Electrochemical Advanced Oxidation of 4, 4′-Sulfonyldiphenol on BDD and Pt Anodes in Aqueous Medium

Naimi Imen1*, Louhaichi Mohamed Radhouan2, Ben Rayana Mohamed Chiheb2 and Bellekhal Nizar1.

1Unité de recherche de Catalyse d’Electrochimie de Nanomatériaux et leurs Applications et de Didactique CENAD, Institut National des Sciences Appliquées et de Technologie (INSAT), B.P.N°676, 1080 Tunis Cedex, Tunisie.
2 Laboratoire National de Contrôle des Médicaments, 11 bis Rue Jebel Lakhdar Bab Saadoun, 1006 Tunis, Tunisie.

Abstract—In this paper, degradation of Bisphenol S (BPS), an environmental endocrine disruptor, in an aqueous medium by the electrochemical advanced oxidation process “Electro-Fenton” is studied using carbon felt as cathode and two different types of anode materials: Platinum (Pt) and boron doped diamond (BDD). The effect of some operating conditions, such as the current density, nature of the supporting electrolyte and catalyst, has been evaluated. The comparative study of BPS removal during the electro-Fenton treatment using Pt or BDD anodes showed that optimal conditions led to total degradation of the pollutant for both anodes but the removal rate with the BDD anode is higher than the Pt anode due to the higher oxidizing power of the BDD anode. Kinetic data showed a pseudo first-order reaction between hydroxyl radical and BPS with an absolute rate constant of $2.22 \times 10^9$ M$^{-1}$ s$^{-1}$ for Pt anode and $4.31 \times 10^8$ M$^{-1}$ s$^{-1}$ for BDD anode. The performance of the process has been followed in terms of BPS conversion to by-products and carboxylic acids using GC-MS and HPLC, respectively.

Keywords—Bisphenol S; Electro-Fenton process; hydroxyl radicals; BDD anode; Degradation.

I. INTRODUCTION

Bisphenol analogues are widely used in industrial and consumer products. Among these compounds is bisphenol A (BPA), produced in quantities of over eight billion pounds each year worldwide, and frequently used in the production of polycarbonate plastics and resin lining of food and beverage cans [1]. BPA has been identified as a weak estrogenic chemical, which modifies natural endocrine functions by binding to the estrogen receptor which consequently causes adverse effects on the human health and wildlife like breast cancer, endometriosis and infertility [2].

Concerns about the health risks of BPA are increasing, and restrictions/regulations have been put forward to limit its application in some consumer products [1] and several manufacturers are gradually replacing BPA with a number of alternatives, such as 4,4′-sulfonyldiphenol known as bisphenol S (BPS) (Fig. 1). BPS is a Bisphenol analogue, used as an anticorrosive agent in epoxy glues and as a reagent in polymer reactions [3, 4]. The production and consumption of the substitute have increased recently [1, 3], leading to its detection as a contaminant in the aquatic environment.

Furthermore, many studies [2, 5-7], have shown that BPS possesses acute toxicity, genotoxicity, and estrogenic activity of a comparable potency to BPA. Beyond health impacts, BPS may also pose risks to the environment. It is not amenable to biodegradation and might be persistent and become an ecological burden. Thus, alternative degradation methods are needed for the removal of BPS in the environment [8].

Advanced Oxidation processes (AOPs) seem to be a useful method to remove or pre-oxidize remaining organic micropollutants from the effluents of waste water treatment plants [9]. These processes involve chemical, photochemical or electrochemical techniques to bring about chemical degradation of organic pollutants. The principal active species in such systems is the hydroxyl radical (•OH), a highly oxidizing agent of organic contaminants [10-16]. These radicals react with organic pollutants and thus lead to their degradation by three modes of action: hydrogen atom abstraction, electrophilic addition to π systems or electron transfer (redox) reactions [17]. During degradation, oxidation intermediates are formed and in their turn are oxidized until complete mineralization to carbon dioxide, inorganic ions and water.

Since it is an economically and environmentally friendly process, Electro-Fenton (EF) is a commonly used Electrochemical Advanced Oxidation process, widely used to remove the toxicity of persistent, non biodegradable and refractory organic pollutants from water such as dyes [14, 17, 18], pharmaceutical and personal care products [9, 10, 12, 15], pesticides [11, 19, 20] and other persistent organic pollutants [16].

![Fig. 1. The molecular structure of Bisphenol S (BPS)](image-url)
In Electro-Fenton process, the source of hydroxyl radical (•OH) is the Fenton reaction (1) in which Fenton reagent is produced electrochemically and regeneraled in situ.

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \quad (1)$$

O₂ or air gas is injected into either the reaction medium or directly at the cathode to generate H₂O₂ via reaction (2).

$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad (2)$$

$$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad (3)$$

H₂O₂ is produced continuously at the carbonaceous cathodes as carbon felt that can provide high yield. Small quantities of Fe²⁺ are usually added to form Fe³⁺ (3) to enhance the zing power of electro-generated H₂O₂.

Using an undivided electrolytic cell for the EF process, the organic compounds can be also destroyed by heterogeneous hydroxyl radicals (M•OH) produced at the anode surface (M) from water oxidation following the (4) thus accelerating the mineralization rate of the pollutants [21].

$$\text{M} + \text{H}_2\text{O} \rightarrow \text{M(OH}^+) + \text{H}^+ + \text{e}^- \quad (4)$$

In the present work, we have undertaken a study on BPS degradation by the Electro-Fenton process in aqueous medium. The experiments are carried out in an undivided cell using Pt or BDD as anodes and commercial graphite felt as cathode. Initially, we investigated the effects of some operating parameters on the removal rate such as current density, catalyst dose and nature of supporting electrolyte. The decay kinetics of BPS were investigated and the absolute rate constant of the reaction between •OH and BPS was determined by using competition kinetics method. Aromatic intermedes were a mixture of water-acetonitrile (70:30, V/V). It was eluted from wa ter oxidation following the (4) thus accelerating the mineralization rate of the pollutants [21].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₁₂H₁₀O₄S</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>250.27</td>
</tr>
<tr>
<td>Solubility (g/L)</td>
<td>1.1</td>
</tr>
<tr>
<td>λₘ₃₆ (nm)</td>
<td>258</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.37</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>240 – 248</td>
</tr>
</tbody>
</table>

Iron heptahydrated sulfate (Fe₂(SO₄)₃·7H₂O) used as a ferrous ion source, was supplied by Prolabo. Anhydrous Sodium Sulfate (Na₂SO₄) used as an inert supporting electrolyte, was purchased from Acros organics. Tetramethylammonium hydroxide (TMAH in water), a derivatisation product, was acquired from Sigma Aldrich. Acetonitrile (HPLC grade) was obtained from Sigma-Aldrich, sulfuric acid (H₂SO₄) from Merck. All the other chemicals were analytically graded from Prolabo and Sigma-Aldrich.

B. Electrochemical system

Experiments, at room temperature, were performed with an open, undivided and cylindrical cell containing a 250mL solution. The carbon felt piece (Carbone Lorraine RVG 4000 Mersen, Paris La Défense, France) was used as a cathode. It was placed on the inner wall of the cell covering the totality of the inner perimeter. The anode is a platinum electrode (Radiometer) or a BDD thin film, having the same surface area (5 cm²), placed on the centre of the cell. The initial pH of the solutions, measured with a Mettler Toledo EL20 pH-meter, was adjusted to 3 by Sulphuric Acid. Prior to the electrolysis, a moderate compressed air is bubbled for 10 min through the cell to saturate the solution, which was agitated continuously by a magnetic stirrer. Fe₂(SO₄)₃·7H₂O is introduced to the cell just before the beginning of the electrolysis. Electrolyses were carried out under current controlled conditions. The current was kept at the desired level with an Amel 2053 potentialstat-galvanostat and samples were withdrawn at regular electrolysis times. The ionic strength was maintained constant by additions of 50 mM Na₂SO₄.

C. Analytical methods

The evolution of BPS concentration was detected using Thermo Separation Products (TSP) High Performance Liquid Chromatography (HPLC) using Spectra system (P1000), equipped with an isocratic pump and UV/Visible detector model Spectra series UV100, fitted with reversed phase C-18 analytical column (Agilent, 5 μm; 4.6 mm × 250 mm). The detection of BPS was carried out at 258 nm. The mobile phase was a mixture of water-acetonitrile (70:30, V/V). It was eluted at a flow rate of 1 mL.min⁻¹. The injection volume was 20 μL. Generated aliphatic carboxylic acids were also identified and quantified by the same HPLC.

TABLE 1. Physicochemical properties of Bisphenol S

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₁₂H₁₀O₄S</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>250.27</td>
</tr>
<tr>
<td>Solubility (g/L)</td>
<td>1.1</td>
</tr>
<tr>
<td>λₘ₃₆ (nm)</td>
<td>258</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.37</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>240 – 248</td>
</tr>
</tbody>
</table>
**III. RESULTS AND DISCUSSION**

**A. Effect of experimental parameters on the BDD degradation**

1) **Effect of the current density on the BPS degradation**

Applied current density is the ratio between the applied current and the surface of the working electrode. It is considered as a key variable parameter for Electrochemical advanced oxidation processes. In order to investigate the effect of this parameter on the degradation of BPS by Electro-Fenton process, several experiments were performed on 10 mg L\(^{-1}\) BPS solution of pH 3 at different current density values, in range of 20 to 80 mA/cm\(^2\), in the presence of 0.2 mM of Fe\(^{2+}\) as a catalyst and 50 mM Na\(_2\)SO\(_4\) as an inert support electrolyte.

Fig. 2 shows that the concentration of BPS decreased exponentially. A very quick drop of BPS concentration for different values of \(j\) over than 20 mA/cm\(^2\) can also be seen. For the EF-Pt treatment (Fig. 2 (a)), the BPS was completely removed at 30, 35 and 40 min for 60, 80 and 40 mA/cm\(^2\), respectively. For the EF-BDD treatment (Fig. 2 (b)) and the same values of \(j\), molecules were eliminated at shorter time of 15, 20 and 25 min. Thus, the BPS degradation kinetic was enhanced by increasing the applied current density. This effect could be explained by increasing the formation rate of the Fenton reagent H\(_2\)O\(_2\) and Fe\(^{2+}\), leading to the generation of a higher amount of •OH from Fenton’s reaction (1).

The BPS degradation kinetic was also enhanced by using a BDD anode. This phenomenon can be explained by the very high O\(_2\) evolution overpotential of BDD electrode (1.27 V) vs. Pt one (0.27 V) since the oxidative action of M(•OH) is rather ineffective for classical electrodes such as Pt but much more efficient for a high O\(_2\) overpotential anode such as BDD [23,24]. Besides having a larger amount of BDD(•OH) generated on the electrodes surface, another advantage of this electrode is that the •OH are physisorbed and thus are labile and more reactive in contrast to Pt one where they are chemisorbed [25] thus relatively strongly attached to the surface and less reactive [26].

It should be noted that for the EF-Pt treatment, the decay of the kinetic curves being closed between 60 and 80 mA/cm\(^2\), and further increase in applied current density do not contribute in any enhancement in degradation rates of BPS. The efficiency of Electro-Fenton is less at higher current density. This is due to the competitive electrode reactions in the electrolytic cell. The discharge of oxygen at the anode (5) and the evolution of hydrogen at the cathode (6) occur at a higher current. These reactions inhibit main reactions such as (7) and (3) [27], which lead to a decrease in the efficiency of the Electro-Fenton [28].

\[
2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{O}_2 + 4 \text{e}^- \quad (5)
\]

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (6)
\]

\[
\text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H}^+ + \text{e}^- \quad (7)
\]

BPS oxidation can be described by a pseudo-first order reaction kinetic, because the concentration of BPS decreased exponentially (Fig. 2). In addition, the inset of the (Fig. 2) highlights the linear correlations obtained for different values of the current density \((R^2 > 0.98)\) of the kinetic analysis. Apparent rate constants for oxidative degradation of BPS, obtained from the slope of the curve of \(\ln (\frac{C_f}{C}) = f (t)\) (Fig. 2), are reported in Table 2. According to the apparent rate constants values given in Table 2, the current density value of 80 mA/cm\(^2\) is the optimal value to degrade BPS by EF-BDD treatment in 15 min with \(k_{app} = 0.316 \text{ min}^{-1}\).

![Degradation Kinetics of BPS by Electro-Fenton process at several current density values (Experimental conditions of Fig. 2)](image)

**TABLE 2. Apparent rate constants of BPS oxidation by Electro-Fenton process (Experimental conditions of Fig. 2)**

<table>
<thead>
<tr>
<th>(J) (mA/cm²)</th>
<th>(k_{app}) (min⁻¹)</th>
<th>(R^2)</th>
<th>(k_{app}) (min⁻¹)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.025</td>
<td>0.99</td>
<td>0.025</td>
<td>0.98</td>
</tr>
<tr>
<td>40</td>
<td>0.111</td>
<td>0.98</td>
<td>0.171</td>
<td>0.99</td>
</tr>
<tr>
<td>60</td>
<td>0.124</td>
<td>0.99</td>
<td>0.228</td>
<td>0.98</td>
</tr>
<tr>
<td>80</td>
<td>0.122</td>
<td>0.99</td>
<td>0.316</td>
<td>0.99</td>
</tr>
</tbody>
</table>
2) Effect of Fe$^{3+}$ concentration

The effect of Fe$^{3+}$ concentration as catalyst on the Electro-Fenton degradation of BPS, using a BDD or Pt anode, was studied in the presence of different initial Fe$^{3+}$ concentrations at a constant Bisphenol S concentration of 10 mg L$^{-1}$ applying a constant current of 200 mA. Fig. 3 shows that the degradation of BPS is significantly affected by the concentration of Fe$^{3+}$ for both of the anodes. The degradation rate increased with decreasing Fe$^{3+}$ concentration from 1 to 0.1 mM, and Electro-Fenton process seems to be more efficient with a low concentration of 0.1 mM of Fe$^{3+}$.

For the EF-Pt treatment, complete degradation can be seen only for the initial Fe$^{3+}$ concentration less than 0.2 mM. Degradation needs more time for a complete removal of the molecule for the initial concentration of the catalyst up to 0.5 mM, and the degradation efficiency of BPS reached only a maximum value of 52 % and 90 % for 1 and 0.5 mM respectively for 40 minutes of electrolysis.

For EF-BDD treatment, a fast and complete degradation of BPS can be seen varying initial Fe$^{3+}$ concentrations from 0.1 to 0.5 mM within 25 to 40 min. However,\fig{3} For 1 mM initial concentration of catalyst, after 40 minutes, the degradation efficiency of BPS enhanced using BDD anode and reached 76 %.

![Fig. 3](image)

Fig. 3. Influence of Fe$^{3+}$ concentration on the degradation Kinetics of BPS by Electro-Fenton process using (a) Pt anode and (b) BDD anode. [Fe$^{3+}$ (mM): I ( ) 1; ( ) 0.5; ( ) 0.2; (x) 0.1, [BPS]s = 0.04mM, pH = 3, [Na$_2$SO$_4$] = 50mM, I = 200mA.

Thus, the removal efficiency declined with the higher Fe$^{3+}$ concentration for both of the anodes. This negative effect of the higher catalyst concentration on degradation kinetics can be related to the increase of the rate of parasitic reaction (8) which is strongly accelerated when much larger amounts of Fe$^{3+}$ are formed from reaction 3 as more Fe$^{3+}$ is added to the starting solution [21].

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^-$$  \hspace{1cm} (8)

3) Effect of supporting electrolyte type

The type of the supporting electrolyte is also an important parameter in the Electro-Fenton process. Indeed, the addition of an electrolyte in a solution can influence the treatment since it modifies the conductivity of the solution, facilitates the passage of the electrical current, and reduces the energy cost of the process. The effect of supporting electrolytes such as NaCl, Na$_2$SO$_4$ and NaNO$_3$ on BPS oxidation at BDD and Pt studied at a BPS concentration of 0.04 mM and applied current density of 40 mA cm$^{-2}$ and the results are shown in Fig. 4. It can be seen, from the kinetic curves of BPS degradation obtained with Pt and BDD anode, complete degradation of the organic matter was achieved in the presence of NaCl and Na$_2$SO$_4$ as a supporting electrolyte. However, the presence of NaNO$_3$ did not accelerate the removal of BPS and the performance of both anodes in this case was weak. This behavior can be explained by the fact that NO$^+$ is a strong oxidant (0.8 V/ESH) at pH 3, so it competes with the chemisorbed O$_2$ for the adsorbed atomic H; suppressing H$_2$O$_2$ production and BPS degradation [29].

Using a Pt anode (Fig 4 (a)), in the presence of Na$_2$SO$_4$ as a supporting electrolyte, the BPS removal occurred slowly, reaching 100 % degradation after 40 minutes of electrolysis. BPS degradation is dramatically enhanced in the presence of NaCl, and achieved after 28 minutes. This behavior can be explained by the fact that Na$_2$SO$_4$ is a stable electrolyte, while chloride ions can be oxidized at the anode surface to active chlorine according to the following equation [21]:

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$$  \hspace{1cm} (9)

The electrogenerated active chlorine can act as an oxidation mediator in the bulk of the solution and a parallel degradation reaction in the solution takes place, accelerating the reaction rate.

Using a BDD anode, (Fig. 4 (b)), the removal of BPS decreased when NaCl was used as a supporting electrolyte instead of Na$_2$SO$_4$. It can be explained by the fact that during electrolysis with the BDD anode, which has a high O$_2$ evolution overpotential, persulfates ions are known to be very powerful oxidants (E$^\circ$ = 2.01 V), and sulfate radicals are generated in situ according to the following equations:

$$2\text{SO}_4^{2-} \rightarrow S_2\text{O}_8^{2-} + 2\text{e}^-$$  \hspace{1cm} (10)

$$\text{OH}^- + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{2-} + \text{OH}^-$$  \hspace{1cm} (11)

$$\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow S_2\text{O}_8^{2-}$$  \hspace{1cm} (12)
The oxidants are either consumed for the degradation of the BPS molecule or coupled with a water molecule to form peroxomonosulfuric acid (H$_2$SO$_5$) which in turn can produce H$_2$O$_2$ [30, 31].

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4$$  \hspace{.5cm} (13)

### B. Determination of the apparent and absolute rate constants

Since hydroxyl radicals are non-selective, have high reactivity towards organic compounds, possess a very short life span of a few nanoseconds, and do not accumulate in the solution, the quasi-stationary state can be applied to their concentration, and the oxidation reaction of organic compounds by •OH can be considered as a pseudo-first-order reaction. Therefore, the following equation can be written:

$$-\frac{d[BPS]}{dt} = k_{BPS} [OH^*][BPS] = k_{app} [BPS]$$ \hspace{.5cm} (14)

Where $k_{BPS}$ is the absolute rate constant and $k_{app}$ the apparent rate constant.

In order to evaluate the reaction rate constant of the BPS degradation by hydroxyl radicals, the competition kinetics method was used choosing benzoic acid (BA) as a standard competitor. The literature value of the absolute rate constant of BA with the hydroxyl radical is $4.3 \times 10^9$ M$^{-1}$ s$^{-1}$. Electrolyses of a mixture of BPS and BA at equimolar concentrations were carried out with the two anodes. The degradation of BPS was studied under optimal conditions determined above for each anode (Fig. 5). The absolute rate constant for BPS can be deduced as follows:

$$k_{BPS} = \frac{k_{app, BPS}}{k_{app, BA}} k_{BA}$$ \hspace{.5cm} (15)

Using the pseudo-first order model, the constant apparent rates of BA and BPS were calculated by linear regression (inset of Fig. 5). For the Pt and BDD anode, the BPS $k_{app}$ values of 0.135 and 0.316 min$^{-1}$ were obtained respectively and the Benzoic acid $K_{app}$ values (data not shown) were 0.261 and 0.315 min$^{-1}$. The value of the constant absolute rate of BPS hydroxylation was $4.31 \times 10^9$ M$^{-1}$ s$^{-1}$ for the BDD anode and was $2.22 \times 10^9$ M$^{-1}$ s$^{-1}$ for the Pt anode.

### C. Identification of by-products during the oxidative degradation of BPS

During the Electro-Fenton treatment, the oxidation reactions produced intermediates, identified in two stages: identification of aromatics and carboxylic acids. The first one included identification of primary aromatic intermediates formed during the oxidation of BPS by GC-MS analysis. The GC-MS spectrums showed the formation only of two intermediates species: Butanol (t$_R$=8.4 min) and (4-hydroxyphenyl)(5-Oxocyclohex-1,3-diene) sulfonylphenol which was the most abundant intermediate detected at t$_R$=10.3 min. This finding evidences that other potential aromatic intermediates are always oxidized at the same rate as formed, without being accumulated in the solution, and they rapidly undergo oxidative ring opening reactions [32].
Thereafter, acetic and maleic acids disappeared within 6 hours. Although, oxalic acid decreased weakly with the electrolysis time and remained present even at the end of the treatment. This is due to the presence of stable Ferric-oxalate complexes formed in the bulk, which are persistent and slowly destroyed by hydroxyl radicals [33–35].

IV. CONCLUSION

The Electro-Fenton process is a very efficient method for the effective removal of BPS from an aqueous medium. Based on the above experiments, it was evident that the efficiency of the Electro-Fenton process depends mainly on the anode material used in the electrolysis. In fact, in optimum experimental conditions, a complete degradation was realized on the BDD anode in a short time due to the high oxidation power of the hydroxyl radicals that were electrogenerated and weakly adsorbed at its surface. However, the degradation processes became much slower using the Pt.

The oxidation of BPS by hydroxyl radicals was found to obey pseudo-first-order kinetics, and the absolute rate constant using the BDD and the Pt anode was determined by the competition kinetic method and found to be $4.31 \times 10^5$ M$^{-1}$ s$^{-1}$ and $2.22 \times 10^4$ M$^{-1}$ s$^{-1}$ respectively.

The identification, using HPLC and GC-MS, of aromatic oxidation products and short-chain carboxylic acids during the treatment, confirmed the effectiveness of Electro-Fenton process to remove BPS from water.

REFERENCES

9. J. Richard, A. Baurers, C. Vom Eyser, K. Bester, J. Tuerk, “Toxicity of the micropollutants Bisphenol A, Ciprofloxacin, Metoprolol and Sulamethoxazole in water samples before and after the oxidative process, confirmed the effectiveness of Electro-Fenton process to remove BPS from water.


