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Electrolytic synthesis of chloroform from carbon tetrachloride in mild conditions. Laboratory approach

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Abstract

A selective electrochemical synthesis of chloroform from carbon tetrachloride (CT) in mild conditions is studied. The voltammetric results show that in a sodium chloride–ethanol:water (4:1) solvent and using carbon as electrode, it is possible to reduce CT to chloroform with very high selectivity and current efficiency adequate for the developing of an industrial process. The influence in the electrochemical potentiostatic reduction of CT of the pH of anolyte and catholyte using a divided electrochemical "H cell", is also investigated. When, as anolyte, a pH 7-buffered solution was used, hydrolysis of the product (chloroform) was observed as a consequence of the basic pH reached in the catholyte. This hydrolysis was not observed when an acid anolyte was used. No other products other than chloroform were detected. Finally, a galvanostatic electroreduction of CT was carried out in a homemade filter-press reactor at laboratory scale. Good current efficiency and material yield were obtained hydrogen being the only sub-product detected.
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1. Introduction

The increase of the social concern about the pollution caused for the chemical industry activity is the origin of the development of new "greener" processes or even the cause of the suppression of some of them. In this way, new strategies to avoid the introduction of pollutants in the environment are being developed by the chemical industry based principally on: (a) promoting "in situ" recycling of contaminants and (b) developing new environmental-friendly processes.

This need for new and more ecological technologies has encouraged the use of electrochemistry as an environmental-friendly technique. Electrochemical processes also offer an easy control over the advance of the process and only need relatively simple equipment to be carried out [1,2].

Carbon tetrachloride (CT) has become one of the most restricted pollutants and its industrial production has been forbidden by the Montreal Protocol [3] because it is a compound that depletes the ozone layer. However, CT is still produced in big amounts as a sub-product in the synthesis of chloromethanes (chloroform, dichloromethane, and chloromethane). However, because CT cannot be commercialised, it must be destroyed, increasing the cost of production of the other chloromethanes.

Many studies have been devoted to the elimination of CT using a wide range of techniques [4–14] some of them related to the elimination in polluted water [12,13]. However, electrochemical reduction of CT has mainly been studied from a mechanistic or kinetic point of view [15–21]. Recently, some reductive electrolytic experiments, all of them over metallic electrodes and at small scale, have been described [22–24] in which mixtures of products have been obtained, including molecules with 2 or 3 carbon atoms [22]. This fact can be a problem for the developing of an industrial process to economically synthesise other chlorinated compounds.

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Because CT is formed in the industrial synthesis of chloroform, it seems interesting to develop a process to transform CT in this compound and, until we know, no attempt has been made to develop an industrial electrolytic process for this synthesis.

Thus, the aim of the present paper is to study the feasibility of an electrochemical process to synthesise chloroform by reduction of CT as the first step in the development of a new industrial process that allows an effective way to transform CT wastes into useful (at the moment) products that could be commercialised. Due to the industrial scope of this work, especial attention has also been paid to the formation of only one product (chloroform) avoiding the formation of other chloromethanes as it has been reported in other works [21–24].

2. Experimental

2.1. Voltammetric experiments

In order to find the potential window for CT reduction, some voltammetric experiments were carried out using a divided ''H cell'' and a 2055 Potentiostat from Amel with a 175 Universal programmer from EG&G. Catholyte and anolyte were separated by a Nafion 450 cation exchange membrane. As working and reference electrodes, glassy carbon (7 mm^2 area, from Metrohm) and Ag/AgCl were employed. The working electrode was previously polished with 1, 0.3 and 0.05 μm alumina. As catholyte, a mixture of ethanol:water (4:1) (ethanol 96%, from J.T. Baker) and NaCl (0.2 M, from Merck) was employed. As anolyte, an aqueous 0.2 M NaCl was used. Solutions were deareated by bubbling Ar for 15 min. In order to avoid the removal of reactives during bubbling, CT or chloroform (both from J.T. Baker) were added after bubbling to get a final concentration of 0.061 M. Data are not corrected for IR drop.

2.2. Electrolysis experiments

Same cell, apparatus and catholyte solution as in the previous voltammetric experiments were employed. An aqueous 0.2 M NaCl solution buffered to pH 7 with Na_2HPO_4/NaH_2PO_4 (from Merck) or an 0.04 M aqueous solution of H_2SO_4 were the anolytes used.

As cathode and anode, graphitised carbon (6.5 cm^2, from Goodfellow) and Ti/Pt were, respectively, employed. A Ag/AgCl reference electrode was placed near the cathode to measure the cathode potential (potentials are not corrected for junction potential). In order to avoid possible emission of Cl_2 to the atmosphere, the gas formed in the anodic reaction was bubbled through a deposit with 2 M NaOH solution. In order to avoid loss of CT or chloroform during the experiment a reflux

column (0 °C) was connected in the gas exit of the catholyte. Before the electrolysis was started, Ar bubbling during 15 min purged the catholyte without CT. CT was then added to get a concentration of 0.061 M and then, the potential was applied. The current was registered until approximately 1/3 of the theoretical charge (2 F/mol) was circulated. Catholyte was continuously stirred with a magnetic stirrer and samples of 5 ml were taken before and after the electrolysis for analysis.

2.3. Galvanostatic electrolysis in a filter-press reactor

Electrolyses at constant current during 120 min (2 F/mol) were carried out in a homemade divided filter-press reactor (Figs. 1 and 2) with a geometric electrode area of 63 cm^2 and Nafion 450 as separator.

Graphitised carbon (from Goodfellow) and carbon felt (RVC 4002 from Carbone–Lorraine) were used as 2D and 3D cathodes. As anode, Ti/Pt was employed. As catholyte, a 0.2 M NaCl + 0.062 M CT in ethanol:water (4:1) solution was used and as anolyte, an aqueous 0.04 M H_2SO_4 solution. Solutions were pumped using two
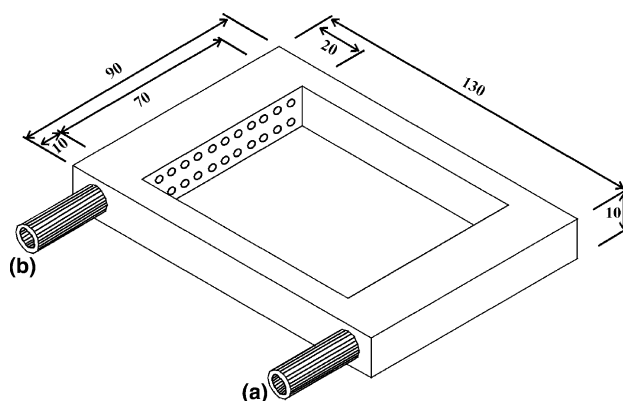
Fig. 1. Schematic representation of one compartment frame for the mod. UA63.10 filter-press reactor: (a) electrolyte inlet port; (b) electrolyte outlet port. Distances are given in mm.
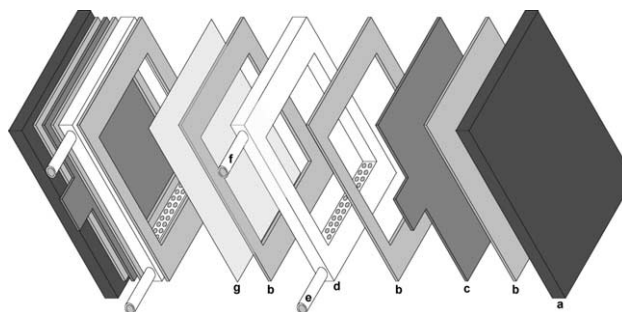
Fig. 2. Schematic representation of the mod. UA63.10 filter-press reactor: (a) end plate; (b) gasket (vyton); (c) planar electrode; (d) catholyte or anolyte frame (nylon); (e) electrolyte inlet port; (f) electrolyte outlet port; (g) Nafion 450 cation exchange membrane.

Plastomec magnetic pumps mod. PO22 at a constant flow rate of 160 L/h. A reflux at 0 °C was connected in the outlet of catholyte in order to avoid loss of CT or chloroform during the electrolysis. Each 30 min, samples of 2.5 ml were withdrawn from the catholyte for quantification via GC, as described in Section 2.4.

2.4. Chemical analysis

Samples were headspace analysed by GC using a HP mod. 5890 Series II GC equipped with a FID detector. A HP Pora Plot Q column (30 m × 0.53 mm, 40 μm film thickness) was used. The head pressure was 35 kPa, and He at flow rate of 1 ml/min and a split of 1:7 was used as carrier gas. The oven temperature was held at 150 °C for 5 min and ramped (2 °C/min) to 177 °C.

The sample was prepared in a 2 ml flask containing 1 ml of electrolysis sample and 50 μl of 0.61 M bromochloromethane (from Aldrich), which was used as internal standard. The flask was hermetically sealed and held at 25 °C for 30 min just before injection. A headspace sample of 50 μl was then injected.

Using the same method, calibration curves for CT, chloroform and dichloromethane were obtained.

3. Results and discussion

3.1. Previous experiences

First of all, some experiments were made in order to check out experimental conditions, electrodes and solvents, to synthesise chloroform as the only reaction product of the reduction of CT (hydrogen is not considered as a final product of the reduction of CT because it can be easily eliminated from the synthesis). Among the solvents studied, ethanol was chosen because only chloroform was obtained being moreover the solubility of CT appropriate for an industrial process. In order to be able to use a low priced electrolyte and increase its solubility, as solvent a mixture of ethanol:water (4:1) was chosen. Addition of water easily provides the protons needed for the reduction of CT to chloroform:

$$CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^- \tag{1}$$
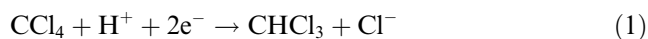
In order to find an optimal background electrolyte for minimizing the ohmic drop in solution as much as possible (decrease of the energetic cost of the synthesis), saturated solutions of some common electrolytes (Table 1) were prepared in ethanol:water (4:1) and their conductivities were measured. Because the saturated sodium chloride (0.2 M) solution has the highest conductivity, being at the same time a very cheap electrolyte, this compound was chosen as supporting electrolyte.

In spite of the fact that metals such as Hg and Pb have the highest hydrogen overvoltage (the hydrogen

Table 1
Conductivity for some saturated solutions of salts in ethanol:water (4:1)

Electrolyte	Conductivity (mS/cm)
Na_2SO_4	0.046
NaCl	7.20
NaOAc	6.59
KCl	3.44

evolution is a competitive reaction with the Cl–R cleavage reaction), carbon was chosen as cathode not only for environmental reasons (Hg and Pb are very toxic) but also because, as a felt, it is a very efficient 3D electrode able to work at high applied currents and at the same time low density currents, increasing in this way the conversion per pass of the reactor and the current efficiency of the process.

As it was said before, in order to fix the window potential of the cathodic reduction of CT, some voltammetric experiments in a H-cell using a glassy carbon cathode were made. Fig. 3 shows the results obtained for
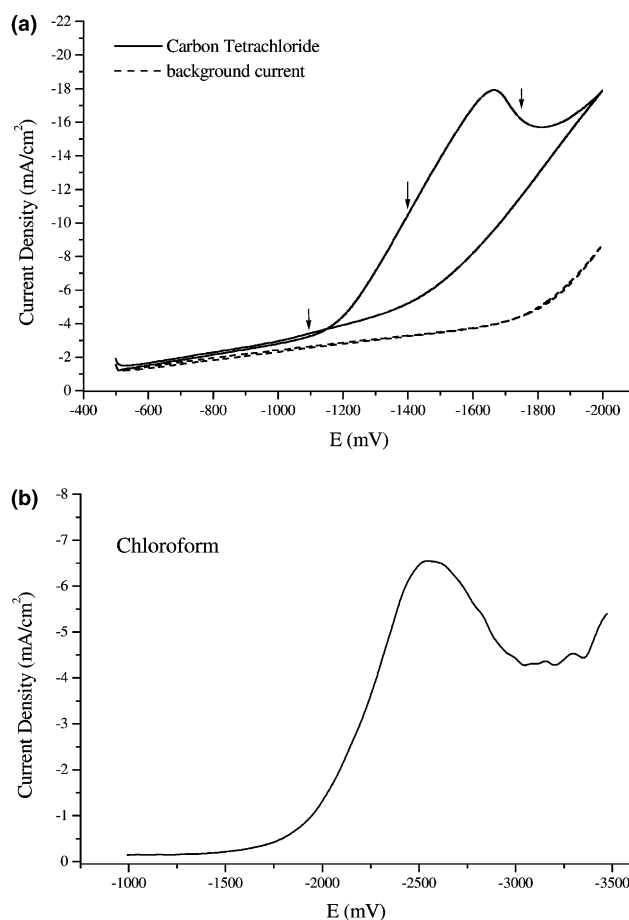

Fig. 3. Linear sweep voltammograms for the reduction of CT (A) and chloroform (B) (both 0.061 M) in ethanol:water (4:1), 0.2 M NaCl. Scan rate: 50 mV/s. Working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/AgCl. Potentials selected to carry out the potentiostatic experiments are marked in the CT voltammogram. Background current has been subtracted in (B).

the reduction of CT and chloroform. No deactivation for the electroreduction was observed and so, this voltammogram was used to select the values of potential to carry out electrolyses at constant potential. Different potentials were chosen in order to check out the behaviour of the cathodic reaction in different regions of the CT reduction curve. As it can be seen in Fig. 3, in ethanol/water solvent, it would be possible to reduce CT without, or very low, formation of dichloromethane, and with an adequate current efficiency (that will increase for low current densities).

3.2. Electrolysis experiments

After the previous voltammetric experiments, some preparative electrolyses in the same electrochemical "H" cell were made. This kind of cell permits to work with catholyte and anolyte solutions separated by a membrane, and it is a good first approach to further experiences with an industrial electrochemical reactor.

As a proton is consumed in the electrochemical reduction of CT (reaction (1)) and the generation of H_2 is a competitive process in CT reduction, the influence of pH was tested. Because our interest is to develop an industrial process, the catholyte composition was fixed as simple as possible, ethanol/water and 0.2 M NaCl, and no other compounds were used. Thus, the initial pH of the catholyte was 6 and two anolytes at different pH were employed. It should be pointed out that no correction for water activity is made for pH measurements.

3.2.1. Potentiostatic electrolysis with a pH 7-buffered anolyte

In the first series of experiences, as catholyte, an aqueous 0.2 M NaCl solution of 0.061 M CT in ethanol:water (4:1) was used. As anolyte, a 0.2 M NaCl solution buffered to pH 7 with Na_2HPO_4/NaH_2PO_4 was employed. With this anolyte, the current from the anolyte to the catholyte was carried out by ionic migration of Na^+ through the cation exchange membrane.

To avoid losses of chloroform and CT, experiments were designed not to last for more than 24 h approximately, that means that, for the less negative applied potential, only 1/3 of the theoretical charge was circulated. This amount of charge was also circulated for electrolysis carried out at the more negative potential. Results of the three experiments carried out at the potentials pointed out in Fig. 3 are shown in Table 2. Current efficiency is defined as the ratio charge employed in CH_3Cl formation/charge passed. Material yield is defined as percentage of CT that has reacted and transformed to chloroform.

As it can be seen in Fig. 4, the intensity remained almost constant during the electrolysis while the pH of the catholyte increased, Table 2. The constant value of the current could be explained by a compensation effect

Table 2
Results for the potentiostatic electrolyses of CT with pH 7-buffered anolyte

	Electrolysis potential (V)		
	−1.1	−1.4	−1.75
Total charge (C)	529	536	545
Total time of reaction (min)	1400	370	150
Current efficiency (%)	5.5	65	91
Material yield (%)	17	65	99
Final pH in catholyte	13.2 ± 0.1	13.1 ± 0.1	13.1 ± 0.1

of the drop of the current by diminution of CT concentration and diffusion drop, and the increase of the current caused by the shift to less negative potentials of the reduction curve when the pH increases [25].

High current efficiencies, over 90%, referred to the synthesis of chloroform, were obtained at −1.75 V. The low current efficiency at −1.1 V is probably due to that at this potential, the background current is of the same order of magnitude that the CT reduction current, as it can be observed in Fig. 3.

Because no other chlorinated reaction products other than chloroform were detected, the material yield (i.e., percentage of CT that has reacted and transformed to chloroform) should be 100%. However, Table 2 shows that this yield decreases with the time of reaction. It is known that in basic medium hydrolysis of the chloroform takes place to mainly yield formate and carbon monoxide [26]. As it can be observed in Table 2, at the end of the electrolysis the pH in the catholyte was very basic, so the loss of the chloroform was probably due to its hydrolysis. The catholyte becomes alkaline because a proton is consumed in the reduction of CT (reaction (1)) and the charge in the electrolyte is transported from anolyte to catholyte by Na^+ ions.

3.2.2. Potentiostatic electrolysis in acid media

In order to test the behaviour of the electrolysis at low pH, some electrolyses were carried out using as anolyte a sulphuric acid solution instead of a pH 7-buffered solution. The concentration of sulphuric acid was chosen in such a way that the anolyte conductivity was the same as before.

As it is shown in Table 3, the pH of the catholyte decreases during the electrolysis due to the consumption of $\frac{1}{2}H^+$ per e^- in the cathodic reaction whereas the charge transports to the catholyte one H^+ per e^- (transport number of the H^+ in the membrane near 1). This pH decrease also shows that the current efficiency for hydrogen evolution is lower than 50%. The decrease of pH increases the current efficiency for hydrogen evolution and, as a consequence, the chronoamperometric curves show a continuous increase of intensity during the electrolysis (Fig. 5). The starting values of
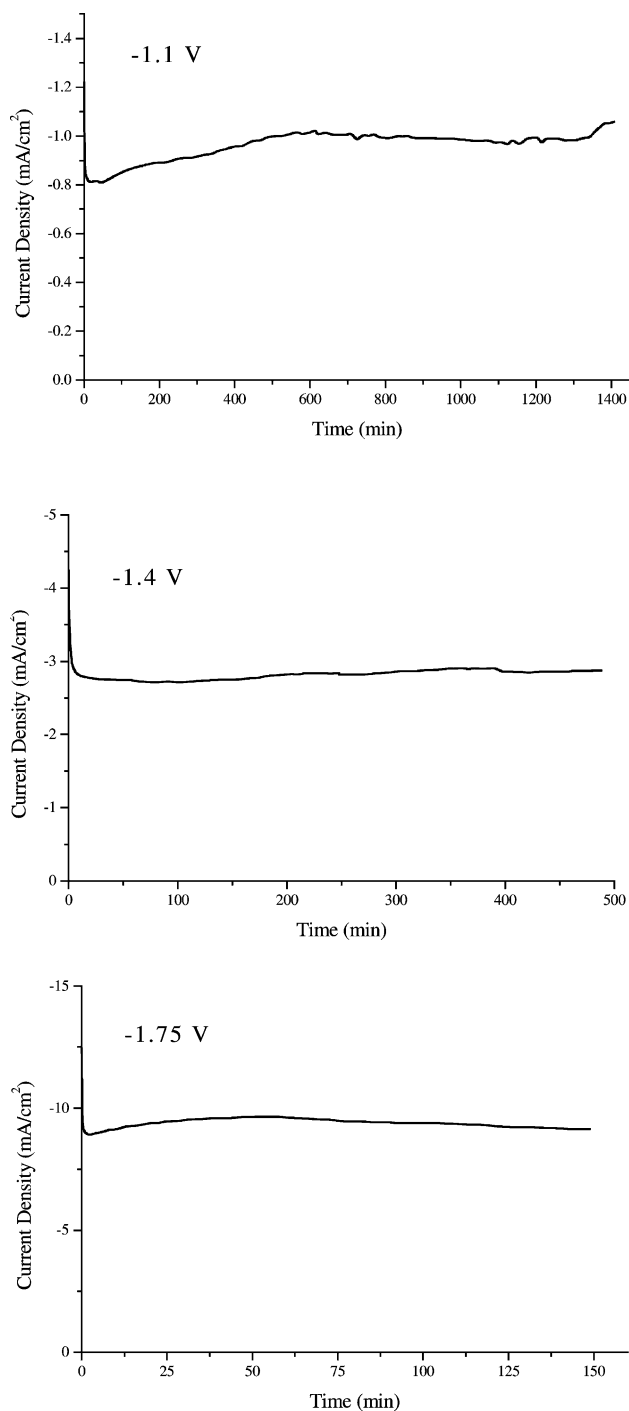
Fig. 4. Current registration corresponding to the potentiostatic electrolysis of 0.061 M CT in an electrochemical "H cell". Anolyte was pH 7-buffered and graphite was used as cathode and anode.

Table 3
Results for the potentiostatic electrolyses of CT using sulphuric acid as background electrolyte in the anolyte

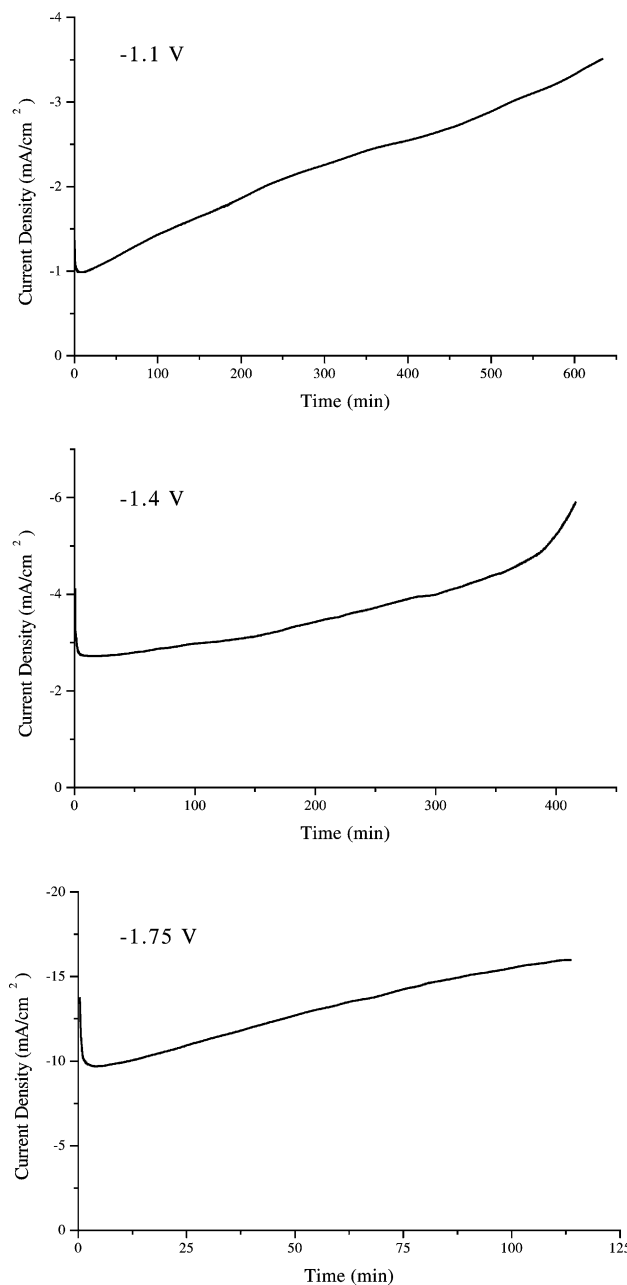|	Electrolysis potential (V)		
	−1.1	−1.4	−1.75
Total charge (C)	560	586	573
Total time of reaction (min)	633	416	114
Current efficiency (%)	55	57	70
Material yield (%)	99	96	99
Final pH in catholyte	1.6 ± 0.1	1.8 ± 0.1	1.7 ± 0.1

Fig. 5. Current registration corresponding to the potentiostatic electrolysis of 0.061 M CT in an electrochemical "H cell". Sulphuric acid was used as background electrolyte in the anolyte and graphite was used as cathode and Ti/Pt as anode.

current were similar to those registered for the buffered anolyte.

Obviously, the current efficiency for the synthesis of chloroform decreased with respect to that obtained for more basic pH because of the competitive reaction of hydrogen evolution. The material yield was this time nearly 100%, showing that no homogenous decomposi-

tion of chloroform takes place at acid pH. No other products other than chloroform were detected.

3.3. Galvanostatic electrolysis in a filter-press reactor

Once the experimental conditions for the electrolysis were tested in the "H" cell, and good current efficiency and material yield were obtained, more adequate electrolyses for developing a pre-industrial process were carried out. For this purpose, a divided filter-press electrochemical reactor was employed, Figs. 1 and 2. The experimental conditions employed were similar to those used in the electrolysis in acid medium and have been described in Section 2.4. A total charge of 2697 C was circulated which corresponds to 110% of the theoretical charge for CT reduction to chloroform (2 F/mol). The electrolysis was carried out at a controlled current density of 6 mA/cm^2 instead of at controlled potential as previously, due to our interest in developing an industrial process.

As it can be seen in Table 4, efficiencies ranging 60% were obtained. The reduction of protons, as a competitive reaction to CT reduction, also took place with a current efficiency ranging 35%. High material yield ranging 96% was achieved at the end of the experiment what newly confirms that chloroform was not hydrolysed in acid medium.

Analysis by GC-FID and GC-MS of the samples from the electrolysis did not show other products than chloroform.

However, this current density was considered too low for an industrial process and, for this reason, new experiments were carried out increasing both the current density and the CT concentration. Table 5 shows the results obtained for a current density of approximately 40 mA/cm^2 and a CT concentration of 0.25 M and a 2D carbon electrode. The increase in the current causes the formation of dichloromethane with a low yield (6% of total products obtained). Because it seems that this formation is related to the current density, a new experiment was carried out at the same apparent current density (referred to the geometric area of the electrode) but using a carbon felt as a 3D electrode. This means that the real current density used with the 3D electrode is going to be much lower than the current density for the 2D electrode. The data obtained are also shown in Table 5. A substantial decrease in the formation of dichloromethane is observed together with an increase in the current efficiency. At the same time, the reactor productivity increases from 14.0 to 16.1 kg/m^2/day (referred to chloroform production) and the energetic cost decreases from 11.0 to 9.0 kWh/kg. More work is in progress in order to optimise this process with a view to develop an industrial synthesis of chloroform from CT.

4. Conclusions

It has been demonstrated that it is possible to synthesise chloroform by electrochemical reduction of CT on carbon electrodes and in ethanol/water solvent using NaCl as supporting electrolyte, with a good material yield and very low production of dichloromethane. If the current density applied is very low, no production of this compound takes place. In spite of the competitive reaction of hydrogen evolution, the electrolysis should be carried out using an acid anolyte and avoiding the basification of the catholyte to prevent a possible hydrolysis of chloroform. An increase of the current density to values used in electrochemical synthesis produces the formation of a 6% of dichloromethane. However, a change from a 2D electrode to a 3D electrode, carbon felt, appreciably decreases the formation of dichloromethane increasing at the same time the current efficiency. Thus, it seems possible to develop an industrial process for the electrochemical synthesis of chloroform from CT.

Table 4
Results for the galvanostatic electrolysis of CT in a filter-press reactor

	Total time of reaction (min)			
	30	60	90	120
Total charge (C)	682	1359	2080	2697
Current efficiency (%)	33.3	56	58	57
Total CT removed (%)	8.7	32	48	65
Material yield (%)	99	98	100	96
Cathode potential (V) (vs Ag/AgCl)	−2.03	−1.88	−1.78	−1.70

Table 5
Comparison between the results obtained using 2D or 3D cathode

	Cathode used	
	2D	3D
Current efficiency (%)	64	77
Total CT removed (%)	87	100
Material yield (%)	94	97
Electric cost (kW h/kg)	11.0	9.0
Production (kg/m^2/day)	14.0	16.1

The charge passed was 2.4 F/mol.

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