Electrochemical degradation of an anionic surfactant on boron-doped diamond anodes

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Abstract

In this work, the electrochemical oxidation on boron-doped diamond of synthetic wastes polluted with surfactant sodium dodecylbenzenesulfonate (SDBS) has been studied. Results show that SDBS can be successfully removed with this technology inside different current densities and concentration ranges. The oxidation of the SDBS seems to occur in two main sequential steps: the first is the rapid degradation of SDBS, and the final is the less efficient oxidation of aliphatic intermediates to carbon dioxide. The nature of supporting electrolyte (NaCl, Na_2SO_4 and K_3PO_4) influences on the efficiency of the electrochemical oxidation process. The treatment of the NaCl solution seems to be more efficient in the chemical oxygen demand (COD) removal, while the sulphate and specially the phosphate media improve the TOC removal. However, in spite of this observation, chemical oxidation of SDBS by different types of oxidants cannot explain alone the results of the electrochemical oxidation with diamond anodes. This suggests that the synergistic effect of the different oxidation mechanisms that occurs into the electrochemical cell (direct oxidation and mediated oxidation by hydroxyl radicals and by oxidants formed from the electrolyte) is the responsible of the great efficiencies obtained with this technology in the treatment of organics.
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1. Introduction

Surfactants are widely used in industry to promote the dispersion of organic species in water. Thus, they are widely used in the formulation of soaps, detergents, inks, etc. They normally consist of large molecules with both, hydrophobic and hydrophilic groups. They are highly soluble in water and persistent, once discharged into a natural environment. Thus, its study is interesting not only for being possible pollutants of industrial effluents but also because they are good models of complex pollutants.

Appropriate treatment of these wastewaters is necessary in order to reduce the impact of their discharge. Different processes have been described in the literature for the treatment of these wastes, but the most commonly used are coagulation, precipitation, and biological methods [1]. In wastewater treatment plants, persistent surfactants can give rise to foaming, adsorp-

tion onto microbial sludge and loading of the purified effluents in concentrations up to ppm range [2].

Conductive diamond is an emergent material with good properties for the electrochemical treatment of wastewaters polluted with organic compounds. In the recent years, a great experimental effort have been made to characterize this material as anode, including lab-scale electrochemical-fundamentals studies in which the properties of the conductive diamond has been clarified and bench-scale electrolytic studies of treatability of synthetic wastewaters polluted with different organics such as phenolic compounds, carboxylic acids, cyanides, herbicides, etc. From these studies [2–16], it was concluded that the use of conductive-diamond electrodes allows to obtain high current efficiencies in the treatment of organics, and also the almost complete mineralization of the organics. These facts have been related to the generation of hydroxyl radicals on the conductive-diamond surface [17]. In this sense, the production of significant amounts of hydroxyl radicals allows to consider conductive-diamond electrochemical oxidation as an advanced oxidation process (AOP) [18]. Other important properties of conductive-diamond electrodes (CDE) are their great chemical

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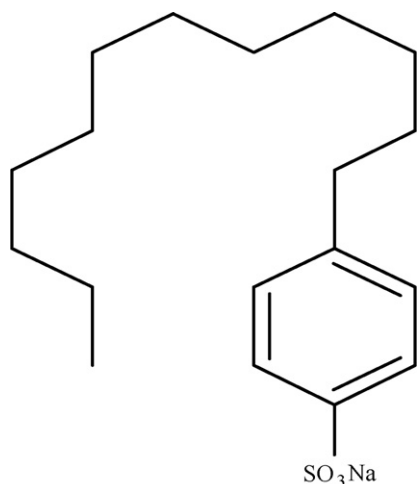
Fig. 1. Chemical structure of sodium dodecylbenzenesulfonate.

and electrochemical stability, which enhance the average life-time of this anodic material and allow its use in the treatment of almost any kind of wastewater.

Sodium dodecylbenzenesulfonate (SDBS) is a chemical species widely used as a model of anionic surfactants. It consists of a benzene ring (Fig. 1) coupled with a large aliphatic chain and a sulphonic group. The benzene ring and the aliphatic chain provide the hydrophobic behaviour while the sulphonic group the hydrophilic behaviour. The treatment of surfactants by electrochemical oxidation was previously studied in literature. Thus, Lissens et al. [2] demonstrated that BDD electrodes show higher surfactants removals compared to plane graphite, and Panizza et al. [19] observed the complete removal of surfactants with Ti–Ru–Sn ternary oxide and BDD anodes operating at different current densities. These authors also observed a mass-transfer control of the electrochemical process (COD removal rate increases with the increase in the electrolyte flow rate) which could be explained by the small concentrations of the surfactant.

The aim of this work has been to study the effect of the supporting electrolyte media on the electrochemical oxidation with BDD anodes of synthetic wastewaters polluted with SDBS, and to try to determine the effect of current density and pollutant concentration on the efficiency of this electrochemical process. To do this voltammetric and bulk electrolyses studies have been carried out. In addition, the results of chemical oxidation tests with hydrogen peroxide (H_2O_2), peroxodisulphate ($S_2O_8^{2-}$), peroxodiphosphate ($P_2O_8^{4-}$), Fenton reagent (Fe^{2+}/H_2O_2) and ozone (O_3) have been used to obtain some insights about the role of the mediated oxidation processes in the electrochemical oxidation of surfactants.

2. Experimental

2.1. Chemicals

Sodium dodecylbenzenesulfonate was of analytical grade and purchased from Fluka. All other reagents used were of analytical grade. All solutions were prepared with deionized water having $18\, m\Omega^{-1}\, cm^{-1}$ resistivity from a Mill-Q^{TM} system. The

synthetic wastes were prepared with a concentration higher than the critical micellar concentration cmc (we dissolved the surfactant in a small amount of water) and then were diluted to obtain a waste that can be used for our research.

2.2. Analytical procedure

The carbon concentration was monitored using Shimadzu TOC-5050 analyzer. Chemical oxygen demand (COD) was determined using a HACH DR2000 analyzer. UV–vis spectra were obtained using a Shimadzu 1603 spectrophotometer and quartz cells.

2.3. Determination of the average current efficiency (ACE) and instantaneous current efficiency (ICE)

The ACE and the ICE were calculated using Eqs. (1) and (2), respectively [20]:

$$ACE = \frac{[COD^0 - COD_t]FV}{8It} \tag{1}$$

$$ICE = \frac{\left[COD_t - COD_{t+\Delta t}\right] FV}{8I\Delta t} \tag{2}$$

where COD^0, COD_t and $COD_{t+\Delta t}$ are the initial chemical oxygen demand (in $g\, O_2\, dm^{-3}$) and the chemical oxygen demand at times t and $t + \Delta t$ (in s), respectively, I is the current intensity (A), F is the Faraday constant ($96487\, C\, mol^{-1}$), t is the time (in s), V is the volume of the electrolyte (dm^3) and 8 is a dimensional factor for unit consistence ($32\, g\, O_2\, mol^{-1}\, O_2/4\, mol\, e^-\, mol^{-1}\, O_2$).

2.4. Determination of the oxygen-equivalent chemical-oxidation capacity (OCC)

To compare the performance of different AOP it is desirable one parameter which quantifies in arbitrary units the oxidants added to the waste. In this work, it is proposed to use the OCC that is defined as the kg of O_2 that are equivalent to the quantity of oxidant reagents used in each AOP to treat $1\, m^3$ of wastewater [21]. The OCC has the same purpose that the frequently used chemical oxygen demand (COD) which quantifies the kg of oxygen required to oxidize chemically any given reduced species present in a wastewater (although the actual chemical oxidation essay is carried out with permanganate or dichromate). The main difference between them is that the COD is used to determine the concentration of organic substrate contained in the waste and the OCC is proposed to quantify the amount of oxidant supplied in the oxidation process. This parameter is related to the different oxidants used in the three advanced oxidation processes studied in this work according to the following equations:

$$OCC(kg\, O_2\, m^{-3}) = 0.298Q(kAh\, m^{-3}) \tag{3}$$

$$OCC(kg\, O_2\, m^{-3}) = 1.000[O_3](kg\, O_3\, m^{-3}) \tag{4}$$

$$OCC(kg\, O_2\, m^{-3}) = 0.471[H_2O_2](kg\, H_2O_2\, m^{-3}) \tag{5}$$

$$OCC(kg\, O_2\, m^{-3}) = 0.0601[K_2S_2O_8](kg\, K_2S_2O_8\, m^{-3}) \tag{6}$$

$$OCC(kg\ O_2\ m^{-3}) = 0.0462[K_4P_2O_8](kg\ K_4P_2O_8\ m^{-3}) \quad (7)$$

These equations are obtained from stoichiometrical calculations, taking into account the number of electrons exchanged in the reduction of the different oxidants (for the case of ozone and hydrogen peroxide) and also the Faraday number in the case of CDEO.

2.5. Conductive-diamond electrochemical oxidation (CDEO)

The oxidation of the different solutions was carried out in a single-compartment electrochemical flow cell, previously described elsewhere [22]. A diamond-based material was used as the anode and stainless steel (AISI 304) was used as the cathode. Both electrodes were circular (100 mm in diameter) with a geometric area of 78 cm^2 each, and an electrode gap of 9 mm. The electrolyte was stored in a glass tank (0.5 dm^3) and circulated through the electrolytic cell by means of a centrifugal pump. A heat exchanger was used to maintain the temperature at 25 °C. The experimental set up also contained a cyclone for a gas–liquid separation, as well as a gas absorber to collect the carbon dioxide contained in the gases evolved from the reaction into sodium hydroxide. Boron-doped diamond films were provided by CSEM (Neuchâtel, Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si(1 0 0) wafers (0.1 Ω cm Siltronise).

Electrolyses were carried out in galvanostatic mode. The natural pH of solutions was about 5 and during electrolysis no control of pH was carried out. The cell potential was constant during each electrolysis reaction, indicating that appreciable deterioration of the electrode or passivation phenomena did not take place. The electrolyte flow rate through the cell was 1.25 dm^3 min^{-1}. The linear velocity of the fluid was 2.31 cm s^{-1}, and the space velocity was 2.08 min^{-1}.

2.6. Voltammetry experiments

Electrochemical measurements were obtained using a conventional three-electrode cell in conjunction with a computer-controlled potensiostat/galvanostat (Auto lab model PGCTAT 30, Ecochemie B.V., Utrecht, Netherlands). Diamond was used as the working electrode, Hg/Hg$_2$Cl$_2$·KCl (saturated) as a reference electrode and platinum wire (Pt) as counter electrode. Voltammetric experiments were performed in unstirred solutions (0.2 dm^3). The anode was anodically polarized for 10 min with a 1 M H$_2$SO$_4$ solution at 0.1 A prior to each experiment.

2.7. Ozonation

Ozonation experiments were carried out by continuously feeding an ozone–oxygen gas stream in a mixed semi-batch bubble reactor (continuous for gas and batch for liquid). This reactor consist of a 2.5 dm^3 jacketed cylindrical Pyrex glass tank equipped with a porous gas distribution plate and baffles to increase the capacity of absorption of ozone. A mechanical stir-

rer (IKA WERKER model EUROSTAR DIGITAL, Germany) and a recycle pump (Emapompe, model P 022 Plastomec) are also used to promote the absorption of ozone and to obtain good mixing conditions. Pure oxygen taken from a commercial cylinder was fed into an ozone generator (Ambizon, Model GMF-10, Sistemas y Equipos de Ozonizacion S.L., Madrid, Spain) which is able to produce a maximum mass flow rate of 10 g h^{-1}. In the generator outlet, the stream was dried with a sample conditioner (Sample conditioning system, model SC-010-R AFX, Sistemas y Equipos de Ozonizacion S.L., Madrid, Spain). The concentration of ozone in the gas at the reactor outlet and inlet was measured with an ozone meter (Ozone analyzer, Model H1 AFX, Sistemas y Equipos de Ozonizacion S.L., Madrid, Spain) and its calibration was carried out iodometrically [23]. Dissolved ozone concentration in the liquid phase was determined spectrophotometrically (600 nm) from discoloration of the resulting solution, by the Karman indigo method [24]. In the experiments described in this work, the ozone–oxygen mixture gas stream was sparged with a constant flow rate of 0.5 dm^3 min^{-1} (flow controller Cole Parmer, model #: 32907-39) and the average production of ozone was around 1 g h^{-1}. The volume of wastewater treated in each assay was 2 dm^3 and it was placed inside the reactor prior to the experiments. To increase the mixing conditions, the stirring rate of the mechanical stirrer was adjusted to 550 rpm and the flow recycled to 67.5 dm^3 h^{-1}. The ozone generator was switched on prior to the experiments, and only when the desired ozone percentage in the ozone–oxygen gas was reached (steady-state conditions) the ozone–oxygen mixture gas stream started to be sparged into the reactor. During the experiments sodium hydroxide was added to the reactor to maintain the pH in a set point close to 12 ± 0.1. According to the literature [25], this is an optimum pH to promote the generation of hydroxyl radicals due to the radicalary decomposition of the ozone molecules. The temperature was also maintained during operation at 25 °C using a thermostatic bath (Tectron, model 3473200 Selecta, Madrid, Spain) by circulating the water through the jacket reactor to ensure a constant temperature inside the reactor.

2.8. Fenton process

Fenton oxidation assays were carried out in lab-scale thermostated mixed batch reactors. The experimental setup consists of a multistirrer device (Ikamag RO 5 power, IKA-WERKE GmbH & Co. KG, Staufen, Alemania) with 15 mixing sites coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain). Pyrex flasks (250 cm^3) hermetically sealed and equipped with magnetic stirrers were used as reactors. They were submerged in the thermostatic bath. In every assay, the reactors were filled with 100 cm^3 of wastewater. Then, the iron dose was added (as FeSO$_4$·7H$_2$O) and the pH was adjusted to 3 ± 0.1 with sodium hydroxide or sulphuric acid. According to literature, this is the optimum pH to promote the formation of hydroxyl radicals in a Fenton process [26–28]. In every case, the reaction was started by adding the dose of hydrogen peroxide. Preliminary experiments were carried out to determine the reaction time needed to meet the steady-state conditions. From these experiments a reaction time of 4 h was selected (more than

three times higher than the worst value obtained in the previous experiments). Once the reaction time was finished COD, UV–vis spectra and hydrogen peroxide were measured in every reactor. Then, the steady-state conditions were assured by a later measure (after 1 h). Hydrogen peroxide was measured according to Eisenberg [29]. The COD value was corrected with the value of hydrogen peroxide to obtain the COD value associated to the organic pollutants contained in the wastes. Several set of experiments were carried out to determine the range of hydrogen peroxide and iron needed to obtain optimum results.

2.9. Peroxodisulphate and peroxodiphosphate oxidation

Oxidation tests with peroxodisulphate and peroxodiphosphate were carried out in lab-scale thermostated mixed batch reactors. The experimental setup consists of a multistirrer device above described (Ikamag RO 5 power, IKA-WERKE GmbH & Co. KG, Staufen, Alemania). Pyrex flasks (250 cm^3) hermetically sealed and equipped with magnetic stirrers were used as reactors. They were submerged in the thermostatic bath. In every assay, the reactors were filled with 100 cm^3 of wastewater. In every case, the reaction was started by adding the dose of the potassium peroxoacid salt. Preliminary experiments were carried out to determine the reaction time needed to meet the steady-state conditions. From these experiments a reaction time of 6 h was selected (more than three times higher than the worst value obtained in the previous experiments).

3. Results and discussion

3.1. Voltammetric study

Fig. 2 shows voltammograms of 0.1 M Na$_2$SO$_4$, NaCl and K$_3$PO$_4$ solutions on boron-doped diamond (100 mV s^{-1}). As it can be observed, only the voltammogram of the K$_3$PO$_4$ solution presents activity in the potential region of stability of the electrolyte, with two anodic peaks situated at 1.75 and 2.5 V (*vs.* SCE). According to the literature [30,31], theses peaks can be explained in terms of the oxidation of the phosphates ions (PO$_4^{3-}$, HPO$_4^{2-}$) to phosphates radicals (PO$_4^{2-\bullet}$, HPO$_4^{-\bullet}$),
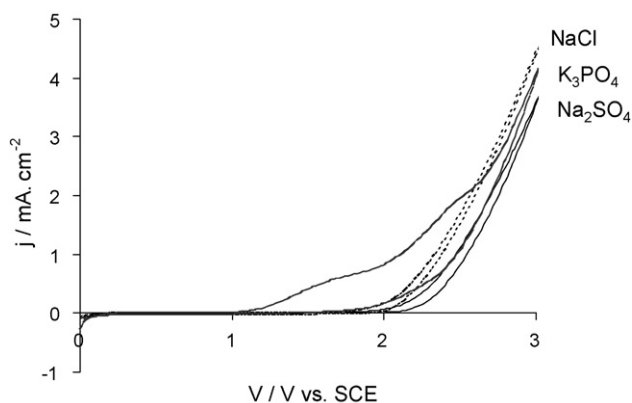
Fig. 2. Cyclic voltammograms on BBD anode of three different supporting electrolytes Na$_2$SO$_4$ 0.1 M (a), NaCl 0.1 M (b) and K$_3$PO$_4$ 0.1 M (c). Auxiliary electrode: platinum. Reference electrode: SCE. Scan rate: 100 mV s^{-1}.

which it is known to be the first step in the formation of the more stable peroxomonophosphate (PO$_5^{3-}$) or peroxodiphosphate (P$_2$O$_8^{4-}$) ions. The oxidation potential of the phosphate radicals increases with their protonation. This explains the two peaks observed in the voltammogram. The voltammograms of the Na$_2$SO$_4$ and NaCl solutions are very similar, although the electrochemical window observed in the sulphate solution voltammogram seems to be slightly wider. This can be explained by the oxidation of chlorides to hypochlorite which overlaps with the oxygen evolution reaction (OER) process and shift the curve towards lower potentials. Although the formation of peroxodisulphates is widely reported in the literature [32] no peaks can be observed in the voltammogram of the sulphate solution. This means that this process should develop in the potential region of water instability.

Fig. 3a–c shows cyclic voltammograms (five cycles) with BDD electrodes of aqueous solutions containing 0.3 g dm^{-3} of SDBS in 0.1 M of Na$_2$SO$_4$, 0.1 M of NaCl and 0.1 M K$_3$PO$_4$, respectively. The curves are obtained with a scan rate of 100 mV s^{-1} in the potential region between 0.0 and 3.0 V (*vs.* SCE). A cyclic voltammogram without organic matter is also plotted in the graphs for the sake of comparison. As it can be observed, the presence of SDBS leads to an anodic oxidation peak around 2.0 V *vs.* SCE. In the case of the phosphate solution, this peak overlaps with the phosphate oxidation process and the OER seems to be shifted towards lower potentials. In the case of the chloride solution, the peak is clearly marked and the OER seems to be shifted towards higher oxidation potentials. This can only be explained by some sort of deactivation of the anode surface after the oxidation of the SDBS which reduces the extension of the oxidation of chlorides to hypochlorites.

In every case, as the number of cycles increase (corresponding to the second, third, fourth and fifth scans), the voltammograms decrease in size. This deactivation of the anode surface can probably be due to the adsorption of SDBS (or some of its oxidation products) and/or the deposition of a polymer film on the electrode surface [5]. However, the anode can restore its initial activity by an anodic polarization at 300 mA cm^{-2} current density during 3 min before scanning other voltammograms. To explain this, it has to be taken in mind that at high anodic current densities, the oxidation of water leads to the formation of significant amounts of hydroxyl radicals [18]. These radicals react rapidly with the organics at the surface of the anode leading to their total mineralization and activating the surface once again. Hence, it seems clear that the SDBS can be oxidized directly on the surface of the BDD in the potential region of water stability. In this oxidation process, the electrolyte has a significant influence as different species can be formed from its oxidation. The oxidation products of the direct oxidation of SDBS lead to a deactivation of the anodic surface (probably fouling) being this problem solved working in the potential region of water oxidation.

3.2. Bulk electrolysis

Fig. 4 shows a typical profile of the variation of COD and TOC with the specific electrical charge passed during electroly-
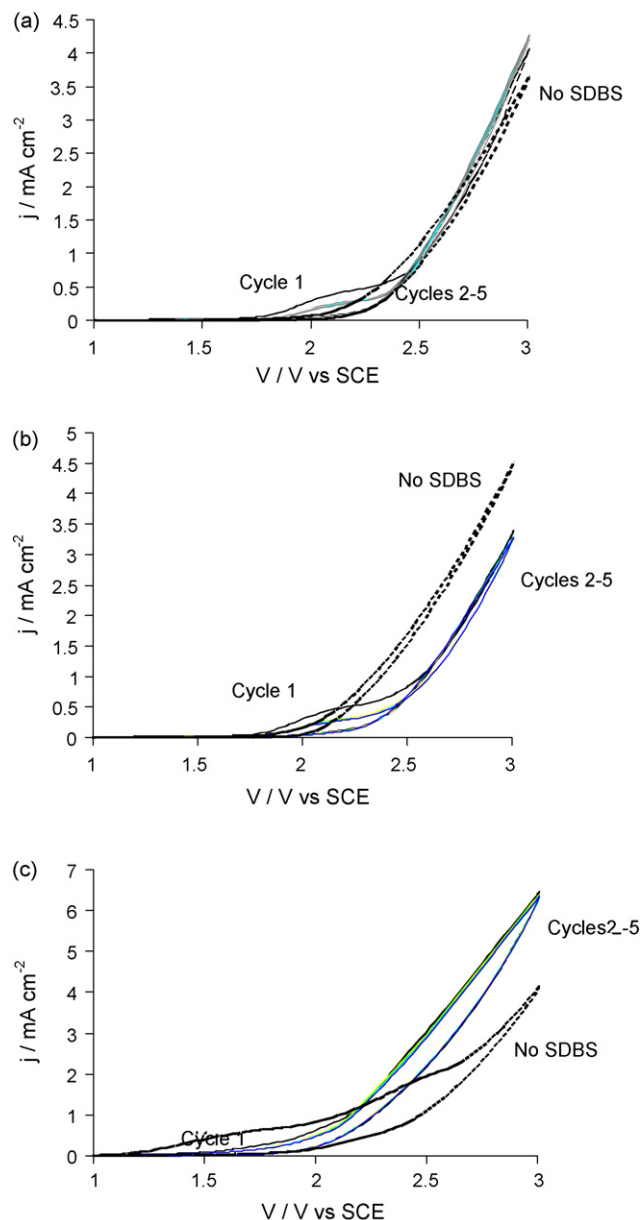
Fig. 3. Cyclic voltammograms on BBD anode of SDBS 0.3 g dm^{-3} on Na$_2$SO$_4$ 0.1 M (a), NaCl 0.1 M (b) and K$_3$PO$_4$ 0.1 M (c) solutions. Solutions with organic matter: cycle (1) thinner dashed line; cycles (2)–(5) continuous grey line (all cycles completely overlapped). Solution without organic matter: thicker dashed line (only shown cycle 1). Auxiliary electrode: platinum. Reference electrode: SCE. Scan rate: 100 mV s^{-1}.

Fig. 4. Bulk electrolysis of SDBS. (a) Changes in the COD ($\blacklozenge$) and in the TOC ($\triangle$) with current charge passed. (b) Changes in the instantaneous current efficiency ($\bigcirc$) and in the COD/TOC ratio ($\blacksquare$). Operation conditions: current density is 30 mA cm^{-2}, $T = 25\,^{\circ}$C. Waste composition: sodium sulphate, 0.1 M; natural pH; initial SDBS concentration, 0.3 g dm^{-3}.

ses of a solution containing 0.3 g dm^{-3} SDBS and 0.1 M Na$_2$SO$_4$ (30 mA cm^{-2}; $T = 25\,^{\circ}$C and natural pH). As it can be observed, both parameters (COD and TOC) are satisfactorily diminished during the treatment. Changes in the TOC indicate that carbon dioxide is formed from the very early oxidation stages. However, as it can be seen in Fig. 4b, the TOC/COD ratio decreases significantly during the first stages (up to current charges around 10 Ah dm^{-3}) and then, it remains constant in a value close to 1. This means that the oxidation of the SDBS can be assumed to occur in two main sequential stages: the first is the rapid degradation of SDBS (average TOC/COD ratio around 1 and disappearance of UV bands) and the final is the less efficient
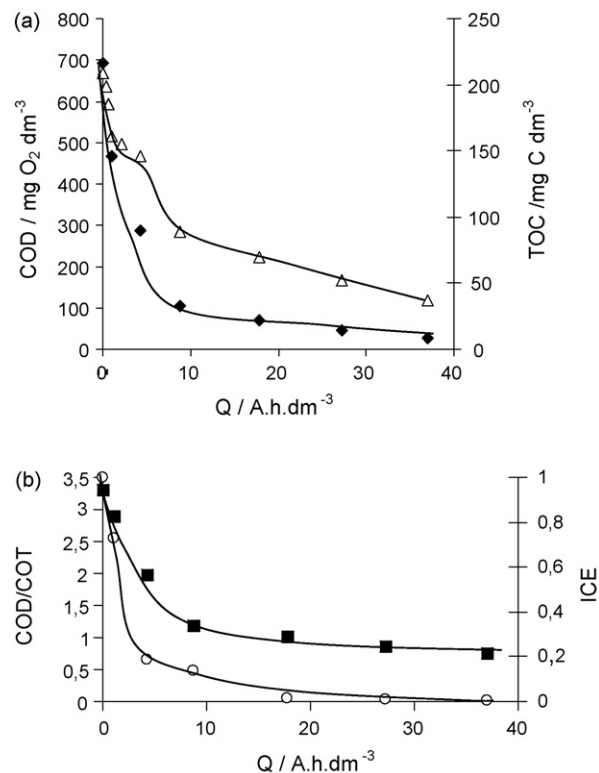
oxidation of aliphatic intermediates to carbon dioxide. In this point it is important to note that the current efficiency (Fig. 4b) decreases rapidly during the treatment being almost negligible in this second stage. This decrease is characteristic of electrochemical wastewater treatment processes, and can be explained in terms of a mass transport control of the overall rate of the process [5,6,9,22]. For the fluid-dynamics and current density conditions used, limit-COD of the electrochemical cell used in this work is around 1700 mg dm^{-3}, for a purely direct electrochemical system (not considering mediated electrochemical oxidation) as it has been obtained by a typical ferrocyanide–ferricyanide test. Taking into account that the maximum tested COD is around 700 mg dm^{-3}, this means that all the SDBS oxidation process is developing under mass transport control.

Fig. 5 compares the changes in the COD and TOC during the electrolyses of SDBS solutions containing different supporting electrolytes (potassium chloride, sulphate or phosphate). The curves show a significant decrease of both parameters during the electrolyses, and a small influence of the supporting electrolyte. Again the accumulation of some slowly oxidizable carbon is observed, as the COD seems to be almost completely disappeared at 35 Ah dm^{-3} while the TOC value remains significant at this current charge. The treatment of the NaCl solution seems to be more efficient in the COD removal, while the sulphate and specially the phosphate media improve the TOC removal. This can be explained assuming that the oxidation with hypochlorites
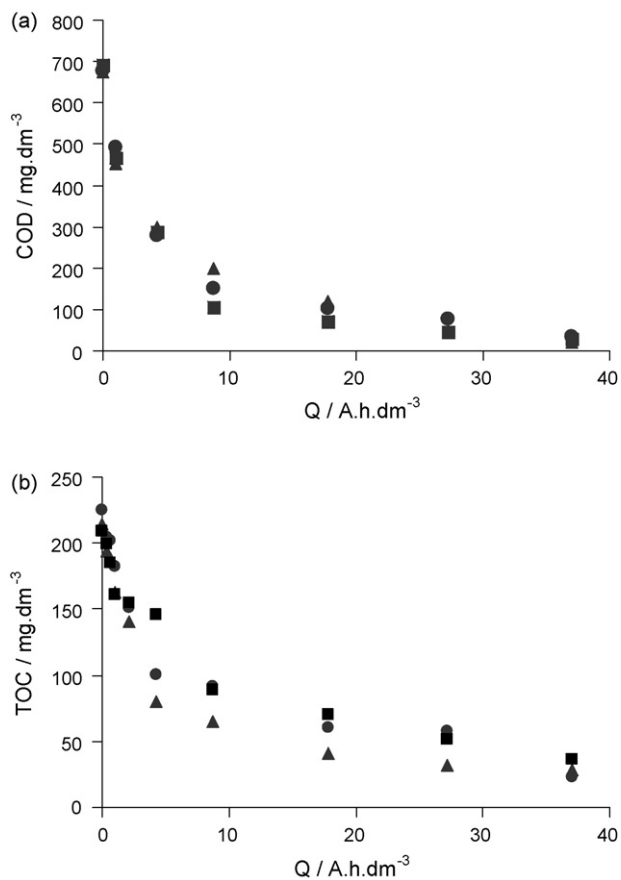
Fig. 5. Influence of electrolyte on the variation of the COD (a) and TOC (b) during electrolyses of SDBS (0.3 g dm^{-3}) on boron doped diamond anodes. (■) NaCl 0.1 M, (●) Na$_2$SO$_4$ 0.1 M, (▲) K$_3$PO$_4$; j = 30 mA cm^{-2}, T = 25 °C.

lead to a very effective oxidation of the SDBS but not of the intermediates formed (probable accumulation of organochlorinated compounds) while the oxidation with peroxodiphosphate or peroxodisulphate seems to be more severe in this second stage and it promotes the formation of carbon dioxide.

These later observations seem to be contradictory to those of Fig. 6. In this figure, the results of some chemical oxidation tests (conventional and advanced) of SDBS with different oxidants are observed. It seems clear that the advanced oxidation technologies (O$_3$/OH$^-$ and H$_2$O$_2$/Fe^{2+}) seem to be more efficient that the oxidation carried out by the two peroxoacids anions (peroxodisulphate and peroxodiphosphate). Even the conventional chemical oxidation carried out by hydrogen peroxide seems to be more effective. In the former case (advanced oxidation) the oxidation is carried out primarily by hydroxyl radicals while in the other two cases the primary mechanisms is expected to be the chemical oxidation by the oxidant molecule. This suggests that peroxoacids are not good chemical oxidants themselves and that maybe is their activation in the anode to form sulphate or phosphate radicals [31] the responsible of the better results (greater mineralization) obtained in the electrochemical treatment of SDBS with sulphate and phosphate supporting electrolytes as compared to those obtained in NaCl media (in which foreseeable many halogenated organic intermediates could be formed).
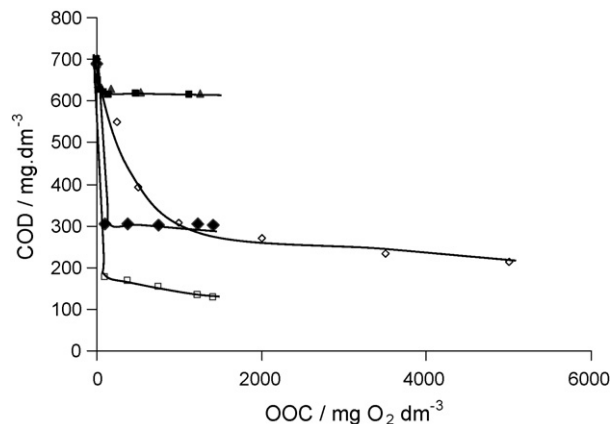

Fig. 6. Chemical oxidation of SDBS. Changes in the COD *vs.* the oxidant dose. Waste composition: SDBS (0.3 g dm^{-3}). Oxidants: (□) H$_2$O$_2$ + Fe^{2+} 270 mg dm^{-3}, pH 3; (◇) O$_3$/OH$^-$ (◆) H$_2$O$_2$, natural pH; (▲) S$_2$O$_8$$^{2-}$, natural pH; (■) P$_2O_8$$^{4-}$, natural pH.

The absorption spectral changes during the galvanostatic electrolyses of SDBS solutions (0.3 g dm^{-3}) at 30 mA cm^{-2} with NaCl, Na$_2$SO$_4$ and K$_3$PO$_4$ supporting electrolytes are shown in Fig. 7. It can be observed that the absorption spectra of SDBS are characterized by the presence of two bands in the UV region at 220 and 250 nm. For the solution containing NaCl, a new band at 292 nm appears. This new band is attributed to the formation of ClO$^-$ ions [33]. For all the electrolytes, the intensity of the first band increases in the initial stages and then it decreases continuously. This observation can be related to the formation of several organic intermediates that appear rapidly during the initial stages of the treatment. In addition it can be observed that the UV–vis spectra obtained during the treatment are very different from one supporting electrolyte to another, suggesting the formation of different intermediate species. This suggests an important influence of the electrolyte on the oxidation process.

Fig. 8 shows the effect of the current density and SDBS initial concentration on the electrolyses results in chloride media. In every case the SDBS is satisfactorily oxidized. It can also be noted two contradictory effects:

(1) a small influence of the current density, suggesting an important role of the volumetric mediated electro-oxidation processes and, at the same time,
(2) the decreases in the COD with the electrical charge are directly related to the concentration, indicating that the process is mass-transfer controlled.

Similar results were obtained in the treatment of SDBS solution with the other two electrolytes used (sulphates and phosphates). This confirms that in addition to mediated processes which depends on the electrolyte nature, processes on the electrode surface which are not exclusively direct oxidation (in this case we would have electrode deactivation) are occurring and hence the electrochemical oxidation results have to be explained by the combined effect of all these mechanisms, as it has been recently proposed in the literature [15,34]. In this con-
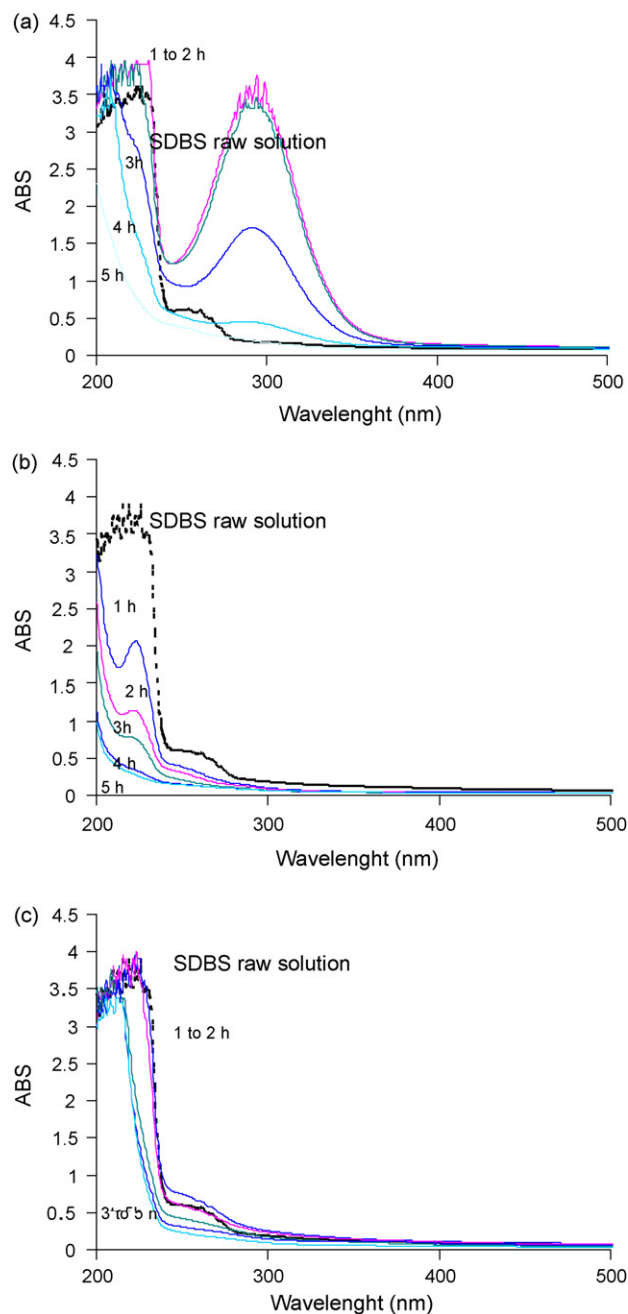
Fig. 7. Influence of the electrolyte on the treatment of SDBS with BDD anodes. Changes with time in the UV–vis spectra during the electrochemical treatment of SDBS solutions ($0.3\,g\,dm^{-3}$) on boron doped diamond anodes. (a) NaCl 0.1 M, (b) Na_2SO_4 0.1 M, (c) K_3PO_4 0.1 M; Operating conditions: natural pH, $T = 25\,^{\circ}C$, $j = 30\,mA\,cm^{-2}$.

Fig. 8. Influence of the current density (a) (♦) $j = 15\,mA\,cm^{-2}$, (■) $30\,mA\,cm^{-2}$, (▲) $60\,mA\,cm^{-2}$ and initial organic load (b) (●) $0.3\,g\,dm^{-3}$ and (■) $0.6\,g\,dm^{-3}$ on the electrolyses of SDBS. Electrolyte 0.1 M NaCl; $T = 25\,^{\circ}C$; natural pH.

text, the action of the hydroxyl radical seems to be not enough to explain the results. As it was pointed out before, the generation of hydroxyl radicals during electrolysis with conductive-diamond electrode was demonstrated by Marselli et al. [18]. These radicals can also be formed with an H_2O_2/Fe^{2+} and with an O_3/OH^- process and according to Fig. 7 they cannot degrade successfully all the organic content of a solution of SDBS. In fact, none of the oxidant system tested was able to reduce completely the COD of the SDBS solution. Hence, it can be pointed that the actual advantage of the diamond electrode electrolyses in
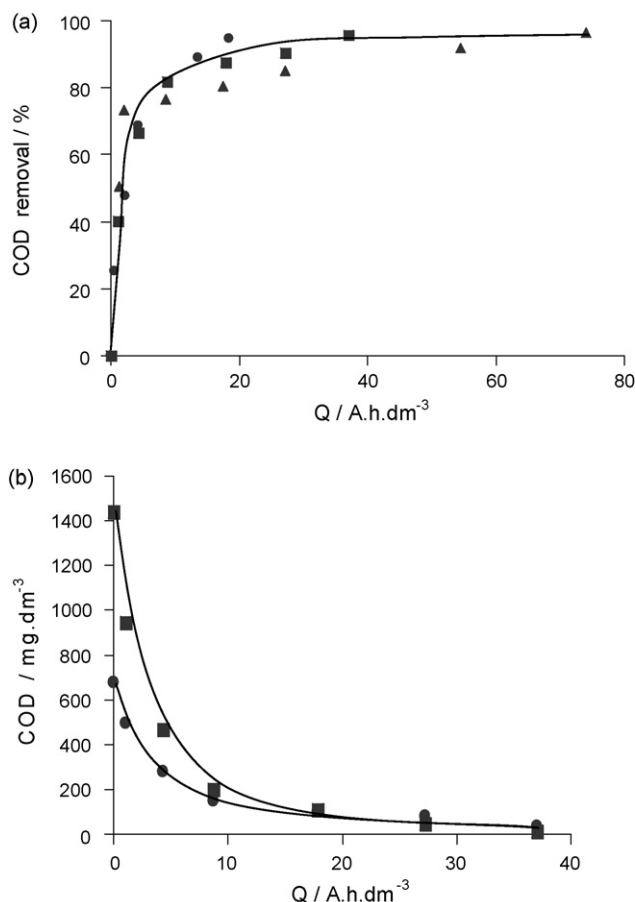
the treatment of organic wastes is provided by the synergistic effect of the different oxidation mechanisms that occurs into the electrochemical cell.

4. Conclusion

The main conclusions of this work can be summarized in the following points:

- Electrochemical oxidation with BDD electrodes can be used successfully to remove the COD and TOC of synthetic wastewater containing SDBS surfactant. The oxidation of the SDBS and its intermediates can be assumed to occur in two main sequential stages: the first is the rapid degradation of SDBS (average TOC/COD ratio around 1 and disappearance of UV bands) and the final is the less efficient oxidation of aliphatic intermediates to carbon dioxide.
- The nature of supporting electrolyte (NaCl, Na_2SO_4 and K_3PO_4) influences on the efficiency of the electrochemical oxidation process. The treatment of the NaCl solution seems to be more efficient in the COD removal, while the sulphate and specially the phosphate media improve the TOC removal. This can be explained assuming that the oxidation with hypochlorites lead to a very effective oxidation

of the SDBS but not of the intermediates formed (probable accumulation of organochlorinated compounds) while the oxidation with peroxodiphosphate or peroxodisulphate seems to be more severe in this second stage and it promotes the formation of carbon dioxide.

- In spite of the important role of mediated electrochemical oxidation processes, chemical oxidation of SDBS by different types of oxidants cannot explain the results of the electrochemical oxidation with diamond anodes. This suggest that the synergistic effect of the different oxidation mechanisms that occurs into the electrochemical cell (direct oxidation and mediated oxidation by hydroxyl radicals and by oxidants formed from the electrolyte) is the responsible of the great efficiencies reached by this technology.

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