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Electrochemical Degradation of Sodium Dodecylbenzene Sulfonate on Boron Doped Diamond and Lead Dioxide Anodes

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Abstract: *In view to carry out a global treatment of used emulsions like that contained in effluents from metallurgic industries, the surfactant behaviour should be known. This paper reports a study of the electrochemical degradation of sodium dodecylbenzenesulfonate (SDBS), a quite common surfactant, encountered in effluents from metal industries. Electrochemical oxidation of solutions containing SDBS at initial concentrations of 25 and 250 ppm was performed in an electrolytic flow cell without separator. A comparison of the performance of PbO₂ and BDD used as anodes in the same electrolysis cell are presented. Today PbO₂ is a material commercially available, while BDD, not yet accessible at large scale is presented as a good candidate for electrochemical treatment of waste waters polluted by organics. Electrolyses monitored by Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and Liquid Chromatography (HPLC) measurements, have shown that BDD is more efficient than PbO₂ for the same operating conditions. The study, focused on the BDD electrode in neutral or acidic media, under different current densities, have shown that SDBS is cut into small carboxylic acids (maleic, oxalic and formic acids), and that the aliphatic chain is attacked before the aromatic ring.*

Keywords: electrooxidation, wastewater treatment, anionic surfactant, boron-doped diamond anode, lead dioxide anode

1. INTRODUCTION

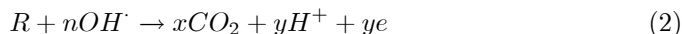
Many wastewaters produced in industrial processes contain organic contaminants. The most important method well established and relatively cheap to decrease the chemical oxygen demand (COD) of wastewaters is based on biological treatment. But, unfortunately, certain substances responsible for COD are not easily biodegradable; other substances which are toxic can inactivate the microorganisms which slow down biological processes. Other methods for COD removal are hence required in the presence of refractory and/or toxic compounds.

Physicochemical methods involving wet chemical oxidation by O₂ (high pressure, high temperature), or hydrogen peroxide (in the presence of catalyst) have given rise to efficient processes, however these technologies are quite expensive. Electrochemistry is an alternative technique which has important advantages. Using only electron as reactant, direct degradation of organics into carbon dioxide and water can be achieved via the electrogenerated hy-

droxyl radicals [1]. This radical is very active in aqueous media in the degradation of organic molecules because of its high redox potential ($E_{\text{OH}^\bullet/\text{H}_2\text{O}}^\circ = 2.41 \text{ V / SHE}$) [2, 3]. Hydroxyl radicals are produced, in the anodic reaction, directly from water according to Equation (1):



The electrochemical oxidation of organics to CO₂ occurs with a significant rate in the potential region of oxygen evolution. The general mechanism of electrochemical incineration is as follow:



Among materials which have been suggested to destroy organics in aqueous effluents, let us quote traditional electrodes like graphite, tin dioxide [4, 5] or lead dioxide [6], but also the recently developed synthetic boron-doped diamond electrodes [1, 7, 8]. However, in view of practical application, the choice of the anodic material having the required catalytic properties is not easy to do. The electrochemical activity and the service life of the electrode

are the main properties having to be considered. Lead dioxide electrodes are commercially available today [9]. This material is efficient to generate hydroxyl radicals for the complete mineralization of organic substances [6, 10-12]. Among new materials, boron doped diamond (BDD) has very interesting electrochemical properties: its electrochemical window is about 3 V for a 1 mol L⁻¹ sulphuric acid solution and its chemical resistance in acid and caustic media is very high [7, 13]. Moreover, BDD is known to have weak adsorption properties; this means low interactions between the electrode surface and both the reactant H₂O and the product OH° (Eq. 1). This material acts mainly via outer sphere reactions and water discharge [1, 14]. In the case of the outer sphere reaction, reactant and product do not interact strongly with the electrode surface while for water discharge hydroxyl radicals formed are considered to be involved in the oxidation of organics in aqueous solutions. The weak interaction of OH radicals with BDD leads to high chemical reaction rate with organic substrates and slow oxygen evolution (high oxygen overvoltage).

Many effluents rejected by metallurgic industries are formed of emulsions containing water, surfactants and lubricants. In view to avoid any reject of polluted water and, better, to recycle the process water, electrochemistry could offer an interesting option. This technique was used by Leu *et al.* [15] to treat surfactant wastewater by electrooxidation of sodium chloride, to produce hypochloric acid, coupled with chemical coagulation. The surfactant removal was increased by addition of hydrogen peroxide producing the Fenton reaction which is efficient in pollution abatement. Lissens *et al.* [16] have studied the electrochemical degradation of cationic and anionic surfactants at carbon-based electrodes. During electrolysis, graphite and carbon felt suffered from abrasion, leading to additional carbon loading of the surfactant solutions. A BDD anode was tested in their study; the TOC removal was higher than obtained with an equal surface of plate graphite. More recently, Panizza *et al.* [17] investigated the degradation of anionic surfactants by galvanostatic electrolysis using Ti-Ru-Sn ternary oxide (on a Ti substrate) and a BDD anode. Using the ternary oxide the complete removal of COD in a solution containing SDBS was obtained only in the presence of chloride anions that act as mediators, while in the case of BDD the total mineralization of SDBS was achieved without chloride; the authors concluded that the process was under mass transfer control. Based on COD measurements, the comparison of the two electrode materials, each under its optimum experimental conditions, showed that faster SDBS mineralization was achieved at the Ti-Ru-Sn oxide anode.

This paper reports a study of the electrochemical degradation of sodium dodecylbenzenesulfonate, a quite common surfactant. Oxidation experiments on SDBS were carried out with a commercially available PbO₂ electrode. A boron-doped diamond anode was tested under the same conditions. A comparison of the performance of each elec-

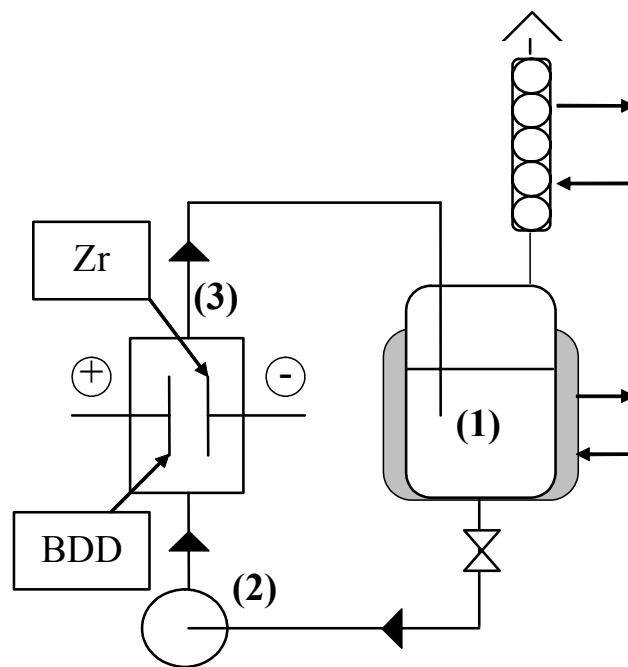


Figure 1. Discontinuous process with a single compartment electrochemical reactor, (1): 1 L tank, (2): centrifugal pump and (3): electrochemical cell.

trode was carried out, and the influence of current density on the efficiency was determined. Though BDD anodes have not yet reached the point of a large industrial scale production [18]; it looks interesting to compare these electrodes, without the presence of any mediator.

2. EXPERIMENTAL

2.1. Electrochemical measurement

Cyclic voltammograms were carried out in a conventional three-electrode cell (30 cm³) using a computer controlled Autolab potentiostat Model 30. Boron doped diamond (0.196 cm²) and lead dioxide (0.600 cm²) were used as working electrode, Pt as counter electrode and Hg/Hg₂Cl₂, Cl⁻ (sat) as the reference electrode.

At first, the electrode was treated under galvanostatic conditions into a molar sulphuric acid solution. Then several scans were successively realized in the SDBS solution on the BDD anode from -1.0 V to 2.2 V vs. SCE, at 50 mV s⁻¹. The limit potential of 2.2 V vs. SCE in oxidation was chosen to avoid oxygen evolution during curve plot. For PbO₂ anode, the reduction potential of PbO₂ must be taken into account (1.2 V vs. SCE); thus, scans were realized in the following potential range: 1.2 V to 2.2 V vs. SCE.

2.2. Electrolysis and electrode materials

Electrolyses were performed in a one compartment electrolytic flow cell under galvanostatic conditions (Fig. 1). Diamond and lead dioxide were used as anodes and zir-

conium as cathode. All electrodes were disks (90 mm diameter) with a geometric area of 63 cm² each. The inter-electrode gap was 10 mm. The solution was stored in a one litre thermoregulated glass reservoir (1) and circulated through the electrolytic cell using a centrifugal pump (2). The flow rate in the electrochemical cell was kept constant during each experiment (42 or 200 L h⁻¹). The range of current density values used was 0.63 – 40 mA cm⁻².

Sodium dodecylbenzenesulfonate (C₁₈H₂₉SO₃Na or SDBS) was used as surfactant model. This anionic surfactant (M = 348.48 g mol⁻¹) is a 12 carbons aliphatic chain with a benzenesulfonate group grafted on to the third carbon. It was supplied by Fluka (80% purity); the remaining 20% are similar alkylbenzenesulfonate compounds with different lengths of aliphatic chains for which one can consider that electrochemical properties are similar. For bulk electrolyses, two different concentrations of SDBS were used 6.15 × 10⁻⁵ and 6.15 × 10⁻⁴ mol L⁻¹ corresponding to 25 and 250 mg L⁻¹ (135 mg L⁻¹ for TOC and 430 mg L⁻¹ for COD in the case of the 6.15 × 10⁻⁴ mol L⁻¹ SDBS solution). The electrolyte used was Na₂SO₄ (Prolabo, Normapur, 99.5% purity) at various concentrations (0.01 to 0.1 mol L⁻¹) and the pH was adjusted with H₂SO₄ (Prolabo, Normapur, 95% purity).

Boron-doped diamond films, Diachem[®], were synthesized by the hot filament chemical vapor deposition technique (HF CVD) on conducting p-Si substrate (0.1 Ωcm, Siltronix). The filament temperature ranged from 2440 to 2560°C and the substrate one was kept at 830°C. The reactive gas used was methane in an excess of dihydrogen (1% CH₄ in H₂). The doping gas was trimethylboron at a concentration of 3 ppm. The gas mixture was supplied to the reaction chamber, providing a 0.24 μm h⁻¹ growth rate for the diamond layer. The diamond films were about 1 μm thick. This HF CVD process produces columnar, randomly textured, polycrystalline films [19].

The anode of lead dioxide was supplied by De Nora (Italy). This electrode was formed by a 1 mm thick coating of PbO₂ deposited on a titanium disk. The material formulation was given by Ueda *et al.* [9].

2.3. Analytical procedures

Electrolyses were followed by Total Organic Carbon (TOC) measurements. TOC analysis was carried out by means of a Shimadzu TOC-VSCN total organic carbon analyzer. The Chemical Oxygen Demand (COD) was determined by common photometric tests using COD test tubes and photometer Dr Lange Lasa 50 system.

In case of incomplete mineralization, aliphatic acids (maleic, oxalic and formic) were obtained. Concentrations of MA, OA and FA were quantified by liquid chromatography (HP series 1100). The column used was Supelcogel C-610H in presence of 0.1% phosphoric acid, and detection was made at 210 nm.

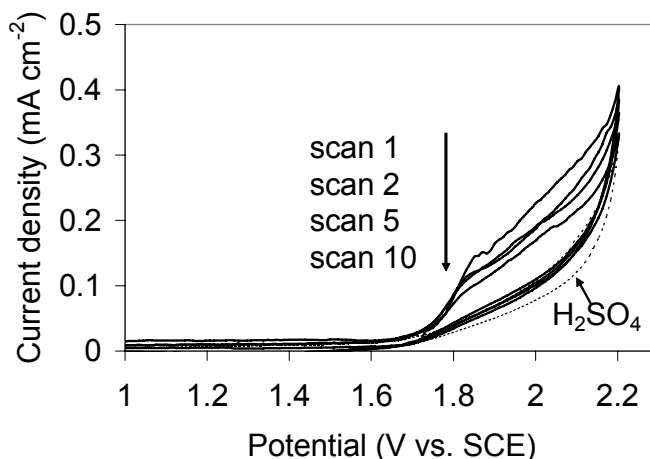


Figure 2. Cyclic voltammograms on BDD electrode (area = 19.6 mm²), scan rate = 50 mV s⁻¹, T = 20°C. Dotted lines: H₂SO₄ 1 M. Continuous lines [SDBS] = 0.3 mM in 1 M H₂SO₄; consecutive scans 1, 2, 5 and 10.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

The cyclic voltammograms (Fig. 2) were obtained at a scan rate of 50 mV s⁻¹ in the potential region between 1 and 2.2 V vs. SCE in a sulphuric acid solution (1 M) with and without sodium dodecylbenzenesulfonate (0.3 mM). Current density, for potentials above 1.7 V, was higher for a solution containing SDBS than without it. This difference is due to SDBS oxidation which appears clearly as an irreversible phenomenon occurring just before the potential region of water discharge (the production of hydroxyl radicals starts theoretically around 2.15 V / SCE).

The decrease of the current density after several cycles (scans 1, 2, 5 and 10, Fig. 2) highlights the modification of the electrode surface. It suggests that during the successive scans, the interface was gradually inhibited probably by polymers formation.

Fig. 3 shows the consecutive cyclic voltammograms obtained in a SDBS solution using a lead dioxide anode. During the first scan, a weak increase of current density compared with the ground current occurred in the range of 1.80 and 1.95 V vs. SCE, this signal corresponds to SDBS oxidation. The following voltammograms (scans from 2 to 10; Fig. 3) show a decrease of the current intensity until a steady state for which it became lower than the ground current of the electrolyte, meaning an inhibition of the electrode.

This deactivation observed by cyclic voltammetry could be explained, for the two materials, by the deposition of a protective film on the surface. The aromatic ring of the SDBS structure is likely to start polymerisation initiated by a direct electron exchange (or by reaction with hydroxyl radicals generated at potential higher than 2.15 V / SCE).

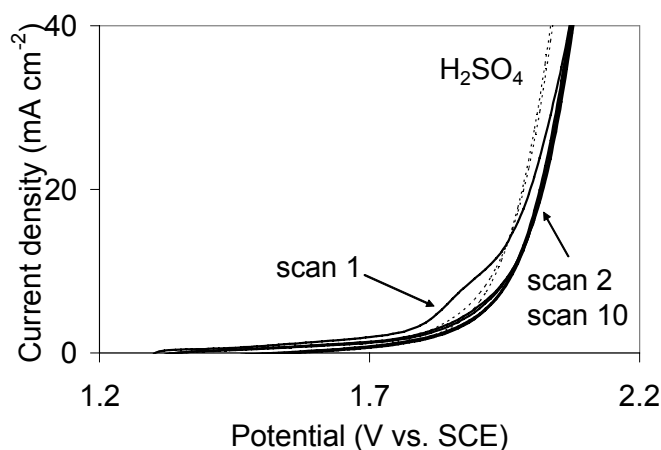


Figure 3. Cyclic voltammograms on PbO_2 electrode (area = 60 mm^2), scan rate = 50 mV s^{-1} , $T = 20^\circ\text{C}$. Dotted lines: H_2SO_4 1 M. Continuous lines $[\text{SDBS}] = 0.3 \text{ mM}$ in 1 M H_2SO_4 ; consecutive scans 1, 2 and 10.

On the other hand, SDBS is a surfactant which can diffuse through the pores of the polymer layer; however the polymer layer strongly decreases the oxidation rate.

3.2. Bulk electrolyses: comparison between BDD and PbO_2 anodes

Fig. 4 shows the TOC removal variation for SDBS electrolyses conducted in the undivided flow cell with two different anodes (BDD and PbO_2), strictly under the same hydrodynamic conditions. The comparison between BDD and PbO_2 -(a) at the same temperature (20°C) shows that, after a charge of 7.5 Ah L^{-1} , the mineralization of SDBS, at the initial concentration of 0.615 mM , reached 85% using a BDD anode whereas, only 25% with a PbO_2 anode. However, previous studies on the oxidation of phenol solutions using a PbO_2 anode have shown that the temperature was an important parameter [6]. Indeed, Belhadj Tahar and Savall highlighted that it was suitable for the complete mineralization of phenol to work in a temperature range of $60 - 90^\circ\text{C}$ [6]. Thus, following this result, experiments were conducted at $T = 65^\circ\text{C}$ on the PbO_2 anode. Comparison between curves (b) and (a) in Fig. 4 shows that an increase in temperature causes rather a decrease in electrochemical performance. So, the behaviour of SDBS on PbO_2 seems to be not in agreement with that of phenol. This disparity between SDBS and phenol oxidation on PbO_2 results probably from the difference in solubility between the intermediaries formed in each case. Benzoquinone (BQ) is formed in relatively important quantity in the course of phenol oxidation [6] and its solubility in water, at 25°C , is $9.26 \times 10^{-2} \text{ mol L}^{-1}$. On the other hand, the concentration of BQ on the anode surface (C_{surf}) can be estimated by using the relation $C_{\text{surf}} = i_{\text{lim}} / (4Fk_m)$. Considering the experimental conditions of Belhadj Tahar et al [6]: current density of 1000 A m^{-2} and mass transfer coefficient

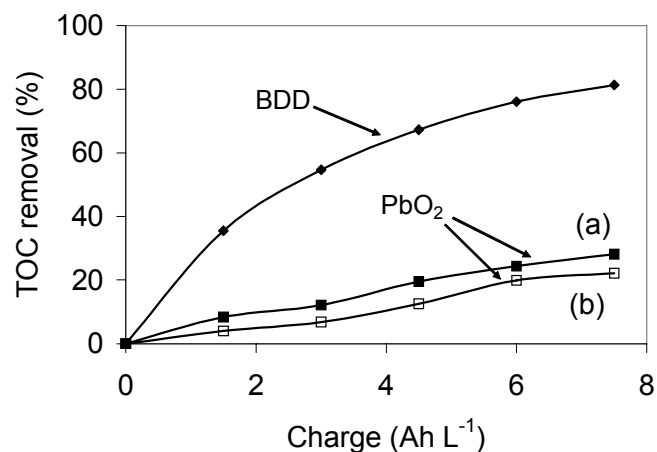


Figure 4. TOC removal variation during electrolysis at BDD and PbO_2 electrodes. Experimental conditions: initial concentration of SDBS = $6.15 \times 10^{-4} \text{ M}$ (TOC = 135 mg L^{-1}); $[\text{Na}_2\text{SO}_4] = 0.118 \text{ M}$; $\text{pH} = 2$ ($[\text{H}_2\text{SO}_4] = 0.005 \text{ M}$); $i = 12 \text{ mA cm}^{-2}$ ($I = 0.75 \text{ A}$); flow rate = 42 L h^{-1} ; $T = 20^\circ\text{C}$ for BDD and PbO_2 (a). $T = 65^\circ\text{C}$ for PbO_2 (b).

cient $k_m = 10^{-5} \text{ m s}^{-1}$, the surface concentration of BQ reaches saturation at 25°C (0.26 mol L^{-1}). In that case, the temperature increase is effective because it avoids BQ precipitation onto the electrode. On the contrary, in the case of SDBS oxidation, insoluble aromatic intermediary does not appear because of the presence of the sulfonate group on the aromatic ring; the temperature increase has no effect.

These results can be explained taking into account the surfactant properties of SDBS. At low concentration (0.615 mM) the surfactant molecules behave like a monomer (without ordered structures formation) while beyond a critical concentration called the critical micellar concentration (CMC), the monomers form aggregates called micelles. The CMC of SDBS in water at $T = 25^\circ\text{C}$ was given by Bakshi *et al.* [20] equal to 2.23 mM . At this temperature SDBS is rather under its monomeric form. Furthermore, adding a counter-ion in solution (like sodium used in the electrolyte Na_2SO_4) has a strong effect on the CMC value: the electrostatic repulsions between head groups of the surfactant are reduced, thus decreasing the value of the CMC. For example, in the case of sodium dodecyl sulfonate (SDS), the corresponding CMC at 20°C is 8 mM [21], while with NaCl (0.1 M) in the solution the CMC value equals to 2 mM [22]. Thus, the SDBS is likely under micellar form at the beginning of the electrolyses conducted at 20°C (Fig. 4). Whatever the SDBS form, we can assumed that for electrolyses conducted at 20°C (Fig. 4) the better performance observed on BDD than on PbO_2 was due to a better electrocatalytic effect; more precisely, BDD compared to PbO_2 has a lower rate of oxygen evolution and a higher rate of OH° production. These radicals weakly

bonded on the BDD surface are available to diffuse and react with micelles on the electrode or monomers into the solution.

In the case of the experiment conducted at 65°C with the PbO₂ anode (Fig. 4; curve b), the system was over the Krafft temperature for which the change of the monomers to micelles occurs. In the case of the SDBS, this Krafft temperature is equal to 57°C [22]. Thus, at 65°C, the solution contained essentially micelles, very large entities diffusing much more slowly than the monomers. If we consider now the mass transfer coefficient, k , defined as the ratio between the diffusion coefficient, D (m² s⁻¹) and the diffusion layer, δ (m) depending on hydrodynamic conditions and physico-chemical properties of the solution, it is possible to evaluate its values for monomeric and micellar structures. A study was carried out by Yeh and Kuwana [23] with ferrocene which forms micelles with Tween 20 ($M = 1650$ g mol⁻¹). These authors highlighted the very great difference between the values of the mass transfer coefficient between monomers and micelles, for similar hydrodynamic conditions. They concluded that : $k_{\text{micelles}} = 10^{-2} k_{\text{monomers}}$. Consequently, at 65°C, the mass transfer to the electrode is strongly decreased due to the presence of micelles; this can explain why increasing the temperature from 20°C to 65°C for experiments conducted with the PbO₂ electrode caused a weakening in electrochemical performance. From the point of view of the material performance it was not considered as essential to pursue the effect of the temperature on the BDD electrode.

Thus, the quasi complete degradation of the surfactant into inorganic species can be accomplished on BDD electrode. Moreover, one can conclude that the BDD electrode has a much higher oxidation power towards SDBS compared to a lead dioxide anode under the same experimental conditions. Lead dioxide and BDD electrodes have both a high overpotential for oxygen evolution compared to platinum. However, the tendency for oxygen evolution is lower on BDD than on PbO₂ (0.77 V lower for a current density of 1 A m⁻²) [8, 24]. This stronger ability for oxygen evolution on PbO₂ makes this material less efficient in mineralization of organics. For these two experiments, the hydrodynamic conditions of the electrolyte circulation in the cell do not depend on the chemical nature of the electrode surface; one can deduce that the electrocatalytic activity of the diamond is higher than that of PbO₂.

3.3. Influence of current density in the case of BDD anode

Let us recall that for electrochemical processes two different kinetic regimes can be defined depending on the value of the current density for a given reactant concentration.

1. If the applied current density is lower than the corresponding limiting current density (cf. Eq. 3): the electrolysis is under charge transfer control, the current efficiency is then 100%.
2. If the applied current density is higher than its lim-

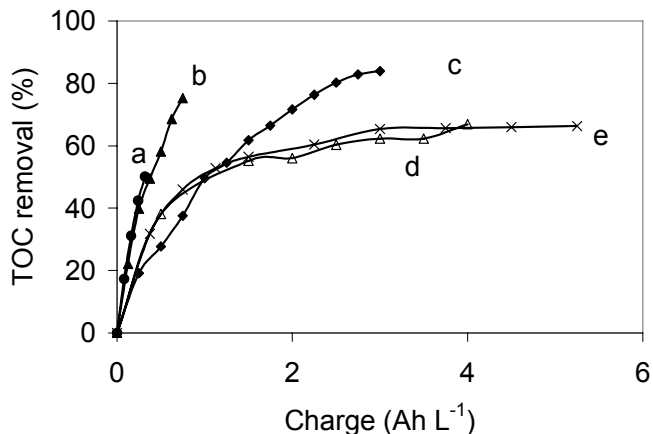


Figure 5. TOC removal during electrolyses under different current densities in mA cm⁻²: (a): 0.63, (b): 1, (c): 4, (d): 8 and (e): 12. Experimental conditions: 20°C, electrolyte: Na₂SO₄ 0.01 M, flow rate: 42 L h⁻¹ and SDBS initial concentration: 6.15×10^{-5} M (TOC = 13.5 mg L⁻¹).

iting value, the electrolysis is under mass transport control; secondary reactions (such as oxygen evolution) occur.

During electrolyses, concentrations of SDBS or intermediate species are unknown, so a limiting current density can be defined by using a global parameter, the Chemical Oxygen Demand (COD), Eq. 3 [25]:

$$i_{\text{lim}} = zFk_m \text{COD} \quad (3)$$

Where i_{lim} is the limiting current density (A m⁻²), F the Faraday constant (96500 C mol⁻¹), $z = 4$ is the number of exchanged electrons considering that the process is similar to the oxidative degradation by molecular oxygen and k_m the average mass transport coefficient in the electrochemical cell (m s⁻¹). For the cell used in this study the value of k_m varies as a function of the flow rate Φ as: $k_m = 2.78 \times 10^{-6} \Phi^{0.38}$ [25]. Although the limiting current is calculated with the initial COD value, the results are presented according to the variation of TOC because of great difficulty of having coherent and reproducible measurements considering the low values of concentration of the SDBS (6.15×10^{-5} M corresponding to 43 mg L⁻¹ of COD).

Fig. 5 shows the TOC removal as a function of the charge per volume for different current densities (from 0.63 to 12 mA cm⁻²). For a SDBS solution at initial concentration of 6.15×10^{-5} mol L⁻¹, and flow rate of 42 L h⁻¹ (in this case, $k_m = 1.14 \times 10^{-5}$ m s⁻¹), the corresponding limiting current is 0.043 A (0.68 mA cm⁻²). One can note that the TOC removal measurements as function of charge for the two lower intensities (0.63 and 1.0 mA cm⁻²) are very close and give better performances. It is assumed that for the two lower intensities, all the hydroxyl radicals produced react with SDBS and its oxidation intermediates.

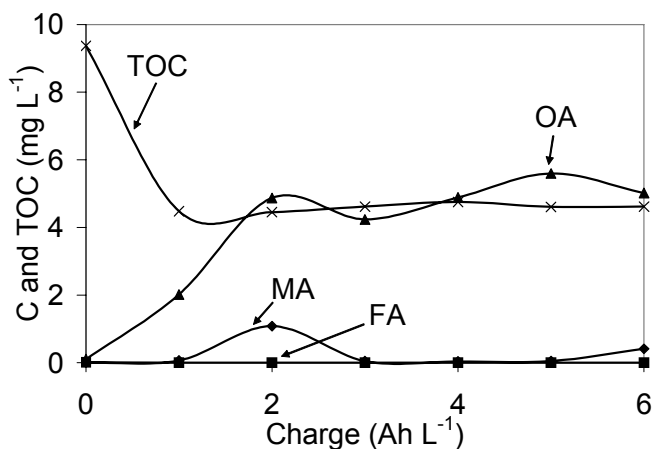


Figure 6. Variation of OA, MA and FA concentrations and TOC variation during electrolysis of SDBS (6.15×10^{-5} M), initial TOC = 13.5 mg L^{-1} ; initial pH = 7, $[\text{Na}_2\text{SO}_4] = 0.012 \text{ M}$, $i = 40 \text{ mA cm}^{-2}$, Volume = 0.5 L , flow rate = 200 L h^{-1} , $T = 20^\circ\text{C}$.

Moreover, at current densities higher than the corresponding limiting value (Curves c, d and e; Fig. 5) the efficiency in the use of the electrical charge decreases. Curves (d) and (e) are quite similar. The profile presents 2 zones: at the beginning of the electrolysis, the TOC removal first increases and then becomes stabilized. The plateau obtained for the highest current densities (curves d and e) corresponds to the lowest TOC removal.

It is assumed that competitive reactions such as oxygen evolution and recombination of hydroxyl radical following Eq. 4 take place in this range of current densities [1]:



Hydrogen peroxide can be further anodically oxidized to oxygen:



The lengths of the chains of the produced intermediaries during the electrolysis at the highest current density are shorter. Thus, it is more difficult for the hydroxyl radicals to react with the species.

To understand the decrease of the TOC removal during electrolysis, the concentration of maleic (MA), oxalic (OA) and formic (FA) acids which are intermediate species formed during electrooxidation of many organic compounds were measured by HPLC. MA and OA are specially formed by oxidation of aromatic ring [6]. Figures 6 and 7 show the TOC variation and the three acids concentration during galvanostatic electrolyses at two initial concentrations of SDBS (25 and 250 mg L^{-1}). One can note that oxalic acid was formed since the beginning of the electrolysis and that the concentration of formic acid was negligible during all the electrolyses. The maximum of

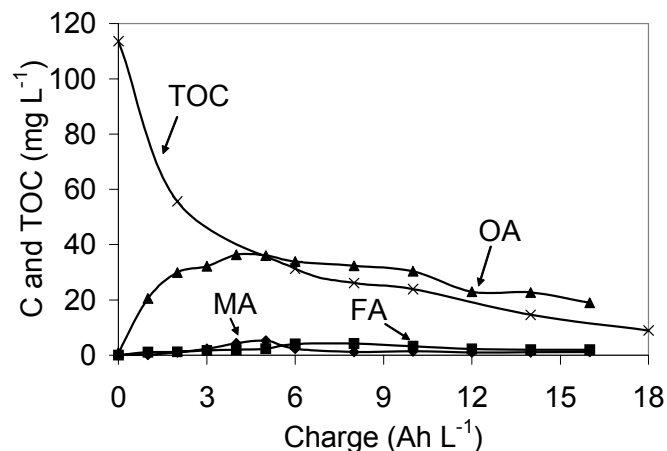


Figure 7. Variation of OA, MA and FA concentrations and TOC variation during electrolysis of SDBS (6.15×10^{-4} M), initial TOC = 135 mg L^{-1} ; pH = 2 ($[\text{H}_2\text{SO}_4] = 0.005 \text{ M}$), $[\text{Na}_2\text{SO}_4] = 0.118 \text{ M}$, $i = 40 \text{ mA cm}^{-2}$, Volume = 0.5 L , flow rate = 200 L h^{-1} , $T = 20^\circ\text{C}$.

the OA concentration was reached when the TOC removal became stabilized. Its concentration presents a very long maximum for the two experiments. On the other hand, maleic acid formation started only as the rate of TOC mineralization stabilized (around 1 Ah L^{-1} ; Fig. 6). The MA concentration reached a maximum and then decreased to a value equals zero. It is known that MA is obtained by oxidation of the aromatic ring when occurs the ring opening [6]. Thus, it is assumed that, during oxidation of SDBS, the aliphatic chain is first attacked to form species with shorter aliphatic chains such as oxalic acid and carbon dioxide. Then, the aromatic cycle which is more stable than aliphatic chains is broken leading maleic acid formation which is then oxidised into OA and FA. When the TOC value is low, there are only species with short chain in the solution which are difficult to oxidize.

Three electrolyses were carried out at different current densities for a concentration range of SDBS which permitted good accuracy in the COD measurements. Under these experimental conditions (SDBS initial concentration = $6.15 \times 10^{-4} \text{ M}$; $\Phi = 200 \text{ L h}^{-1}$; $k_m = 2 \times 10^{-5} \text{ m s}^{-1}$), the initial limiting current density expressed as a function of COD (Eq. 3) was 12 mA cm^{-2} . Fig. 8 represents the COD removal variation during galvanostatic electrolyses at current densities of respectively: 1 , 12 and 40 mA cm^{-2} . In the same time, the faradic efficiency, η , was calculated using the global parameter COD as followed:

$$\eta = \frac{\Delta \text{COD}_{\text{exp}}}{\Delta \text{COD}_{\text{th}}} = \frac{[\text{COD}^\circ - \text{COD}(t)]}{I \times t \times M_{\text{O}_2}} \times 4 \times F \times V \quad (6)$$

COD° , $\text{COD}(t)$ are respectively the COD concentration (g L^{-1}) at initial time and at time t (s); I , constant intensity (A); M_{O_2} , molecular weight of dioxygen (g mol^{-1});

Table 1. Current efficiency for 0.615 mM SDBS electrolysed on BDD in 0.118 M Na₂SO₄ at initial pH = 2. T = 20 °C.

COD removal (%)	Current density (mA cm ⁻²)	Charge (Ah L ⁻¹)	Time (h)	Efficiency
50%	12	1.8	1.5	0.41
	40	2.25	0.56	0.37
70%	12	3.8	3.17	0.27
	40	5.7	1.43	0.18

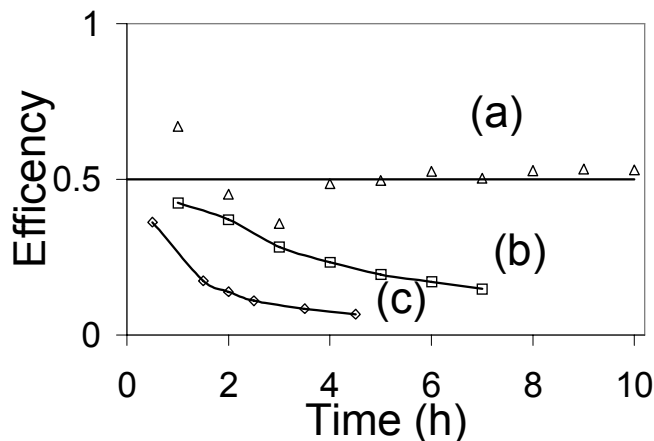


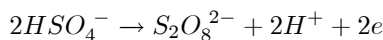
Figure 8. Variation of COD removal as function of charge and variation of efficiency based on COD measurements as function of time for three current densities: (a): 1; (b): 12 and (c): 40 mA cm⁻². SDBS initial concentration = 6.15 × 10⁻⁴ M (COD = 430 mg L⁻¹), initial pH = 2 ([H₂SO₄] = 0.005 M) and [Na₂SO₄] = 0.118 M in 0.5L solution, flow rate = 200 L h⁻¹.

F, Faraday constant (C mol⁻¹); V, volume of the solution (L).

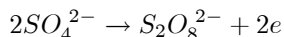
Curves (a), (b) and (c) in Fig. 8, and Table 1, show that, for a given charge, the COD removal decreased as current density increased. The plot of the efficiency, η , versus time reveals that the smaller the current was, the higher the efficiency. Curve (a) shows that the current efficiency did not vary during the electrolysis and was equal to 50%. Under this experimental condition, the electrolysis was under charge transfer control ($i < i_{lim}$). The efficiency was not 100% in this case probably because a part of SDBS was in the form of micelles and diffused very slowly at the electrode. However hydroxyl radicals are extremely reactive, but unselective agent and a bigger part reacts by re-combination of radicals according to Reaction (4) which can be followed by Reaction (5).

For electrolyses conducted at 12 mA cm⁻² and 40 mA cm⁻² (Curves b and c, Fig. 8), the process is controlled by mass transfer; thus, in both cases, the efficiency decreases continuously. Progressively, the part of the current used to oxidize the SDBS decreases, other reactions take place essentially leading to the formation of the persulfate anion

(Eq. 7 and 8) and dioxygen [26].



$$E^\circ = 2.123 \text{ V vs. SHE} \quad (7)$$



$$E^\circ = 2.01 \text{ V vs. SHE} \quad (8)$$

Table 1 gives the electrolysis time and the corresponding current efficiency for COD removals of 50 and 70% obtained on the BDD anode.

4. CONCLUSION

The cyclic voltamograms of SDBS carried out with boron-doped diamond and lead dioxide electrodes have revealed that the oxidation of sodium dodecylbenzene sulfonate occurs in the potential region just before water discharge probably via direct electronic exchange giving rise to the formation of oligomeric products which inhibit the electrodes.

Galvanostatic electrolyses, carried out with the two materials strictly under the same experimental conditions, have shown that boron-doped diamond is very efficient to oxidize and mineralize SDBS in aqueous solution. On the other hand, the commercial electrode made of lead dioxide on titanium was not so active. Increasing temperature decreased weakly the performance of lead dioxide. This fact was explained assuming that the number of micelles in the solution was higher at 65°C than at 20°C.

Increasing the current density on the BDD anode favours competitive reactions such as oxygen evolution or oxidation of sulphate ions. The concentration measurement of maleic, oxalic and formic acids which are intermediate species formed during electrolyses have proved that the aliphatic chain is attacked before the aromatic cycle.

5. ACKNOWLEDGMENT

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