant concentration with prolonging the electrolysis time causes limiting the diffusion of organic molecules towards the anode surface. It could also be attributed to the formation of carboxylic acids, which are known to degrade more slowly comparing the other intermediate compounds. The current efficiency was found to be decreased with increasing the I_{appl} and drops down from 3.4% at 0.4 A h dm⁻³ to 2.65% at 0.5 A h dm⁻³ for 14.28 and 35.7 mA cm⁻², respectively. At higher current densities, the O₂ evolution, which is an undesired parallel reaction, is yielded in higher extent at the detriment of the main oxidant •OH [18]. However, the MCE does not seem to vary much between the higher current densities 25 and 35.7 mA cm⁻², as the concomitant generation of •OH greatly enhance in these cases. It can also be observed that the MCE increases linearly

with increasing initial concentration of BPA at constant I_{appl} value 35.7 mA cm⁻². This is because the relatively higher concentration of organic pollutants making a possibility of utilizing the larger proportion of •OH so as to minimize the evolution of O₂ and weaker oxidants generation. These results allow to conclude that MCE was influenced by I_{appl} and initial concentration of BPA and in particular, found to be a maximum for high pollutant concentration and low I_{appl} value. The specific energy consumption for a solution containing 20 mg dm⁻³ of BPA with 100% TOC elimination was calculated as 28.67 Wh l⁻¹.

3.4. Effect of electrolyte variables

The possible effect of electrolyte variables such as initial pH and supporting medium were studied at constant I_{appl} 35.7 mA cm⁻² of BPA concentration 20 mg dm⁻³ to clarify the optimization of experimental conditions. Firstly, the electrolyte pH was found to have strong influence on anodic oxidation of BPA with BDD as shown in Fig. 5(a) and (b). It is very clear that the concentration of BPA and TOC value decreased in higher rate with electrolysis time at pH 10. However, the total mineralization was accomplished only at pH 6 with comparatively lesser electrolysis time of 14 h. The trend observed for the reaction rate at pH 10 could be explained with the pK_a value of BPA molecule. BPA molecule has two ionisable hydrogen atoms with a pK_a value of 9.59 and 10.20 and it exists predominantly in the ionised form at pH 10. Therefore, it could be more readily attacked by the electrophilic •OH and rapidly oxidized. At pH 10, the TOC removal rate becomes slower after 3 h of electro-

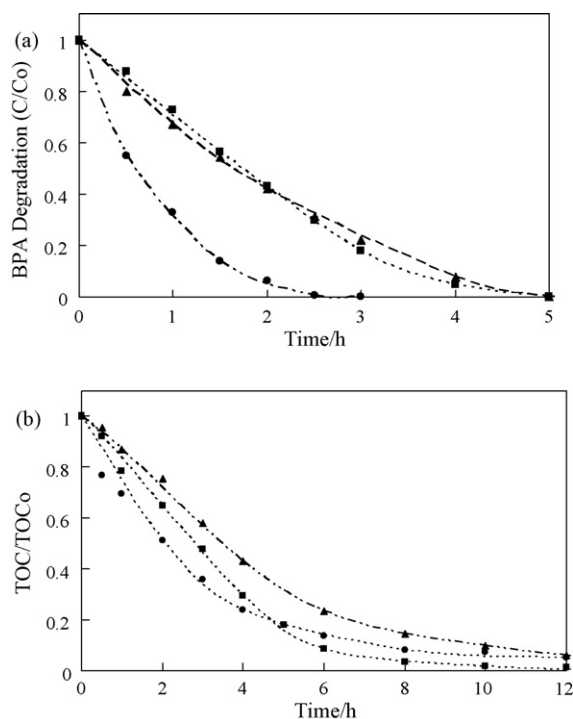


Fig. 5. (a) Degradation and (b) mineralization of BPA with respect to initial pH of the electrolyte at BDD anode (BPA, 20 mg dm⁻³; I_{appl} , 35.7 mA cm⁻²; T, 25 °C; electrolyte, 0.1 M Na₂SO₄) (▲) pH 2, (■) pH 6 and (●) pH 10.

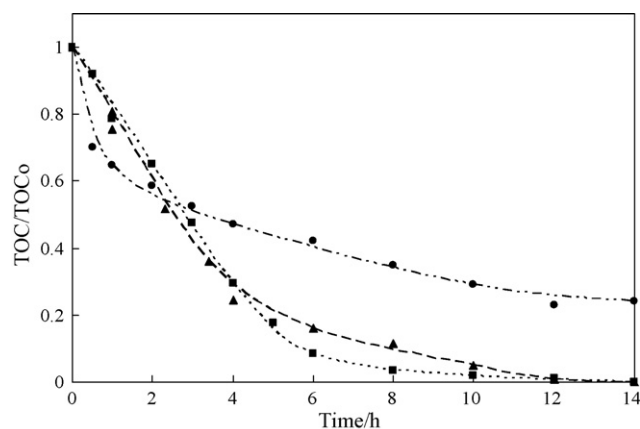
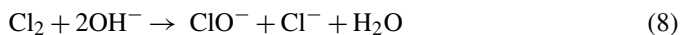


Fig. 6. Effect of supporting medium on BPA removal with BDD anode (BPA, 20 mg dm^{-3} ; I_{appl} , 35.7 mA cm^{-2} ; pH 6; T , 25°C) (■) Na_2SO_4 , (▲) NaNO_3 and (●) NaCl .

ysis period. It could be justified that the fast removal of TOC observed in the beginning stage up to 3 h electrolysis time at pH 10, only due to the rapid degradation of BPA molecule (anionic form) rather than intermediate products. After 3 h of electrolysis time, the slow down rate reflects a slower mineralization of the intermediate products. Also, this result seems to agree with the phenomenon that the oxidative potential of $\bullet\text{OH}$ decreases as the pH value increase [22]. In comparison, pH 2 shows low efficiency for TOC removal since a part of the hydroxyl radicals are neutralized as the concentration of H^+ increases in the acidic region. During the electrolysis a slight fall in pH was observed in the experiment starting from the initial pH 6, as a result of short chain aliphatic acid formation originated from BPA molecule breaking and ring fission reactions [18]. The pH decay during the electrolysis was found to be negligible at experiments start with pH 2 and 10, since the electro generated aliphatic acids were not strong enough to make the impact in these extreme pH values.

As far as the role of the supporting electrolyte concerned, this parameter seems to have a markedly influence on BPA removal with BDD anode as shown in Fig. 6. As seen for the mineralization trend, almost no influence was observed between the supporting electrolytes Na_2SO_4 and NaNO_3 . It has been proved in the literature [18,23], that electrolytes containing SO_4^{2-} will lead to the generation of $\text{S}_2\text{O}_8^{2-}$, which exists for longer time and diffuses to the bulk of the electrolyte resulting a mediated homogeneous reaction with organic pollutant. Conversely, no such oxidants would be generated while the electrolyte solution containing nitrate ion. But in our case, the extent of TOC removal was observed to be the same up to 3 h electrolysis time for the experiments with Na_2SO_4 and NaNO_3 as supporting electrolyte. This confirms that the majority of the BPA and intermediate molecules were oxidized by hydroxyl radicals formed on the electrode surface rather by inorganic oxidizing intermediates such as $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 . Similar behavior was observed by Flox et al. [20] for the degradation of herbicides at BDD anode. The quicker mineralization found at the initial period when using NaCl , can be related to the existence of chlorine (Cl_2) and hypochlorite (ClO^-), generated from the oxidation of

chloride ion at BDD according to the reactions:



Obviously, these oxidants have been observed to be able to degrade the organic pollutant effectively [24,25]. However, in the present study, the mineralization efficiency became very slow after 0.5 h electrolysis time. This might be due to the formation of chlorinated organic intermediates which are less rapidly degraded even with chlorine-based oxidizing reagents (Cl_2 and ClO^-). Although the Cl_2 and ClO^- are strong enough to degrade the chlorine-free organic compounds, it fails to show the effective degradation for the chlorinated organic compound. It can thus be concluded that the overall poor mineralization using NaCl is due to the formation of chlorinated organic compounds.

3.5. A study on influence of the anodic materials

Electrolysis were carried out with solution containing constant initial concentration (20 mg dm^{-3}) of BPA under similar experimental conditions (35.7 mA cm^{-2} , $0.1 \text{ M Na}_2\text{SO}_4$) with an equal surface area of Pt and GC each as anode, to compare the corresponding oxidizing ability with BDD anode. As can be seen in Fig. 7, the results are quite explicable in terms of the $\bullet\text{OH}$ generation behavior of anodes. It could be seen that the anodic oxidation with BDD yields a continuous TOC removal up to the total mineralization of BPA within electrolysis time of 14 h whereas in the case of Pt as anode, hardly 20% TOC removal was obtained under the similar experimental conditions. The better efficiency of BDD with a comparison of Pt can be accounted for the larger generation of oxidant $\bullet\text{OH}$ on its surface as it exhibits a “non-active” behavior. The surface of the BDD has less interaction on electrogenerated $\bullet\text{OH}$, resulting in the larger generation of $\bullet\text{OH}$ without forming as higher oxides. It is already well documented in our previous study [16] on degradation of 17β -estradiol at BDD anode. Although, poor efficiency of TOC removal was observed for Pt anode, the substrate compound (BPA) degrades completely within 10 h of electrolysis time (data not shown). It evidences the less but constant generation of the main oxidant

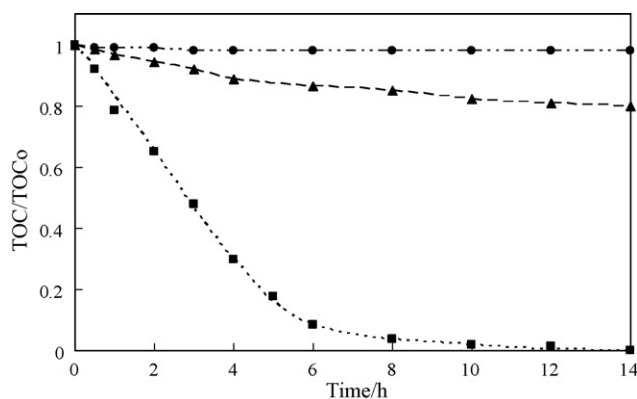


Fig. 7. Comparative study of different anodic materials for mineralization of BPA with equal surface area of 7 cm^2 (BPA, 20 mg dm^{-3} ; I_{appl} , 35.7 mA cm^{-2} ; electrolyte, $0.1 \text{ M Na}_2\text{SO}_4$; pH, 6; T , 25°C) (■) BDD, (▲) Pt and (●) GC.

$\bullet\text{OH}$ at the surface of Pt anode. The earlier study on oxidation behavior of SnO_2 and Pt electrodes proved that the former is showing the better efficiency to degrade the organic pollutants [26]. However, SnO_2 has major drawback of having lower electrochemical stability and limited service life and it is proved to be inferior to BDD anode for the degradation of dye molecules [27]. GC anode surface was found to be undergone severe deterioration during the electrolysis and not potent enough to mineralize the BPA due to its less electrochemical stability.

3.6. Oxidation products and proposed reaction mechanism

To predict the reaction mechanism of BPA degradation at BDD anode, a preparative electrolysis was performed at 35.7 mA cm^{-2} of solution containing 20 mg dm^{-3} BPA in $0.1 \text{ M Na}_2\text{SO}_4$. The sample was siphoned out from the cell and saturated with NaCl salt followed by a successive extraction (three times) with diethyl ether. GC–MS analysis of the extracted sample gave three main intermediates at different retention time (t_r) as follows: (a) phenol ($m/e = 94$, $t_r = 6.81 \text{ min}$), (b) benzoquinone ($m/e = 108$, $t_r = 6.15 \text{ min}$) and (c) hydroquinone ($m/e = 110$, $t_r = 7.66 \text{ min}$). According to the literature [28], the reaction intermediates from the oxidation of phenolic compound are expected to be mainly quinone products and short chain carboxylic acids. Based on the results obtained from galvanostatic study and the three intermediate products, the possible degradation pathway is proposed as shown in Fig. 8. The oxidation of BPA by $\bullet\text{OH}$ leads to the appearance of phenol and isopropylene alcohol by breaking the bonds adjacent to the methyl bridge. Isopropylene alcohol molecule will undergo further oxidation by $\bullet\text{OH}$ to give short chain carboxylic acid molecule. The hydroxylation of phenolic ring might be having a possibility to form catechol, resorcinol and hydroquinone compounds as mass spec-

trum shows a species at $m/e = 110$. However, it is only expected to be hydroquinone from earlier investigations [29]. Subsequently it forms as quinone by dehydrogenation reaction with $\bullet\text{OH}$. All these phenolic ring molecules can be oxidized and converted to ring cleavage small fragmented products which would be eventually give short chain aliphatic acids (maleic, fumaric, oxalic, acetic and formic acid) by $\bullet\text{OH}$ attack. The formations of all these aliphatic acids were not identified but can be easily understood bearing in mind that pH decay during the galvanostatic electrolysis of BPA. Moreover, it is proved in the earlier studies [29], that aliphatic acids are formed in the final step prior to CO_2 conversion, when phenolic compounds undergo the electro-oxidation process. Finally, these short chain aliphatic acids were destructed resulting in a complete oxidation of BPA.

4. Conclusions

The feasibility of BPA removal by anodic oxidation using BDD electrode was studied in bulk electrolysis varying the operating and electrolyte conditions. The voltammetric study indicates that BPA gets oxidized at 1.2 V vs. SCE and deposited as polymer on the surface of the BDD anode, causes the decrease of electrode activity. The experimental results suggest that the initial concentration of BPA and applied current density (I_{appl}) could affect the mineralization efficiency especially in the initial phase of the reactions. Kinetic studies show that the BPA oxidation reaction was a I_{appl} controlled process and faster at higher current density. The complete mineralization of BPA was always accomplished with all the experimental conditions studied, and the mineralization current efficiency was found to be increased with increasing initial concentration and decreasing I_{appl} value. It was also observed that high initial concentration and low I_{appl} value were beneficial to remove BPA with less energy consumption. The electrolyte pH has a significant role on degradation rate of BPA, being faster at pH 10. No considerable effect was observed between the supporting electrolytes Na_2SO_4 and NaNO_3 demonstrating that $\text{S}_2\text{O}_8^{2-}$ is not able to degrade the more resistant intermediate molecules. The overall mineralization efficiency was found to be very poor when NaCl was employed as supporting medium. It was speculated from the HPLC analysis that this might be due to the formation of chlorinated organic intermediates. A comparative study of different anodic material (Pt and GC) confirms that the BDD anode is the most effective electrode for BPA mineralization. Three intermediate products, identified by GC–MS structural analysis and the observation from the galvanostatic studies were allowed the reaction pathway that the oxidation of BPA leads to the appearance of phenol, isopropylene alcohol and quinonic compounds and subsequently these organics are transformed into short chain aliphatic acids and eventually this reaction completes with the formation of CO_2 and water.

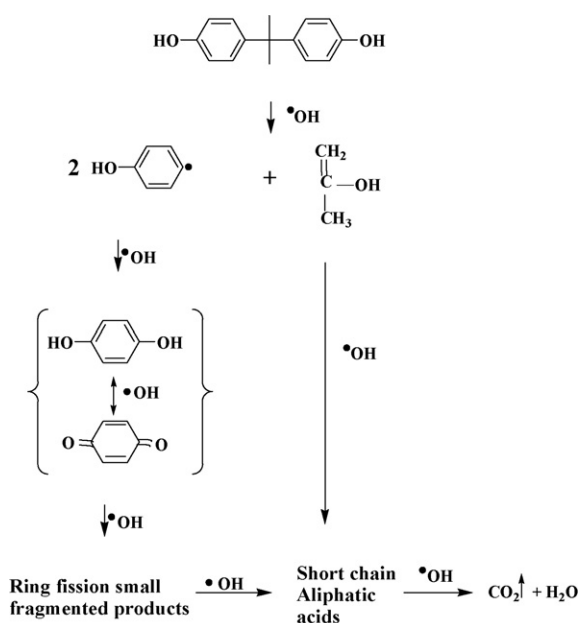


Fig. 8. Proposed reaction mechanism for the anodic oxidation of BPA with BDD electrode.

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