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

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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 2.22×10^9 M^{-1} s^{-1} for Pt anode and 4.31×10^9 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].
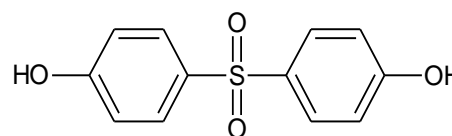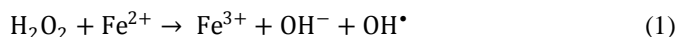

Fig. 1. The molecular structure of Bisphenol S (BPS)

In Electro-Fenton process, the source of hydroxyl radical (•OH) is the Fenton reaction (1) in which Fenton reagent is produced electrochemically and regenerated in situ.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

O_2 or air gas is injected into either the reaction medium or directly at the cathode to generate H_2O_2 via reaction (2).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

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

H_2O_2 is produced continuously at the carbonaceous cathodes as carbon felt that can provide high yield. Small quantities of Fe^{2+} are usually added to form Fe^{3+} (3) to enhance the zing power of electro-generated H_2O_2.

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].

$$M + H_2O \rightarrow M(OH^\bullet) + H^+ + e^- \qquad (4)$$
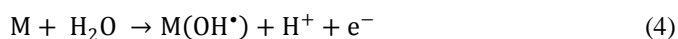
In the present work, we have undertaken a study on BPS degradation by the Electro-Fenton process in aqueous medium. The experiments are carried out in an undivided cell using Pt or BDD as anodes and commercial graphite felt as cathode. Initially, we investigated the effects of some operating parameters on the removal rate such as current density, catalyst dose and nature of supporting electrolyte. The decay kinetics of BPS was investigated and the absolute rate constant of the reaction between •OH and BPS was determined by using competition kinetics method. Aromatic intermediates were identified by gas chromatography-mass spectrometry (GC–MS). Carboxylic acids were also identified and quantified by HPLC.

II. MATERIALS AND METHODS

A. Chemicals

4,4'-dihydroxydiphenyl sulfone (BPS, purity 98%) was purchased from Sigma–Aldrich. Table 1 summarizes the major physicochemical properties of BPS.

TABLE 1. Physicochemical properties of Bisphenol S

Parameter	Range
Molecular formula	$C_{12}H_{10}O_4S$
Molecular weight (g/mol)	250.27
Solubility (g/L)	1.1
λ_{max} (nm)	258
Density (g/cm^3)	1.37
Melting point (°C)	240 – 248

Iron heptahydrated sulfate ($Fe_2(SO_4)_3 \cdot 7H_2O$) used as a ferrous ion source, was supplied by Prolabo. Anhydrous Sodium Sulfate (Na_2SO_4) 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 (H_2SO_4) 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 internal perimeter. The anode is a platinum electrode (Radiometer) or a BDD thin film, having the same surface (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. $Fe_2(SO_4)_3 \cdot 7H_2O$ 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 potentiostat-galvanostat and samples were withdrawn at regular electrolysis times. The ionic strength was maintained constant by additions of 50 mM Na_2SO_4.

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 at room temperature. The detection was performed at 210 nm with a mobile phase of 4 mM H_2SO_4 at a flow rate of 1 mL.min^{-1}.

Intermediates of Electro-Fenton treatment of BPS were directly deduced from mass spectra obtained from GC-MS applications. Sample preparation for GC-MS analysis consisted of dissolving 4 mL of the BPS solution treated in 2 mL of methanol. Prior to the measurement, 10 μL of (0.25 M) TMAH (10% water) was added to 100 μL of the BPS derivatives. The mixture was allowed to stand for 1 h prior to analysis. The analyses were performed with a 6890 Agilent gas chromatograph. The flow rate was 1.9 mL/min. The temperature of the oven program of the gas chromatograph started at 100 °C with increments of 15 °C/min immediately up to 320 °C. This temperature was kept for 5 min. For mass spectral detection, a MS 5973 was used. The Selective Ion Mode (SIM) of the mass spectrometer was applied for the quantification of BPS [22].

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/cm², in the presence of 0.2 mM of Fe^{2+} as a catalyst and 50 mM Na_2SO_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/cm² 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/cm², 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_2O_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/cm², 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].

$$2H_2O \rightarrow 2H^+ + O_2 + 4\ e^- \tag{5}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{6}$$

$$H_2O \rightarrow OH^\bullet + H^+ + e^- \tag{7}$$

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 (C_0/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/cm² is the optimal value to degrade BPS by EF-BDD treatment in 15 min with k_{app} of 0.316 min^{-1}.
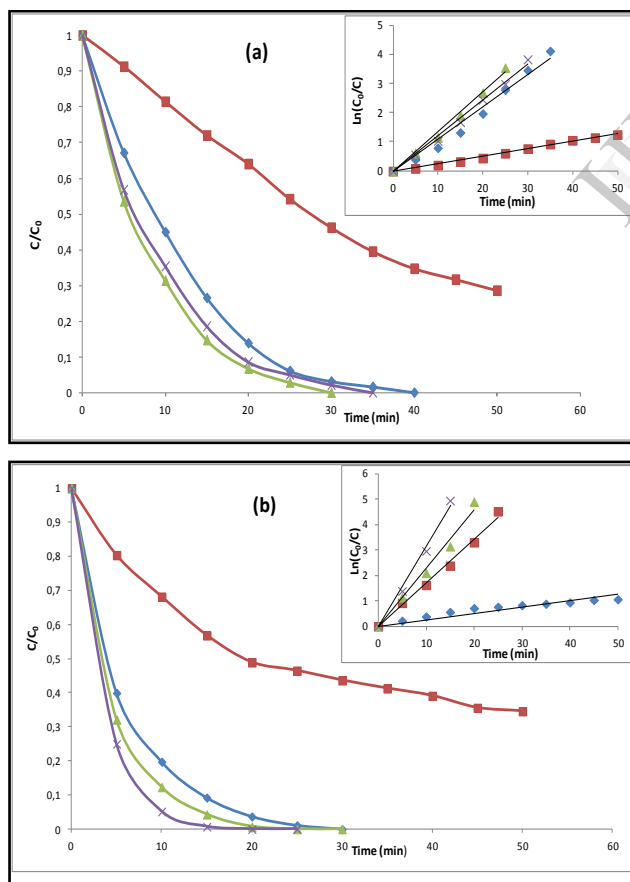

Fig. 2. Degradation Kinetics of BPS by Electro-Fenton process at several current density values using (a) Pt anode and (b) BDD anode. Current density (mA/cm²): (■) 20; (♦) 40; (▲) 60, (x) 80. [BPS]$_0$ = 0.04 mM, pH = 3, [Fe^{3+}] = 0.2 mM, [Na$_2$SO$_4$] = 50 mM

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

J (mA/cm²)	Pt		BDD	
	K_{app} (min^{-1})	R^2	K_{app} (min^{-1})	R^2
20	0.025	0.99	0.025	0.98
40	0.111	0.98	0.171	0.99
60	0.124	0.99	0.228	0.98
80	0.122	0.99	0.316	0.99

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, for 1 mM initial concentration of catalyst, after 40 minutes, the degradation efficiency of BPS enhanced using BDD anode and reached 76 %.
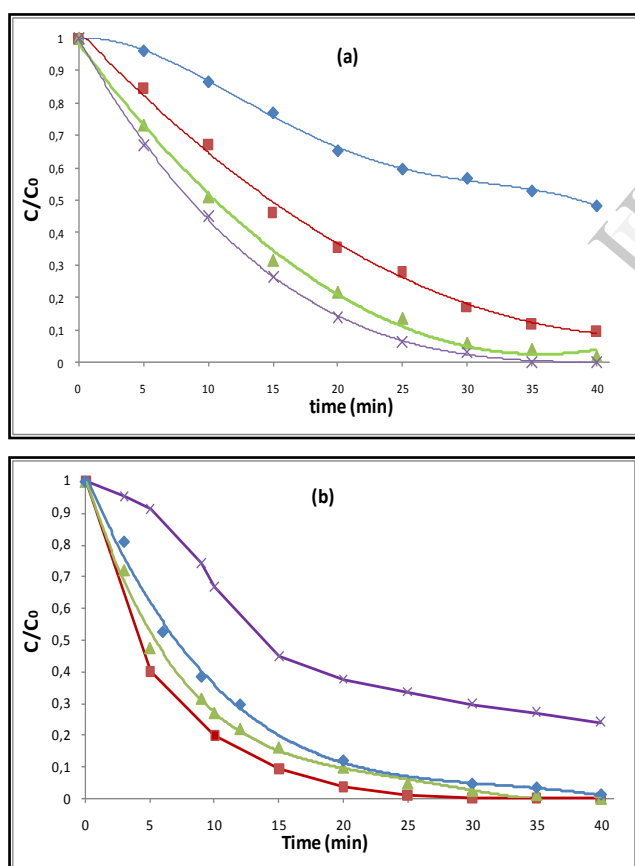

Fig. 3. Influence of Fe^{3+} concentration on the degradation Kinetics of BPS by Electro-Fenton process using (a) Pt anode and (b) BDD anode. [Fe^{3+}] (mM) : (◆) 1; (■) 0.5; (▲) 0.2, (x) 0.1. [BPS]$_0$ = 0.04mM, pH = 3, [Na$_2$SO$_4$] = 50mM, I = 200mA.

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^{2+} are formed from reaction 3 as more Fe^{3+} is added to the starting solution [21].

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{8}$$

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_2SO_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_2SO_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^{3-} 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_2O_2 production and BPS degradation [29].

Using a Pt anode (Fig 4 (a)), in the presence of Na_2SO_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_2SO_4 is a stable electrolyte, while chloride ions can be oxidized at the anode surface to active chlorine according to the following equation [21]:

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-} \tag{9}$$

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_2SO_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° = 2.01 V), and sulfate radicals are generated in situ according to the following equations:

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^{-} \tag{10}$$

$$OH^{\bullet} + SO_4^{2-} \rightarrow SO_4^{-\bullet} + OH^{-} \tag{11}$$

$$SO_4^{-\bullet} + SO_4^{-\bullet} \rightarrow S_2O_8^{2-} \tag{12}$$

Fig. 5. Normalized concentration decay of BPS with electrolysis time during Electro-Fenton treatment using (x) Pt anode and (◆) BDD anode. Inset: corresponding kinetic analysis.
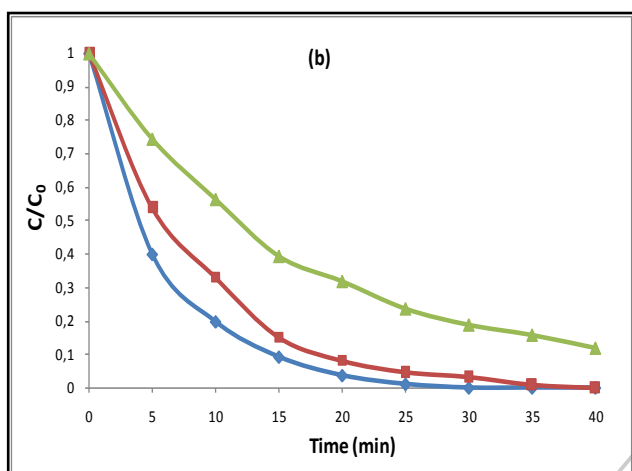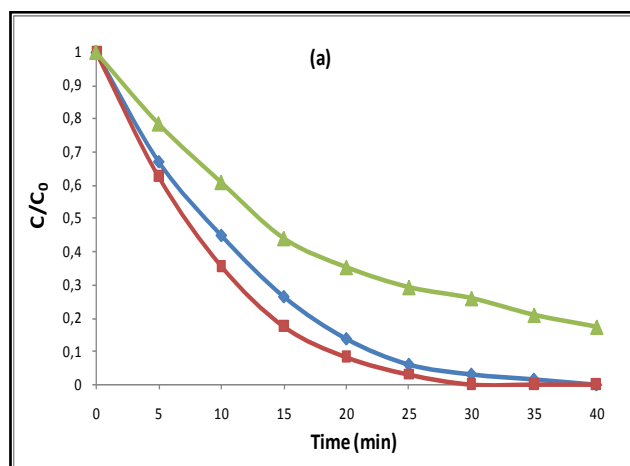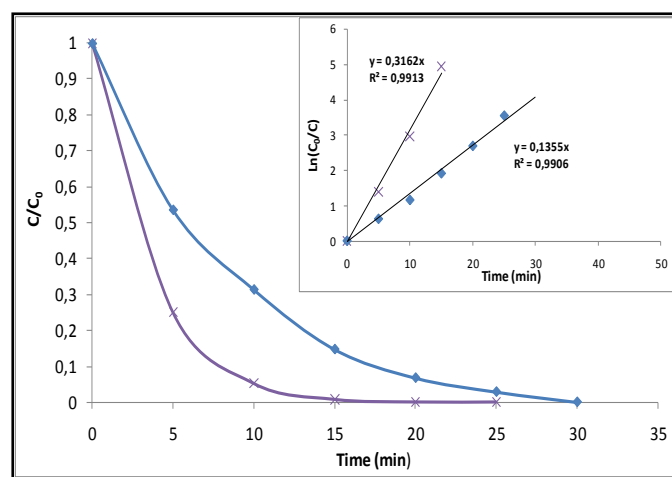
Fig. 4. Influence of electrolyte support on the degradation Kinetics of BPS by Electro-Fenton process using (a) Pt anode and (b) BDD anode. Electrolyte support: (■) NaCl; (◆) Na_2SO_4; (▲) $NaNO_3$. $[BPS]_0 = 0.04$ mM, pH = 3, [electrolyte support] = 50 mM, I = 200 mA

The oxidants are either consumed for the degradation of the BPS molecule or coupled with a water molecule to form peroxomonosulfuric acid (H_2SO_5) which in turn can produce H_2O_2 [30, 31].

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \qquad (13)$$

B. Determination of the apparent and absolute rate constants

Since hydroxyl radicals are non-selective, have high reactivity towards organic compounds, posses 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:

$$-\frac{d[BPS]}{dt} = k_{BPS}[OH^\bullet][BPS] = k_{app}[BPS] \qquad (14)$$

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 4.3×10^9 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:
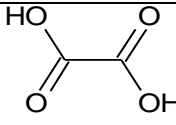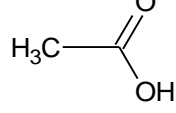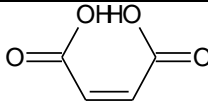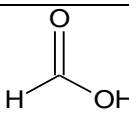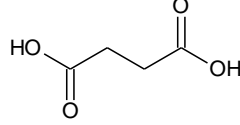
$$k_{BPS} = \frac{k_{app\ BPS}}{k_{app\ BA}}\ k_{BA} \qquad (15)$$

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 4.31×10^9 M^{-1} s^{-1} for the BDD anode and was 2.22×10^9 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].

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TABLE 3. The detected carboxylic acids during the degradation of BPS by Electro-Fenton process using Pt anode.

Carboxylic acid	Chemical structure
Oxalic acid	
Acetic acid	
Maleic acid	
Formic acid	
Succinic acid	

In the second stage, aromatic intermediates were oxidized in their turn to the formation of short-chain carboxylic acids before complete mineralization. In order to identify and follow the evolution of the carboxylic acids generated during BPS removal by the Electro-Fenton process, a 0.04 mM BPS aqueous solution was treated. The carboxylic acids detected are presented in table 4. Oxalic, Acetic and maleic acids were identified at significant concentration and their evolutions are presented in Fig. 6, while succinic and formic acids were detected at a low concentration.

As can be seen in Fig. 6, Oxalic, Acetic and Maleic acids are generated as soon as the electrolysis is started, reaching their maximum concentrations after 3 to 4 h of treatment
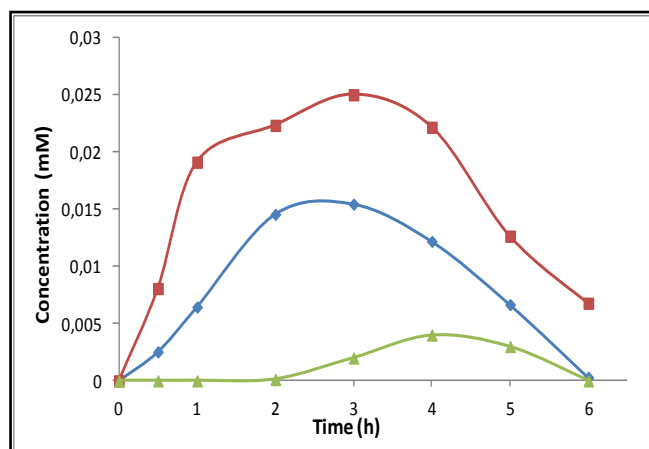

Fig.6. Evolution of carboxylic acids during the Electro-Fenton treatment of BPS aqueous solution

$[BPS]_0 = 0.04$ mM, pH = 3, I = 300 mA, $[Fe^{3+}] = 0.1$ mM, V = 205 mL.

(■) Oxalic acid, (◆) Acetic Acid and (▲) Maleic acid.

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 4.31×10^9 M^{-1} s^{-1} and 2.22×10^9 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.

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