

Synthesis of novel oxidants by electrochemical technology

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Abstract In this work it has been studied the electrochemical production of different oxidants with conductive-diamond anodes. This technology was found to allow the production of stable oxidants that can not be easily synthesized using other electrodes or by other more usual techniques. Thus, it has been found that monoperoxophosphoric acid, and peroxodiphosphate, peroxodisulphate and ferrate salts can be easily produced by this technology, when the right operation conditions are used. In contrast, the production of pure hypochlorite is not favoured, because this technology leads to the formation of a mixture of hypochlorite with other oxoanions of chlorine in a higher oxidation state, particularly chlorates and perchlorates, which seems to be the final product in these electrolyses. The production of perbromates salts has also been pointed, although in this case only preliminary results are shown. In every case, it has been observed two marked trends in the process efficiency as function of the current density applied. This fact can be explained in terms of the contribution of hydroxyl radicals in the oxidation mechanisms that occur on diamond surfaces. Results obtained in this work also allow explaining the influence of the electrolyte salt on the efficiency of the electrochemical oxidation of wastewaters.

Keywords Electrosynthesis · Oxidants · Boron doped diamond

1 Introduction

During the recent years, many works have been focused on the study of electrochemical oxidation with diamond anodes as an alternative technology for the treatment of a great variety of wastewaters. Compared with other electrode materials, conductive-diamond has shown a higher chemical and electrochemical stability, and also a higher current efficiency in many oxidative processes. In addition, the high overpotential for water electrolysis is the more important property of conductive-diamond in the processing of aqueous solutions. This electrochemical window is large enough to produce hydroxyl radicals with high efficiency, and this species seems to be directly involved in the oxidation mechanisms that occur on diamond surfaces.

Thanks to these good properties, the use of conductive diamond in the electrochemical treatment of wastewaters has allowed achieving great results (in both efficiency and yield) in comparison to other electrodes materials [1–10]. Likewise, as it has been reported better results are obtained when supporting electrolytes (such as chloride, sulphate...) are added to the reaction system to increase the conductivity of the solution. In these cases, besides hydroxyl radicals oxidation mechanism, the global oxidation process in conductive-diamond anodes is known to be complemented by mediated oxidation by other oxidants electrogenerated on the surface from the electrolyte salts [11, 12]. This fact is not observed when other electrodes are used. From this observation, electrochemical oxidation with conductive-diamond anodes can be considered as a very promising technology in the electrosynthesis of powerful oxidants.

In this point, during the recent years, some studies have been focused on the use of diamond electrodes for the synthesis of oxidants that can be difficult to be generated by more usual synthesis methods. Thus, several studied have

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been published in which the generation of, peroxodiphosphate [13], peroxomonophosphate [14], peroxodisulphates [15], ferrates [16–18] and oxoanions of chlorine [19–22] by electrochemical techniques are described.

The aim of this work is to increase the knowledge about the production of different oxidants with conductive diamond electrode, comparing the results obtained in the production of several known oxidants in terms of the possible mechanisms that explain their formation, and giving some new information about new possible oxidants that can be produced with this technology.

2 Experimental

2.1 Analytical procedures

The oxidants produced were determined by titration. To measure peroxomonophosphate and peroxodisulphate, I_2/I^- assays were performed. This technique quantifies by potentiometric titration with thiosulphate in acid media all the oxidants capable of oxidizing I^- to I_3^- . To measure peroxodiphosphate, Fe^{2+}/Fe^{3+} assays were performed. This technique quantifies by titration with permanganate in acid media all the oxidants capable of oxidizing Fe^{2+} to Fe^{3+} . The concentration of ferrate was analyzed by the chromite method [23]. The soluble iron concentration was measured using an Inductively Coupled Plasma LIBERTY SEQUENTIAL VARIAN according to a standard method (Plasma Emission Spectroscopy).

The chlorine species were determined by ion chromatographic (column, Metrosep A Supp 4; mobile phase, 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$; flowrate, 1 mL min^{-1}), in the case of hypochlorite, the peak of chromatogram interfere with the chloride peak, therefore, the determination is realized by titration with As_2O_3 in NaOH 2 M.

Due to the non-commercial availability of perbromates standards, the concentration of this species was followed by titration of the total oxidants and by ionic chromatography (column, Metrosep A Supp 4; mobile phase, 20 mM $PhONa$; flowrate, 1 mL min^{-1}).

2.2 Electrochemical cell

The electrosynthesis was carried out in a double-compartment electrochemical flow cell. A cationic exchange membrane (STEREOM L-105) was used to separate the compartments. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm^2 each and an electrode gap of 15 mm. The anolyte and the catholyte were stored in dark glass tanks and

circulated through the electrolytic cell by means of a centrifugal pump. A heat exchanger was used to maintain the temperature at the desired set point. The pH was monitored by means of the WTW-InoLab pHmeter.

2.3 Experimental procedures

Bench scale electrolyses under galvanostatic conditions were carried out to determine the influence of the main parameters in the process. The anolyte and the catholyte consisted of solutions of K_3PO_4 (0.5 M to 2 M), H_3PO_4 (0.5 M to 2 M), Na_2SO_4 (1 M to 2 M), NaOH (5 M to 14 M) with $Fe(OH)_3$ for the synthesis of peroxodiphosphate, peroxomonophosphate, peroxodisulphate and ferrates, respectively. In the case of chlorine compounds, the raw material consists of a solution of NaCl 0,1 M and in the perbromate production, the initial solution study is $KBrO_3$ 0,4 M. The range of current densities employed was 130–2,300 $A m^{-2}$ in the synthesis of peroxosalts and 20–130 $A m^{-2}$ in the synthesis of ferrate. The range of temperatures studied was 15–60 °C. The anolyte and the catholyte were stored in dark glass tanks (500 mL) and circulated through the electrolytic cell by means of a centrifugal pump (14 dm^3/h).

3 Results and discussion

Figure 1 shows the effect of the electrolyte salt on the electric charge required to remove 80% of the initial organic load contained in different types of synthetic wastewaters. It can be clearly observed that both, the particular pollutant and the supporting electrolyte, influence significantly on the efficiency of the processes. In addition, contrary to what it

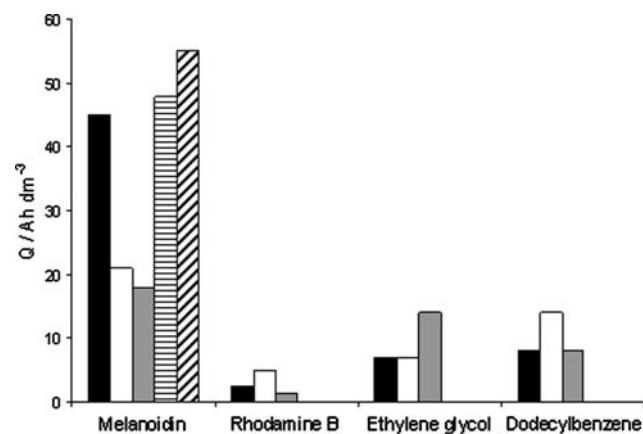


Fig. 1 Electrical charge passed required to remove 80% of the initial organic load contained in several types of synthetic wastewaters (1,000 ppm COD, natural pH, 25 °C, 300 $A m^{-2}$) containing different supporting electrolytes (0.1 M). ■ Na_2SO_4 , □ Na_3PO_4 , ■ NaCl, ▨ HNO_3 , ▩ $HClO_4$

can be expected; chloride media is not the most efficient but the one of the worst media for carrying out electrolysis with diamond electrodes. In fact, it only shows advantages in the treatment of wastewaters polluted with ethylene glycol, but the efficiencies obtained in the other cases shown in the figure are around half of the obtained using other supporting media. This is important because in the electrolyses of wastewaters containing chlorides, it is very well documented [24–26] the effect of the gaseous chlorine, hypochlorite and other chlorine-based oxidants formed anodically during the treatment of the pollutants. Consequently, these results can only be explained if it is taken into account the formation of other powerful oxidants during the electrolyses with conductive diamond electrodes of wastewaters containing different salts. These oxidants can improve the results of the electrolyses, oxidizing chemically the organic matter contained in the wastewater [6, 12, 27–31].

Figure 2 shows the formation of oxidants during the electrolysis of solutions of different salts. Oxidants have been quantified by a standard titration procedure. It is observed that within all media, the formation of significant amounts of oxidants is obtained. All these oxidants are relatively—stable (additional measurements were carried out at least 90 min after the sample collection to confirm stability), but the final concentration and the efficiency of the processes are very different, being greater in chloride, sulphate and alkaline phosphate media and smaller in acid phosphate and iron media. In every case, the presence of significant amounts of ozone, peroxocarbonates or hydrogen peroxide was not found. Just on the contrary, by different techniques some interesting oxidants were

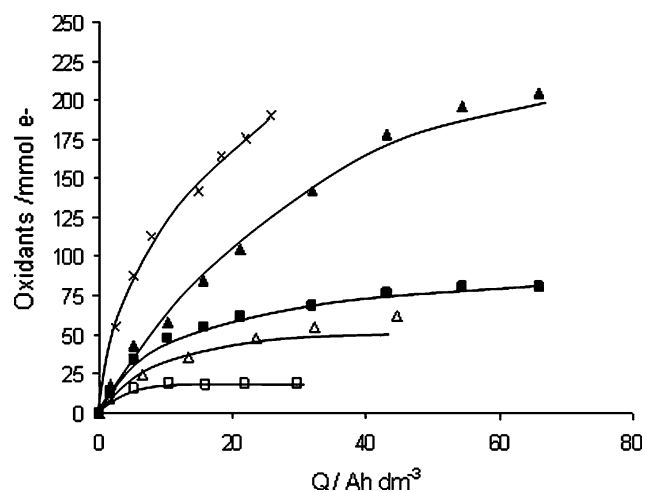


Fig. 2 Variation of the concentration of stable oxidants with the electrical charge passed during the BDD-electrolysis of aqueous solutions containing different supporting electrolytes. (Δ) 1 M H_2SO_4 ; pH 2, $1,000 \text{ A m}^{-2}$, 10°C ; (\blacktriangle) 1 M K_3PO_4 , pH 12.5, $1,000 \text{ A m}^{-2}$, 10°C ; (\blacksquare) 1 M H_3PO_4 , pH 1.5, $1,000 \text{ A m}^{-2}$, 10°C ($[\text{ox}] \cdot 10^2$); (\square) 10 M KOH + iron powder, $1,000 \text{ A m}^{-2}$, 30°C ($[\text{ox}] \cdot 10^2$); (\times) 0.1 M NaCl, pH 10, 300 A m^{-2} , 35°C

identified such as peroxophosphates, peroxosulphates, ferrates and a mixture of oxoanions of chlorine, for phosphate, sulphate, iron and chloride media, respectively. Therefore, these results seem to validate the formation of oxidant species during the electrolyses of wastewaters, and they also confirm the feasibility of using BDD anodes for the synthesis of stable oxidants that can not be easily generated using other electrodes or by other more usual techniques.

It is also important to notice the changes in the concentration of oxidants with the electrical charge passed during each electrolysis. As it can be observed, the concentration of oxidants increases progressively until achieving a constant value for a given electrical charge passed. This decrease of the generation rate can be explained in terms of a progressive decrease in the efficiency of the process due to both, mass transfer limitations (in the batch system studied the concentration of reactant decreases continuously) or by some sort of electrochemical or chemical destruction of the oxidants formed (stability of the oxidant). A clear example of this explanation is the lower efficiency of the electrogeneration of oxidants during the electrolysis of phosphate solutions at acidic pH if compared to that obtained at alkaline conditions. According to literature, this is related to the nature of the oxidant electrogenerated in both cases [13, 14]. Thus, the most important oxidant reagent produced in the electrolyses of phosphates solutions at alkaline pH is peroxodiphosphate ion ($\text{P}_2\text{O}_8^{4-}$). This reagent shows a great stability at these alkaline pH conditions. On contrary, peroxomonophosphoric acid (H_3PO_5) is the primary oxidant produced at acidic pH. This is a very reactive species and it could suffer a significant rapid chemical decomposition.

It is also remarkable the low efficiency obtained in the electrogeneration process from the electrolysis with BDD of iron hydroxide solutions. This behavior was observed in all the experiments carried out with this electrolyte [17, 18] and it could be related to the available concentration of soluble iron (III) species. This fact influences strongly the performance of the process due to the low available amount of iron (III) ready to be oxidized in the reaction system. The small concentration of soluble iron species can lead to a diffusion-controlled rate of the oxidation process, and hence it can explain the significant decrease in the oxidation rate. Thus, it can be suggested that the small amounts of available iron can limit markedly the efficiency of the electrosynthesis process.

A last point that should be marked from Fig. 2 is the formation a mixture of oxoanions of chlorine in different oxidation states during the BDD-electrolysis of chloride solutions. In this context, Fig. 3 shows the variation of the concentration of the main oxidant species generated during the electrolysis of a 0.1 M NaCl solution. As it can be observed, hypochlorite, chlorite and chlorate are the species produced in higher concentrations. Likewise, from a

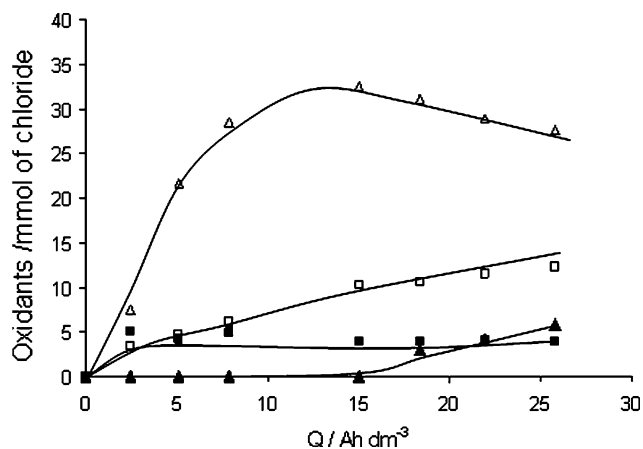


Fig. 3 Variation of the concentration of chloride species electrogenerated during the BDD-electrolysis of NaCl aqueous solutions (0.1 M, pH 10, 300 A m⁻², 35 °C). (Δ) ClO⁻; (■) ClO₂⁻; (□) ClO₃⁻; (▲) ClO₄⁻

given electrical charge passed, significant amounts of perchlorate begin to be detected in the reaction system. At the same time, the concentration of species of lower oxidant stage starts to decrease. These results are opposite to those obtained with other electrodes such as DSA. As it is well documented [32], DSA electrodes can be successfully used for the electrochemical generation of hypochlorite, although they are not able to attain significant concentrations of perchlorate salts.

At the light of this observation, it can be established that conductive-diamond allows great improvements in the synthesis of oxidant reagents as compared to more usual electrodes. This is important because this electrode could be used for the synthesis of oxidants that up to now have been difficult to obtain with classical techniques. In this way, Fig. 4 shows preliminary results about the production of perbromate during the oxidation of bromate solutions at

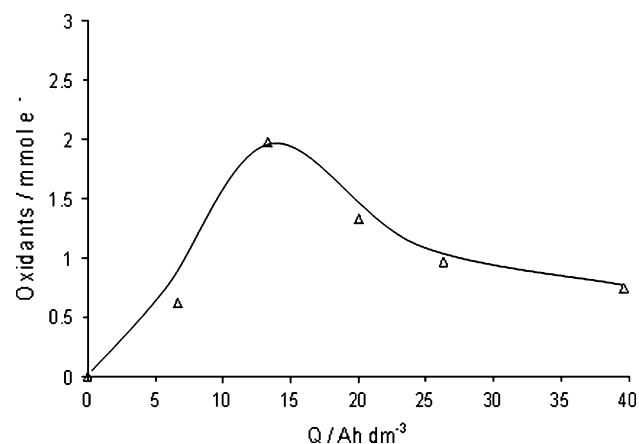


Fig. 4 Variation of the oxidant concentration with the electrical charge passed during the BDD-electrolysis of aqueous solutions containing bromate (0.4 M, pH 10, 641 A m⁻², 45 °C)

strongly alkaline media. It can be easily verified that conductive-diamond allows the further oxidation of bromate ions, giving to the formation of Br(VII) species. This observation is a very important insight because, to the authors' knowledge, the electrochemical generation of perbromate has not been previously reported by electrochemical methods in aqueous media. However, at the present moment the low concentration attained and the low current efficiency warning about the use of this electrochemical technique as a promising synthesis method. So, further studies must be done to establish the optimum operating conditions that allow improving the current efficiency and the generation of large amount of perbromate.

Another very interesting point that should be mentioned in this work is the fact that the voltammetric behaviours are also completely different (Fig. 5) and within the region of supporting electrolyte stability, it is only observed direct oxidation of the salt ions in the cases of alkaline phosphate and chloride (irreversible anodic oxidation peaks). However, in the other cases a small shoulder can be clearly observed in the water oxidation region. Likewise, in the case of sodium hydroxide solutions, it can be observed that the presence of iron favour a slight shift of the oxygen evolution toward lower anodic potential. This suggests that in every case, oxidants can be produced by direct electrolyses from the salts contained in the solutions. This observation is supported by the fact that the previously marked oxidation potentials appear around those expected from the standard values reported in the literature (1.48, 2.12, 2.07, 2.20 V vs.

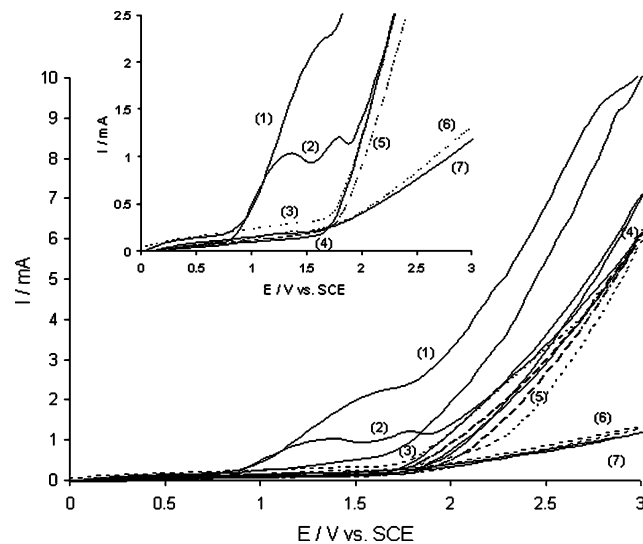
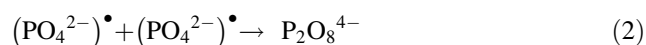


Fig. 5 Cyclic voltammograms on BDD anodes of different electrolytes. Auxiliary electrode: stainless steel AISI 304. Reference electrode: SCE. Scan rate: 100 mV s⁻¹. (1) 0.1 M KH₂PO₄, pH 12; (2) 0.1 M NaCl, pH 12; (3) 0.1 M Na₂SO₄, pH 2; (4) 0.1 M NaCl, pH 2; (5) 0.1 M KH₂PO₄, pH 2; (6) 0.001 M NaOH + Fe(OH)₃; (7) 0.001 M NaOH

NHE for hypochlorite, peroxodisulphate, peroxodiphosphate and ferrates, respectively) [15, 33–35].

It is important to point out that the formation of stable oxidants is not usually a direct electrochemical process but a sequence of electrochemical and chemical stages. A clear example is the production of peroxodiphosphate. In these cases, the electrochemical reaction leads to the formation of the peroxophosphate radical (Eq. 1) which is responsible of the peak observed in the voltammogram. The later combination of peroxophosphate radicals allows the production of the more stable peroxodiphosphate anion (Eq. 2) [36].



However, recently it has been also demonstrated the production of hydroxyl radicals [37] during the electrochemical oxidation of water solutions with diamond electrodes (Eq. 3).



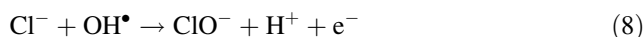
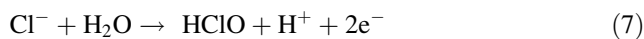
This is a very important point, because these powerful oxidants can also promote the formation of stable oxidants. An example of this mechanism is the formation of the peroxosulphate radical proposed in Eq. 4. This radical can be chemically combined with other radicals to yield peroxodisulphate anion (Eq. 5).



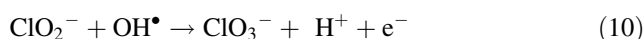
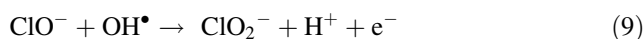
Likewise, the action of hydroxyl radicals can help to explain the formation of other stable oxidants such as the monoperoxophosphoric acid (Eq. 6)



In the oxidation of chloride solutions the hydroxyl radical can also play an important role, because both, the direct and the mediated oxidation mechanisms have been demonstrated (Eqs. 7 and 8).

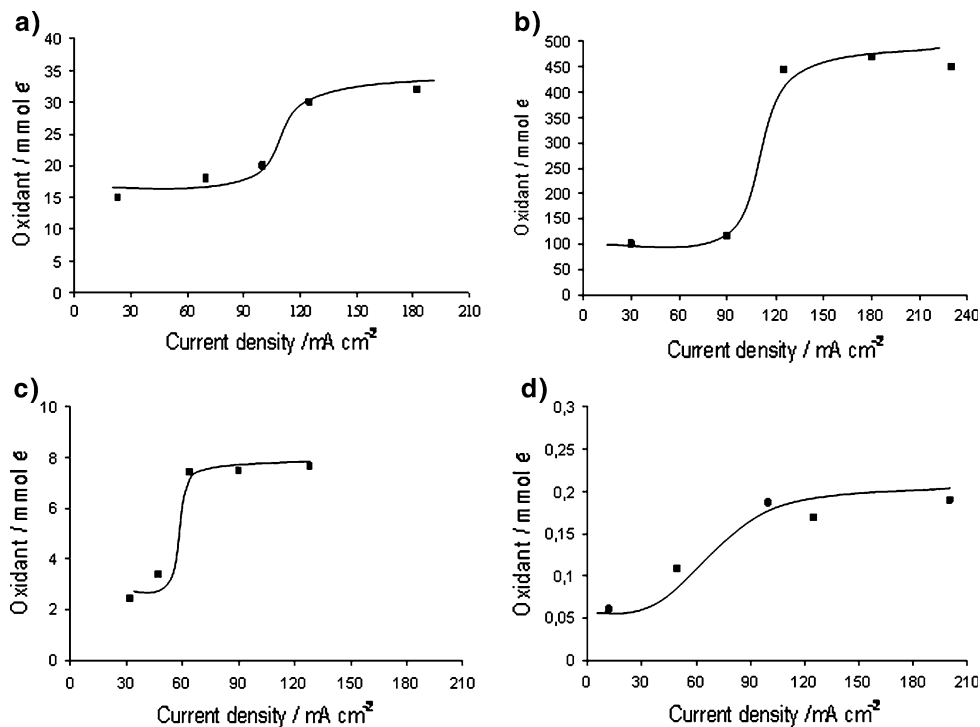


However, the significant electrochemical production of perchlorate with conductive diamond electrodes has to be explained by the effect of the hydroxyl radicals according to Eqs. 9–11. This may allow explaining the impossibility of formation of perchlorates with other electrode materials.



The effect of the hydroxyl radical has to be noticed not only in the product distribution but on the efficiencies of the bulk electrolyses. This can be clearly observed in Fig. 6, which compares the production of different oxidants

Fig. 6 Variation of the maximum oxidant concentration with the current density, in the electrolysis of different supporting electrolytes. **a** 1 M Na_2SO_4 , pH 2, T: 10 °C; **b** 1 M KH_2PO_4 , pH 12.5, T: 10 °C; **c** 1 M KH_2PO_4 , pH 2.5, T: 10 °C; **d** $\text{Fe}(\text{OH})_3$ solutions, 10 M KOH; T: 30 °C



for a given specific current charge passed as a function of the current density used in the galvanostatic electrolyses.

As it can be observed, the concentration of oxidants generated strongly depends on the current density and it suffers a huge increase in every case when the current density increase over $1,000 \text{ A m}^{-2}$, leading to two different efficiency zones. In this point, it is important to note that although the experiments were carried out galvanostatically, the cell potential was observed to be almost constant during all the experiments, and that the boundary current density may correspond to the anodic potential in which hydroxyl radicals can be formed massively in the system. Thus, in the essays carried out below the water oxidation potential, the generation of hydroxyl radical (Eq. 3) does not take place. In these cases, the direct mechanism should be the only responsible of the oxidant generation and, therefore, lower efficiencies are obtained. On the other hand, at higher potentials, both direct and hydroxyl radical mediated mechanisms contribute to the oxidant generation and therefore, the process is more efficient. The small shifts observed in the value of the boundary current densities for different experiments can be easily explained taking into account that the four series were not carried out simultaneously. Thus, small modifications in the electrochemical cell assemblage (wirings, electrodes contacts, etc.) produced modification in the cell current–potential relationship.

4 Conclusions

From this work, the following conclusions can be drawn:

- The electrochemical oxidation of wastewaters with conductive diamond electrodes is strongly influenced by the salts contained in wastewaters. This is due to the formation of oxidants during the treatment process. These oxidants can improve the results of the electrolyses, oxidizing chemically the organic matter contained in the wastewater.
- Conductive diamond electrolyses allows to produce stable oxidants that can not be easily synthesized using other electrodes or by other more usual techniques. Ferrates, peroxosulphates and peroxophosphates are among this type of oxidants.
- The electrolysis of chloride solutions leads to the formation of a mixture of oxoanions of chlorine, ranging from hypochlorite to perchlorate. The oxidation of bromate solutions leads to the production of perbromate.
- During the production of oxidants, two marked trends in the process efficiency are obtained as function of the current density applied. This fact can be explained in

terms of the contribution of hydroxyl radicals in the oxidation mechanisms that occur on diamond surfaces.

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