A comparison between flow-through cathode and mixed tank cells for the electro-Fenton process with conductive diamond anode

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Abstract

This work focusses on the production of hydrogen peroxide and in the removal of bromacil by the electro-Fenton process using two different electrochemical cells: mixed tank cell (MTC) and flow-through cell (FTC). Both cells use boron doped diamond (BDD) as anode and carbon felt as cathode to promote the formation of hydrogen peroxide. In the case of the MTC, two surface area ratios, $A_{cathode}$ / A_{anode}, have been used. Results show that the H_2O_2 produced by MTC and FTCPSC increases with the time until a stabilization state. For the FTCPSC, the average hydrogen peroxide concentration produced increases progressively with the current, while for MTC the maximum values are found in applying very low current densities. In addition, the FTCPSC provides higher concentrations of hydrogen peroxide for the same current density applied. Regarding the MTC, it can be stated that the higher the area of the cathode, the higher is the amount of H_2O_2 produced and the lower is the cell voltage (because of a more efficient current lines distribution). The initial oxidation of bromacil is very efficiently attained being rapidly depleted from wastewater. However, the higher production of hydrogen peroxide obtained by the FTCPSC cell does not reflect on a better performance of the electro-Fenton process. Thus, bromacil is better mineralized using the MTC cell with the lowest cathode area. This observation has been explained because larger concentrations of produced hydrogen peroxide seems to benefit the oxidation of intermediates and not the mineralization.

Keywords:

Flow-through; mixed tank; electro-Fenton; diamond anodes; bromacil; hydrogen peroxide

Highlights

- Rapid depletion of bromacil was obtained using MTC and FTC cells
- Significant differences in mineralization efficiency were found for MTC and
- The MTC is more efficient for the electro-Fenton process than the non-optimized FTC
- FTC is more efficient for the production of hydrogen peroxide than MTC
- Higher production of hydrogen peroxide in FTC is not beneficial to electro-Fenton

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1. Introduction

Production of strong oxidants for being used in environmental applications and degradation of pollutants does not always need for the same cells, despite in both cases a huge production of oxidants is demanded (Sirés et al., 2014). The use of the cathode to promote the formation of hydrogen peroxide has been postulated as an important breakthrough concept in environmental technology (Scialdone et al., 2015; Petrucci et al., 2016), because it may help to increase the efficiency of the degradation of pollutants (Martínez-Huitle et al., 2015; Martínez-Huitle and Panizza, 2018). It is particularly important in the development of electro-Fenton process, because it allows to provide continuously the hydrogen peroxide by reduction of oxygen contained in air (Yu et al., 2014; Oturan and Oturan, 2018). This process is typically carried out in mixed tank cells with a vigorous stirring in order to favor transport processes (Ding et al., 2012; Isarain-Chavez et al., 2013; Sarkka et al., 2015). To promote the formation of hydrogen peroxide, gas diffusion electrode (GDE) or other carbon electrodes with a high volumetric area are used (Brillas et al., 2009; Brillas, 2014). In the second case, aeration with very small bubbles is required to reach a very efficient process (Petrucci et al., 2016). In addition, the relative size of the cathode (with respect to the area of the anode) is another key parameter because the cathodic area does not only affect the capacity of the production of the hydrogen peroxide but also to the reduction of the iron(III) to iron(II) species, which is key for a successful catalysis of the whole process (Sirés et al., 2007).

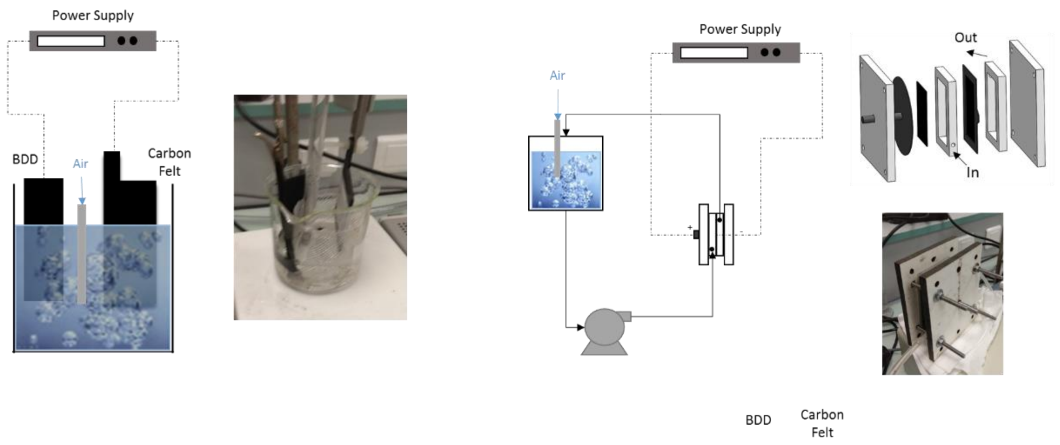
Very recently, a new type of cells has been proposed to produce efficiently hydrogen peroxide. These cells are based on the use of flow-through electrodes instead of single cathodes or GDEs (Salazar and Ureta-Zanartu, 2012; Pérez et al., 2016, 2017a, 2017b, 2018a, 2018b, 2018c; Rodriguez et al., 2018). In addition, oxygen is provided by using the highly effective Venturi aerator and their combination with other two important concepts, the use of high pressure and the microfluidic (Geng and Duan, 2010), have allowed to reach productions of hydrogen peroxide as high as 750 mg L^{-1} with high current efficiencies and working with current densities over 50 mA cm^{-2}.

The success in the use of these cells is an attention call indicating perhaps the focus on the research in environmental electrochemistry is not well placed. Thus, typically, more attention is paid to electrodes than to cell design, while very often this latter input is more important to achieve a highly efficient process (Salazar and Ureta-Zanartu, 2012; Borras et al., 2013; Moreira et al., 2013; Panizza et al., 2013; Scialdone et al., 2013; Yu et al., 2015).

This paper focused on the comparison of two concepts of cell design for electro-Fenton process: the stirred tank cell and the single pass with flow-through cathode cell. This latter cell was found to produce hydrogen peroxide in a very efficient way when combined with Venturi and high pressure (Pérez et al., 2018b) although in this work, it is going to be compared barely in the same conditions of the mixed tank, that is, with the same oxygen supply, at the same operation pressure and with a standard cell design (not microfluidic). In addition, in order to point out the relevance of the ratio of electrodes surfaces, $A_{cathode}/A_{anode}$, the same tests are going to be carried out with a mixed tank cell in which this parameter is changed by 3.4 times. Both the production of hydrogen peroxide in these non-optimized conditions and the degradation of a model persistent pollutant, bromacil, herbicide selected due to its potential carcinogenicity, liver toxicity and its occurrence in natural water bodies, will be studied to shed light on the goal of the present work.

2. Materials and Method

Fig. 1 shows the two cells used in this work. Fig. 1a shows the conventional mixed tank cell (MTC) typically used for electro-Fenton processes, for which air is dosed directly by means of a diffuser connected with a fisheries air pump, which attains at the same time a good mixing (Diagne et al., 2007). Fig. 1b shows the flow–through cell (FTC)for which the same aerator was used and in which the flow direction of the waste during the treatment is indicated (Moraleda et al., 2016; Llanos et al., 2018). No Venturi, no microfluidic and no high pressure is applied, that is, the bare configuration is tested in order to do not favor the second cell with additional very efficient processes. Just the Flow-through cathode is going to be responsible for the differences found. In both cases, the geometrical area of the cathode (carbon felt from SFL Group, Germany) was 32.0 cm^2, which was higher than the geometrical area of the anode (12.2 cm^2). As well, in both cases the anode was boron-doped diamond supplied by Adamant (Switzerland) (currently NeoCoat, France). For comparison purposes, prototype 1 was also tested with a larger cathode of 108 cm^2, which means that the cathode/anode area ratio was enlarged from 2.6 to 8.9. All current densities are referred to the anode area.



a) prototype 1: Mixed tank cell.

b) Prototype 2: Flow –through cell.

Fig. 1. Electrochemical cells compared in this work

For the production of hydrogen peroxide, the supporting medium was a solution of Na_2SO_4 (20 mM). For the electro-Fenton process, wastewater consists of synthetic solutions containing Bromacil (0.1 mM). As catalyst it was used 0.1 mM Fe^{2+} and pH around 2.5 – 3.0. Test duration was 8 h. Current was modified within the range from 0.1 to 1.2 A.

The decay kinetics of bromacil was followed by high-performance liquid chromatography (HPLC). The analyses were carried out by Merck-Hitachi Lachrom equipped with a RP-18 (Merck, France), 5 µm, 250 mm x 4.6 mm column at 35 ºC and coupled with a L-7455 UV-Vis detector selected at optimum wavelength of 258 nm. The mobile phase was composed of methanol-water 70:30, each solution containing 1 % acetic acid. A flow rate of 0.5 cm^3 min^{-1} was used. Under these conditions, bromacil exhibited a well-defined peak retention time of 2.5 min. The analysis time was 30 min. The Total Organic Carbon (TOC) of treated solutions was determined on a Shimadzu VCSH analyzer. The injecting volume was 4 cm^3, making measure in triplicate. The analysis of TOC was based on the production of CO_2 from the combustion of organics (680 ºC), which was then analyzed by infrared method. Hydrogen peroxide was determined by potassium titanium (IV) using the oxalate method (Eisenberg, 1943). The absorbance was determined at 410 nm by an Agilent 300 Cary series UV-vis spectrophotometer. The titanium solution was supplied by Fluka.

3. Results and Discussion

Fig. 2 shows the changes in the production of hydrogen peroxide with the two cells evaluated in this work. Fig. 2a gathers the evolution of the concentration of hydrogen peroxide when an electric current of 0.8 A is applied in discontinuous electrolysis for 8 h, meanwhile Fig. 2b shows the average hydrogen peroxide concentration produced within an 8h-electrolysis for increasing values of current density. It has to be taken into account that the range of intensities used in this work was chosen in order to optimize the role of the diamond anode (8-100 mA cm^{-2}) and it is particularly high for the efficient production of hydrogen peroxide, as compared to other ranges for which this production is optimized according to the literature (10-50 mA cm^{-2}) (Yu et al., 2015; Pérez et al., 2016, 2017b, a, 2018b, a).

In the case of the MTC, two cathode sizes were used leading to $A_{cathode}/A_{anode}$ ratios of 2.6 (small cathode, SC) and 8.9 (large cathode, LC). As expected, the concentration of hydrogen peroxide increases during the electrolysis up to a certain value, from which it remains approximately constant or even decrease. The stabilization is explained in terms of the equilibrium reached between formation (Eq. (1)) and depletion of hydrogen peroxide, as this latter reaction depends on the concentration of this species in the bulk. The destruction of the hydrogen peroxide can be caused by further reduction on the cathode into water (Eq.(2)) or by oxidation in the anode into oxygen (Eq. (3)). In addition, it can also be destroyed by thermal decomposition (Eq. (4))

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \qquad (1)$$

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2\ H_2O \qquad (2)$$

$$H_2O_2 \rightarrow O_2 + 2e^- + 2\ H^+ \qquad (3)$$

$$H_2O_2 \rightarrow H_2O + 1/2O_2 \qquad (4)$$

Likewise, other oxidants produced on the anode (such as peroxosulfates) may oxidize hydrogen peroxide to oxygen, contributing more to their depletion and explaining the final decrease observed, which is especially important in the case of the mixed tank with the larger cathode and, in lower extension, in the flow-through cell (FTC).

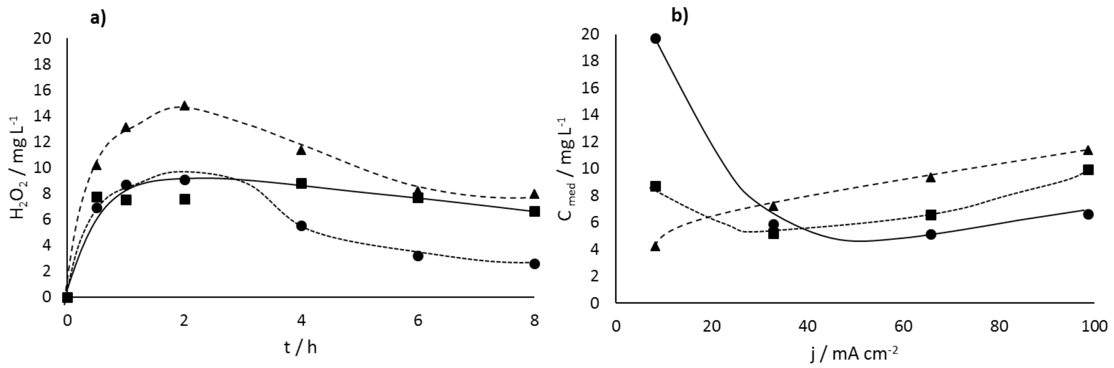


Fig. 2. Production of hydrogen peroxide with the two cells tested. a) Changes in the concentration of hydrogen peroxide at 800 mA. b) Average hydrogen peroxide concentration produced within an 8h-electrolysis. MTC-SC (■); MTC-LC (●) and FTC (▲). Current densities are calculated vs anode area.

The role of current density is reflected in Fig. 2b, where it can be observed that the maximum average concentration of hydrogen peroxide is reached by the mixed tank cell equipped with the large cathode (MTC-LC) operating at low current (where destruction is not favored). In this cell, the average production of hydrogen peroxide decreases initially when increasing the current density and then, it increases slightly. These changes indicate a modification in the mechanisms involved in the production of hydrogen peroxide. At very low current densities only the cathode affects significantly to the production. Opposite, at higher current densities, the oxidants produced on the anode surface may be affecting the process either in a positive way (formation of additional hydrogen peroxide by combination of hydroxyl radicals formed anodically, Eqs. (5) and (6)) or in negative way (oxidizing the cathodically formed hydrogen peroxide to oxygen on the anode surface or by consumption of other oxidants electrogenerated in the anode).

$$H_2O \rightarrow \bullet OH + H^+ + e^- \qquad (5)$$

$$2\ \bullet OH \rightarrow H_2O_2 \qquad (6)$$

The influence of the current density on the production of hydrogen peroxide is not the same in the FTC. In this case, an increase in the production is observed in the complete range evaluated, with average concentrations that are over those produced in the MTC and that lead to a more efficient production of hydrogen peroxide, in particular when using current densities over 16 mA cm^{-2}. This current density is just in the range of values proposed in previous works for the efficient anodic production of hydroxyl radicals (Cañizares et al., 2007), indicating the significance of the anode in keeping a high concentration of hydrogen peroxide. Thus, in that work, it was shown how operating at low current densities with diamond anodes makes the direct oxidation be the controlling mechanisms while over a given current density (15 mA cm^{-2}) oxidation by hydroxyl radicals begins to control the process.

In order to check if the anode material can have an influence on the production of hydrogen peroxide, additional tests were carried out in the MTC equipped with small cathode (MTC-SC) using different anode materials (BDD and carbon cloth) and working at low current densities. Thus, Fig. 3a indicates the significance of the anode material on the production of hydrogen peroxide by comparing the average production of hydrogen peroxide for the MTC-LC at the lowest current densities used.

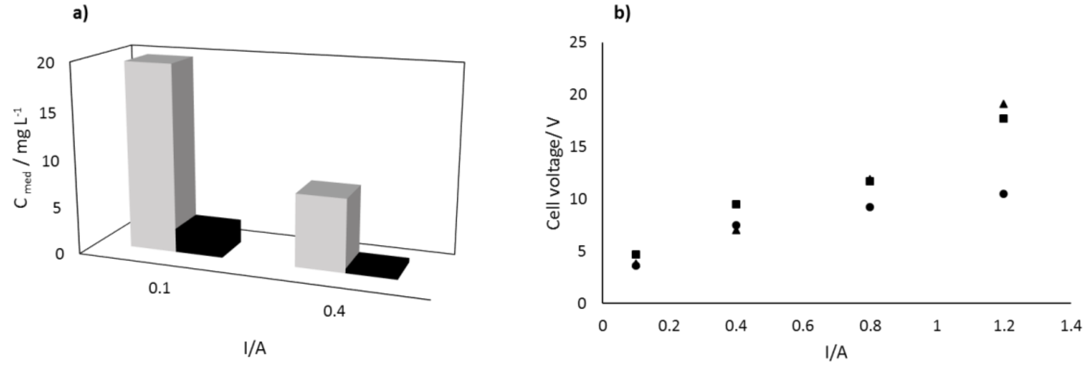


Fig. 3. Other factors affecting the production of hydrogen peroxide. a) Comparison between the average concentrations of hydrogen peroxide obtained after 8-h discontinuous electrolysis with BDD (■) and with carbon cloth (■) as anodes. b) Influence of the current intensity on the resulting cell voltages. MTC-SC (■); MTC-LC (●) and FTC (▲).

The most important observation is that production of hydrogen peroxide decreases very importantly when using carbon cloth instead of BDD, indicating a higher destruction of the hydrogen peroxide produced with the carbon cloth anode than with the BDD. This may indicate that the oxidants produced on the anode (which are negligible in the carbon cloth electrode) can help to stabilize partially the concentration of hydrogen peroxide and that when no hydroxyl radicals are formed, hydrogen peroxide is consumed in the anode. Thus, it can compete with organic matter for being oxidized and lead to less efficient processes.

Fig. 3b shows the resulting cell voltages of the two cells for the different current densities applied. As seen, no important differences are observed between the MTC and the FTC when the same size of cathode is used. This can be explained because, despite the cells are very different, the interelectrode gap is very similar and the electrolyte used is the same. In addition, the use of a larger cathode has a positive influence on the cell voltage leading to lower values, which can be explained because of a more effective distribution of the current lines.

Once evaluated the H_2O_2 generation with the two cells, their performance is going to be compared for the degradation of bromacil by electro-Fenton (EF) using 0.1 mM Fe^{2+} as catalyst. Fig. 4 shows the changes in the concentration of bromacil during the electro-Fenton with the two cells. As it can be observed, the concentrations decrease down to zero very quickly at the beginning of the treatment (Fig. 4a). In the case of the FTC, it can only be seen concentrations over the detection limit of the HPLC for the lowest intensity and for reaction times shorter than 1 h (Fig. 4b). In the case of the MTC, the concentrations of bromacil also decrease very rapidly, although slower than in the case of the FTC. This can be explained by the higher concentration of hydrogen peroxide produced in this latter cell. The oxidation of the functional groups of bromacil is a simple process, which can be easily carried out by the hydrogen peroxide either alone or activated by the iron (II). Hence, the higher the concentration of hydrogen peroxide, the higher is the oxidation rate of bromacil expected.

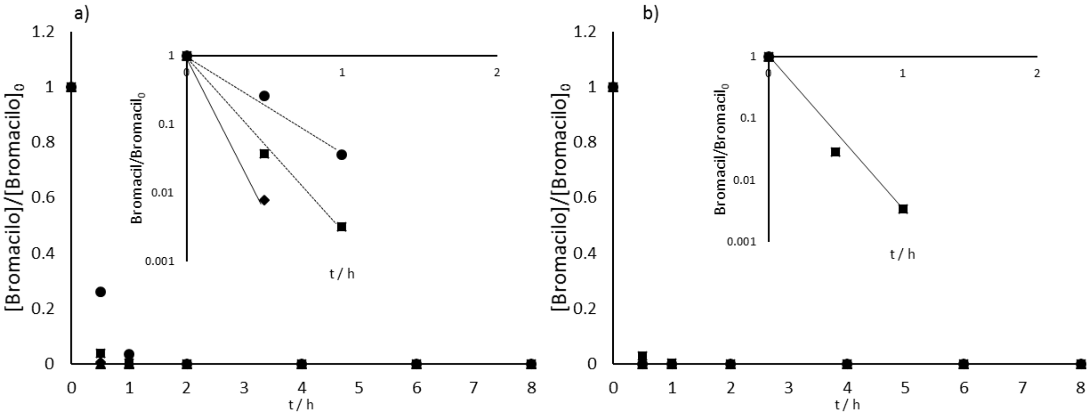


Fig. 4. Changes in the concentration of bromacil during the electro-Fenton with a) the MTC-SC and b) the (FTC) at 0.1 A (■), 0.4 A (●), 0.8 A (▲) and 1.2 A (◆). Inset: Semi-logarithmic plot for obtaining pseudo-first order kinetic constants.

Anyway, bromacil is depleted from the experimental system with the two cells. However, the better performance of the FTC reverses when the mineralization is evaluated (Fig. 5). As seen, higher mineralization rates are obtained in the MTC than in the FTC and this can be explained because hydrogen peroxide is not effective in the complete mineralization of the bromacil but just in its conversion into its oxidation intermediates, because the Fenton reagent is not very efficient in the degradation of carboxylic acids. At this point, the higher production of hydrogen peroxide can become negative, because this reagent can compete with the intermediates for being oxidized on the anode surface (direct oxidation mechanisms) and it can also consume part of the oxidants generated anodically. As a clear example, the presence of high H_2O_2 concentration makes the reaction expressed by Eq. (7) competitive with the degradation of organics, thus consuming the hydroxyl radicals and decreasing the overall efficiency of the process. In all cases, hydrogen peroxide can be transformed into the non-efficient oxygen. This reaction became competitive with oxidation of organics when $[H_2O_2]$ becomes high, particularly towards the end of treatment, when the solution contains mainly carboxylic acids for which rate constants are close to that of wasting reaction noted above.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad k = 2.7 \times 10^{7}\ L\ mol^{-1}\ s^{-1} \qquad (7)$$

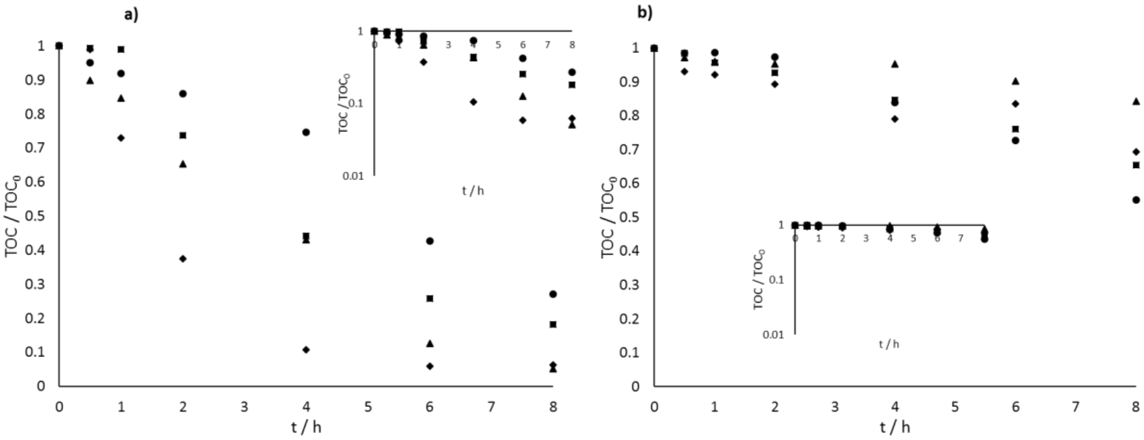


Fig. 5. Changes in the mineralization of bromacil solution during the electro-Fenton with a) the MTC-SC and b) the FTC at 0.1 A (■), 0.4 A (●), 0.8 A (▲) and 1.2 A (◆). Inset: Semi-logarithmic plot for obtaining pseudo-first order kinetic constants.

This consumption of oxidants can also be responsible for the less efficient mineralization in the case of using a larger cathode. Thus, Fig. 6 indicates that the increase in the surface area of the cathode in MTC-LC shows a negative effect on the mineralization, leading to a slower process. The higher the size, the more H_2O_2 generated and this benefits the oxidation of bromacil to intermediate products and not the mineralization.

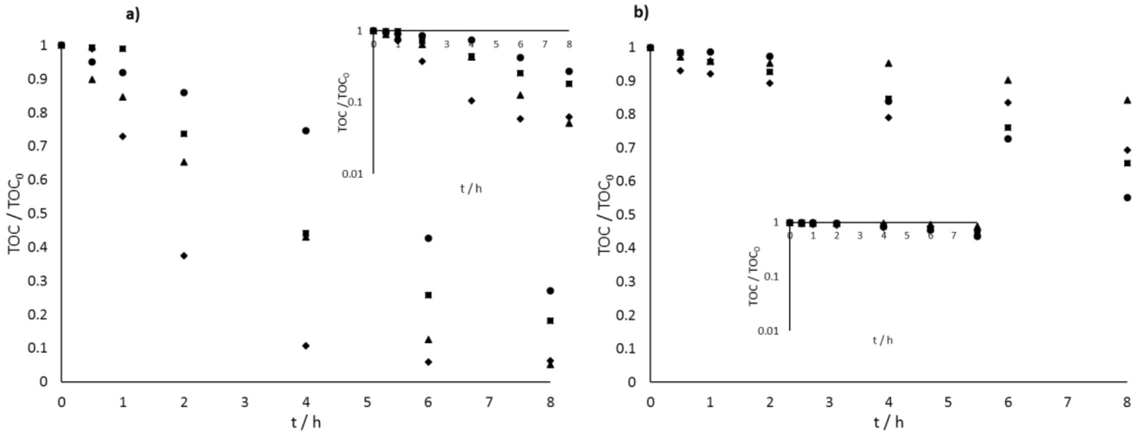


Fig. 6. Changes in the concentration of a) bromacil and b) TOC during the electro-Fenton with the MTC-LC at 0.1 A (■), 0.4 A (●), 0.8 A (▲) and 1.2 A (◆).

On the other hand, in all figures, the semilogarithmic plot of experimental results show a linear trend, indicating that kinetics fit well a first-order model. Values of the kinetic constants obtained are shown in Table 1.

Table 1. First-order kinetic constants for the oxidation and the mineralization of bromacil with the different cells tested in this work.

Intensity (A)	Bromacil degradation (s^{-1})			Mineralization (s^{-1})		
	MTC-SC	MTC-LC	FTSPC	MTC-SC	MTC-LC	FTSPC
0.1	5.90	3.50	5.98	0.21	0.08	0.05
0.4	3.20	*	*	0.14	0.02	0.06
0.8	*	*	*	0.33	0.06	0.02
1.2	9.69	*	*	0.49	0.03	0.04

(*) Bromacil disappeared completely in the first sample, so the kinetic constant could not be calculated.

Hence, the type of reactor has a very important influence on the efficiency of the electro-Fenton process and this opens new ways to optimize this treatment technology. A higher production of hydrogen peroxide does not assure a better performance when the anode used is BDD, because the hydrogen peroxide can compete with the intermediates by oxidation on the anodic surface and consume part of the oxidants generated anodically.

4. Conclusions

From this work, the following conclusions can be drawn:

- The H_2O_2 produced by MTC-SC, MTC-LC and FTC increases with the time until a stabilization state, that can be explained in terms of equilibrium reached between formation and depletion of H_2O_2. For FTC, the average hydrogen peroxide concentration produced increases progressively with the current, while for MTC the maximum values are found in applying very low current densities. Except when working at low current density, the FTC provides higher concentrations of hydrogen peroxide for the same current density applied. Regarding the MTC, it can be stated that the higher the area of the cathode, the higher is the amount of H_2O_2 produced and the lower is the cell voltage (because of a more efficient current lines distribution). BDD show better results than carbon cloth anode because of the high anodic contribution to the formation of H_2O_2.
- The initial oxidation of bromacil is very efficiently attained by the three cell designs and it is rapidly depleted from wastewater. However, the higher production of hydrogen peroxide obtained by the FTCPSC cell does not reflect on a better performance of the electro-Fenton process. Thus, bromacil is better mineralized using the MTC-SC cell. This observation has been explained because larger concentrations of produced hydrogen peroxide seems to benefit the oxidation of intermediates and not the mineralization. Formation of $HO_2^\bullet$ can be

competitive with oxidation of organics when concentration of hydrogen peroxide becomes high, particularly towards the end of treatment, when the solution contains mainly carboxylic acids for which rate constants are close to that of wasting reaction noted above.

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