



Reprint

Hydrodehalogenation of Polychloromethanes on Silver-Based Gas Diffusion Electrodes

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Dedicated to Prof. Jean-Michel Savéant

This work reports the electroreduction of a volatile organic halide (trichloromethane) from an airborne stream. In the past years, we highlighted the role of polycrystalline silver as powerful electrocatalyst for the electroreductive hydrodehalogenation of volatile organic halides (VOH) in water/organic solvent mixtures, from 0 to 100% of the aqueous component. The successful conversion of trichloromethane and 1,1,1-trichloroethane to the relevant dehalogenated compounds, methane and ethane have prompted us to extend the investigations to the treatment of gaseous effluents, adopting a silver Gas

Diffusion Electrode (Ag-GDE) and the appropriate cell design. In the field of electroreduction processes the possibility of using GDE to treat gaseous effluents for the removal of volatile organic pollutants represents an electrochemical challenge, and the treatment of N₂/CHCl₃ gas mixtures fed into the cathodic Ag-GDE compartment demonstrates the feasibility of the electroreductive detoxification process. Our results will be presented and discussed in terms of CHCl₃ removal efficiency, selectivity and energy consumption in preparative electrolyses.

1. Introduction

The electroreduction of organic halides has played a key role in organic electrochemistry^[1,2] since the early works of Winkel and Proske^[3] and of von Stackelberg and Stracke^[4] on the treatments of organic halocompounds. In the last thirty years, the removal of halogen groups from organic substrates has gained a strong attention due to the possibility of applying this process for environmental purposes,^[5–12] being more effective than the most popular electrooxidative process of total degradation. The interest in oxidative processes is confirmed by recent reviews^[13–20] and different papers on the mineralization of chlorophenoxy herbicides,^[21–23] mono- and poly-halogenated phenolic wastes,^[24–26] and other chlorinated organic compounds.^[27–29] Oxidative electrochemical processes are more widely used and studied because these treatments can lead to the total degradation (mineralization) of the compounds.^[16,17] In this class of treatments, both direct and indirect oxidations together with the emerging coupled technologies (e.g. electro-Fenton, photoelectron-Fenton, and so on) have been deeply unravelled showing quite a few advantages, such as outstandingly efficiency, mild operative conditions, versatility and ease of automation.^[20] Nevertheless, some limitations are still evident as low current efficiency under some conditions and

short lifetime that hinder their industrial applicability.^[20] Rodrigo et al. largely investigated the coupling of two or more (photo-) electrooxidation processes, such as photo-electrooxidation coupled to zero-valent iron (ZVI), resulting in a very high (around 100%) removal of chloro-containing compounds in both drinking water and soil effluents.^[30–32] However, their potential scale-up is still rather difficult. Besides, electroreductive processes have gained a large scientific attention due to either their potentiality in chemical recovering/recycling or in the value-added substance productions,^[33–37] in particular when halocompounds in wastewater streams have to be treated.^[38,39] Indeed, on one hand, the cathodic reaction can be used to produce energy as molecular hydrogen, while performing the solution decontamination via the anodic process, on the other it can concomitantly play a pivotal role in the degradation of organics.^[19] Both the direct reduction of the pollutant at the cathode and the electrogenerated H₂O₂-mediated decontamination are the two most relevant cathodic processes.^[20]

As far as it concerns the degradation of organic halides, they are present in many industrial processes as solvents and are (or have been) involved in a large number of chemical preparations and processes. Moreover, some halocompounds can be formed as secondary pollutants in primary waste treatments (e.g. in thermal decomposition plants,^[40–42] in oxidative degradations^[43–46] and so on), and in productive processes.^[5,47,48] Organic halocompounds occupy a large part of the list of the persistent organic pollutants catalogued in the Stockholm Convention and its successive amendments,^[49] due to their toxicity with high chemical stability, lipophilicity and long-range diffusivity.

For this reason, soil and ground-water remediation become key issues of the environmental protection and restoration, and electrochemical methods have been proven to be very effective in the waste detoxification, as reported by both literature and industrial/pilot plants.^[50–53] As such, these treatments have

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An invited contribution to a joint Special Collection in memory of Prof. Jean-Michel Savéant

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gained interest over the more popular physico-chemical techniques (e.g., thermal degradation or chemical oxidation). Moreover, they allow for mild reaction conditions, avoiding the secondary pollution effects linked to the excess of reagents, and they are easily adapted even to small-size treatment needs.

In this context, it has been demonstrated that silver possesses a strong electrocatalytic activity for organic halide electroreduction,^[6,54–57] due to its affinity for halides with which interacts, producing an attenuated radical intermediate ($R...X...Ag$) in which C–X bond has been strongly weakened.^[58] Recently, silver nanoparticles have been used also for analytical purposes, with the possibility of detecting organic chlorinated compounds and carbon dioxide.^[59–62] This characteristic can be favourable if applied to wastewater treatment since it leads to the production of dehalogenated organic molecules,^[6,7,63] that can be easily digested by microorganisms. Moreover, in the field of electroreduction processes, the possibility of using gas diffusion electrodes (GDEs) to treat gaseous effluents and/or non-conductive streams represents a significant challenge for electrochemistry.^[8,64] In this paper, silver-based GDE for the hydrodehalogenation of polychloro-methanes will be presented and discussed in terms of organic substance removal efficiency, selectivity and energy consumption in preparative electrolyses.

Experimental Section

Two different GDE were prepared: Ag-GDE and B-GDE, the latter used as blank electrode. Both electrodes were prepared using a silver-covered nickel net support, whose two sides were treated differently. The electrolyte side was covered with a slurry containing the electrocatalyst, using a roll to distribute the ink homogeneously on the surface. The gas side was covered with a mixture of SAB[®]

(Shawinigan Acetylene Black) and PTFE (Polytetrafluoroethylene), 50:50. The electrolyte side was covered by a slurry containing Vulcan XC72R[®] + PTFE (1:1), B-GDE, or Ag + Vulcan XC72R[®] and PTFE (1:1), see Figure 2B. This last ink was prepared as follow: 1.5 g of microcrystalline Silver was mixed with 6 g of Vulcan XC72R and dispersed in Milli-Q water. The slurry was sonicated for 10 minutes. The slurry was then transferred in a beaker and magnetically stirred. 75 g of a solution of PTFE in water (10%w) was added to the slurry under stirring. The final slurry was filtered, and the mud was deposited with a spatula onto the electrolyte side of silver-covered nickel net support. The ink was homogeneously dispersed on the net using a roll. Finally, the GDE was hot-pressed at 25 Kg/cm², 150 °C, for 10 minutes. Preparative electrolyses were performed in a divided filter-press flow cell, already described in^[63] (Figure 1). Rapidly, the cell consisted in an anodic chamber (500 cm³) separated from the cathodic compartment by a cation exchange membrane, Nafion 117[®], provided by Sigma Aldrich. The cathodic section was in turn divided into a gas chamber, connected to a gas pipe to feed N₂ saturated with CHCl₃ at 20 ± 1 °C, and a liquid chamber by the GDE (Ag- or B-), 22 cm long and 7 cm large, whose exposed area was 5 × 20 cm². The plexiglas[®] electrolytic cell, 30 cm x 10 cm, was mounted with the short side in vertical position, in order to decrease the liquid pressure on the GDE cathode thus limiting flood problems, see Figure 2A. The anode was a Pt sheet of 13 cm², divided in three different slices. For on-line analysis during electrolyses, the exhausted gas was sent to a Gas Chromatograph HP5890 (GC/FID), equipped with a FID detector and a 30 m length capillary column (with 0.32 mm diameter) AT624[®] (Alltech). The head pressure was 55 kPa at 150 °C; He was used as carrier (2.0 ml/min) and Make Up (28.0 ml/min) gas. FID was fed with air, 400 ml/min, and H₂, 50 ml/min. The injector was a sample valve with a 125 µl sampler loop at 150 °C. The oven temperature ramp was: 40 °C for 10 minutes, ramp of 30 °C/min up to 150 °C, 150 °C for 2 minutes. Applying these conditions to the GC/FID analysis, the following retention times were obtained: methane 2.17 min; monochloromethane 3.07 min; dichloromethane 10.74 min; trichloromethane 12.78 min. Some runs were performed connecting the exhausted pipe to a CG-Mass analyzer in order to recognize the

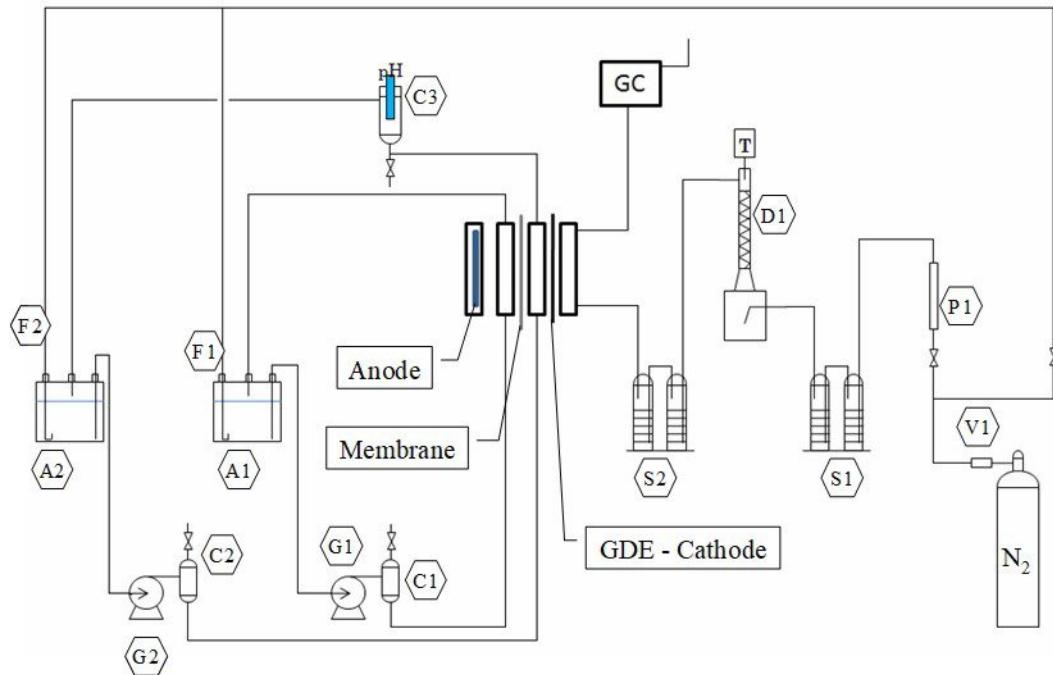


Figure 1. Process flow chart.

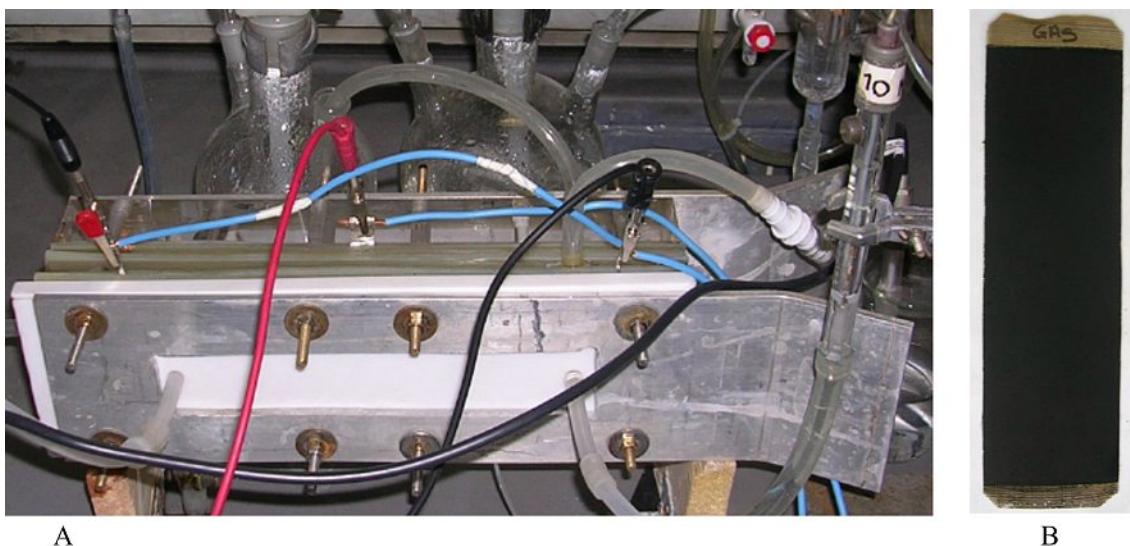


Figure 2. A – Cell disposition. B – One cathode used in the present work.

dehalogenated products and to confirm the reaction pathway. GDE potential was measured versus Saturated Calomel Electrode (SCE). Figure 1 shows a flow chart of the electrolysis process. Two pumps (G1 and G2), connected to damper flasks (C1 and C2) fed anolyte and catholyte aqueous solutions to the cell, at $60 \text{ dm}^3\text{h}^{-1}$ and $18 \text{ dm}^3\text{h}^{-1}$, respectively, drawing the solution from two tanks (A1 and A2) degassed with N_2 by two bubblers (F1 and F2). Catholyte pH was monitored by a glass electrode positioned in (C3). Nitrogen (5.5 SIAD) was fed, at a flow rate of $25 \text{ cm}^3\text{min}^{-1}$ controlled by a flowmeter (P1) and adjusted with a needle flow control valve (V1), to two presaturators (S1) filled with CHCl_3 and followed by a reflux flask (D1) maintained at 20°C , in order to have a N_2 gas saturated with CHCl_3 at 20°C . Before entering into the gas chamber, N_2 was fed into two demisters (S2) to remove last CHCl_3 drops. Exhausted gas, coming from the electrolytic cell, was sent to the sample valve of the CG/FID for online analysis of effluent to analyse the dehalogenated products. The catholyte solution was periodically sampled to monitor the chloride concentration by AgNO_3 titration. All chemical reagents were provided by Sigma-Aldrich and used as received.

Results and Discussion

In our studies we changed both the gas flow rate, changing in turn the retention time for the cathodic chamber (ranging from 60 s to 120 s), and the current density, ranging from 25 mA/cm^2 to 50 mA/cm^2 . Here, we discuss the best experimental conditions we found in our experiments: 25 mA/cm^2 for current density and 120 s for retention time. For the other experimental conditions, we verify that, by increasing the current density, it is possible to faster remove chloroform from gaseous flow, but by producing, at the same time, more partially dehalogenated products, thus reducing the methane conversion. In summary, 25 mA/cm^2 is the best balance between the necessity of a rapid pollutant abatement, from gaseous effluent, and the importance of a complete dehalogenation of the organic pollutant. Thus, all preparative electrolyses here described were carried out at room temperature using a constant current density of

25 mA cm^{-2} , two different anolytes: Na_2SO_4 0.1 M or NaOH 0.5 M, and one catholyte: Na_2SO_4 0.1 M. The electrolysis progress was followed by monitoring gaseous effluent by GC/FID, whose typical data are presented in Figure 3, for an Ag-GDE at the first run. Left axis represents gas chromatographic area (Arbitrary Unit) obtained analyzing the gaseous effluent, thus allowing for the determination of product chemical speciation and quantitative analysis of reagents and products. Right axis shows the Ag-GDE electrode potential versus SCE. Notably, for all the preparative electrolyses the main product was methane, the compound of the complete dehalogenation, followed by the intermediate dehalogenation products, i.e., dichloromethane and monochloromethane, whose amount increased with the electrode deactivation. In few minutes, after the beginning of the electrolysis, chloroform removal reached the maximum grade (see the steep decrease of CHCl_3 gas chromatographic area in Figure 3) and remained constant for about 150 minutes, during which a large methane production occurred. After 200 minutes the decrease in methane produc-

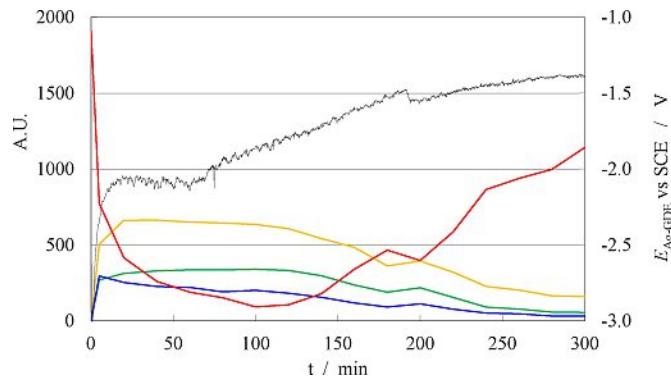


Figure 3. Left axis: gas chromatographic area, in Arbitrary Unit, of gaseous outlet from the electrolytic cell: red line = CHCl_3 , blue line = CH_2Cl_2 , green line = CH_3Cl , orange line = CH_4 ; right axis, black line: Ag-GDE potential versus SCE.

tion, strictly correlated with the augmentation of CHCl_3 in the outlet gaseous flux, was probably due to the mechanical degradation of Ag-GDE with the subsequent electrode flooding and diminishing of the electrocatalytic activity. The material degradation is probably due to the interaction between the plastic component of the electrode and the organic molecule present in the gas, an effect already described by Sugiyama and Okajima.^[65,66] The diminishing of electrode performance was also evidenced by the decrease of electrode potential (right axis of Figure 3) probably caused by flooding. By analyzing the GC/FID peak area reduction of CHCl_3 , which confirms the CHCl_3 conversion, the lifetime of Ag-GDE has been determined after re-using it for different electrolyses. Figure 4 clearly shows the obtained results (the cathode was stored at 60°C for 16 hours between each run). It is evident the increase of electrode performance during the first four runs and the subsequent drop of electrocatalytic activity of the material. By performing optical microscopy analyses, it was possible to correlate this behavior to the wettability of the liquid-side electrode surface.

Indeed, in the first run the wettability of the electrode liquid-side surface was too low to have a high active area for the electrochemical reaction, for which triple contact (gas, liquid and metal) was necessary; very likely the prolonged contact between the liquid-side electrode surface and the electrolyte solution improved the wettability, as well as the performances, thus improving the removal of CHCl_3 from the gaseous flux.

However, the continuous increase of electrode surface wettability, which occurred with the repeated usage of the electrode (for the mechanical degradation of the diffuser layer, as previously described - after some runs GDE has a consistency of a sponge) produced a reduction of the electrode performance, witnessed by the reduction of the capability of CHCl_3 removal (5th run in Figure 5). The wettability increase led to a flooded electrode, as it can be seen in Figures 5a, b and c which show the electrode surface whose data are presented in Figure 4, after the relevant runs (it must be remembered that cell has been placed with the longest side as base).

The reduction of droplets number on the electrode surface is a clear proof of flooded electrode (increase wettability). A sharp separation (Figure 5, gray line) between a too wetted electrode surface (bottom - homogeneous black colored surface) and a less wetted one, with a high number of droplets, is visible in Figures 5b and c, which are related to runs 4th and 5th of Figure 4. Then, it is well-observable the correlation between the cathode wettability and the electrode potential. For a new electrode the cathode potential was less negative with respect to an aged one, i.e. repeatedly used. With the runs increase, the potential became more and more negative, very likely due to the increasing overvoltage linked to the active sites number decrease. It is important to stress that, at the very beginning of the electrode life, the cathode potential was less negative (low energy consumption), but the CHCl_3 conversion was very low. However, after some runs, the electrode reached a good wettability and the dehalogenation process presented high CHCl_3 conversion, still having a low energy consumption, i.e. around 340 Wh per mol of CHCl_3 removed. On the other hand, an aged electrode exhibited high wettability and low CHCl_3 conversion, thus indicating the end of the electrode service-life. In summary, there is an evolution for the electrocatalytic activity of the Ag-GDE, witnessed by both its potential and its wettability: good performances (high CHCl_3 conversion and high selectivity) were observed for intermediate electrode wettability, which readily favors the gas-liquid contact and the exchange of chloride ions and protons between the two phases, and potential.

Some electrodes showed a good wettability at the first run, thus having immediately high CHCl_3 conversion. In the case of E6, Figure 6, there was only a small increase of CHCl_3 conversion

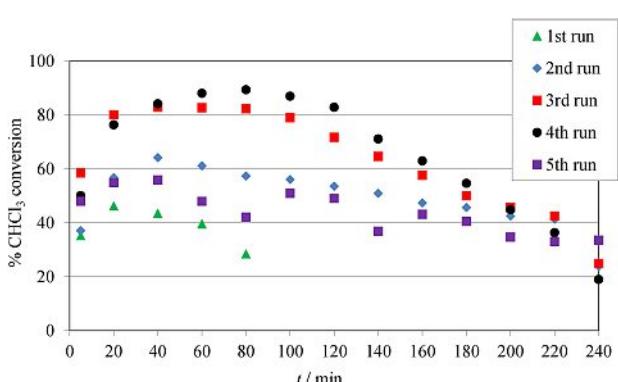


Figure 4. % CHCl_3 conversion for different runs of the same electrode (E5).

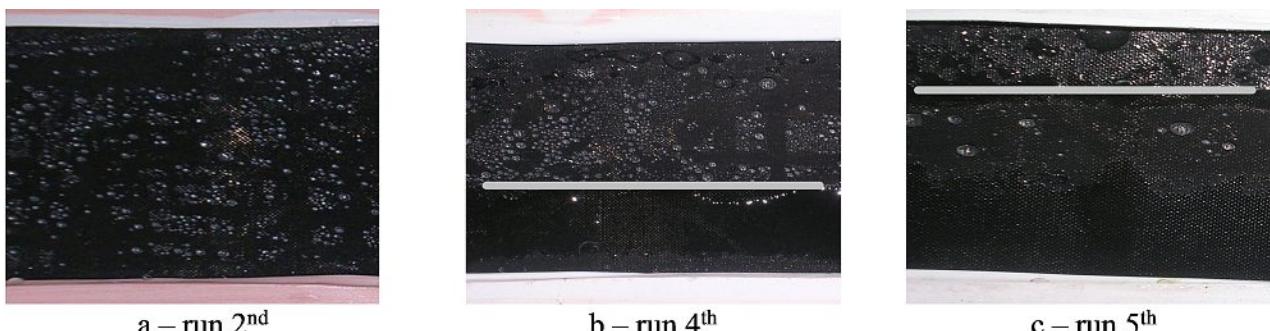


Figure 5. Ag-GDE surface after different runs. Grey line divides flooded electrode (bottom part) from right wetted electrode (upper part with droplets).

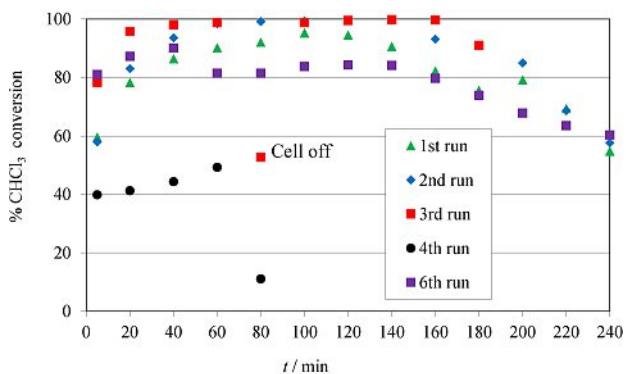


Figure 6. % CHCl_3 conversion for different runs of the same electrode (E6).

between the first and the second run, as the electrode can absorb the right amount of water already at the first run.

Electrode E6 was also used to investigate anolyte pH influence on the CHCl_3 conversion, current efficiency and electrode lifetime. During electrolyses there was a catholyte pH variation due to the process reactions [Eqs. (1)–(3)]:

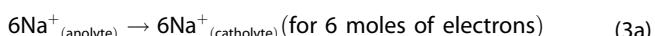
at the cathode



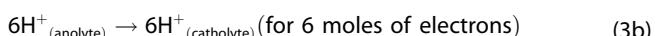
at the anode



and transport in the cationic membrane

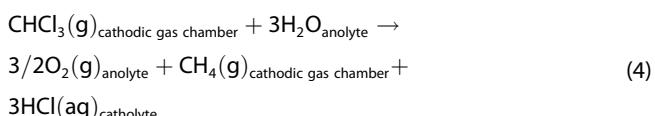


at the beginning



after the consumption of Na^+

In the hypothesis of a total conversion of trichloromethane to methane, the overall cell reaction [Eqs. (1)+(2)+(3b)] is [Eq. (4)]:



When a neutralized solution (Na_2SO_4 0.5 M) was used as catholyte and anolyte, catholyte pH increased at the beginning due to the consumption of H^+ (reaction (1)), which was not balanced by the inlet of Na^+ . Nevertheless, after adequate time (depending on the catholyte volume), Na_2SO_4 concentration and other cell parameters, pH decreased (Figure 7) due to the unbalance between H^+ inlet [Eq. (3b)] and H^+ consumption [Eq. (1)] per mole of electrons. The catholyte pH decrease can reduce the selectivity of the cathodic process, because high H^+

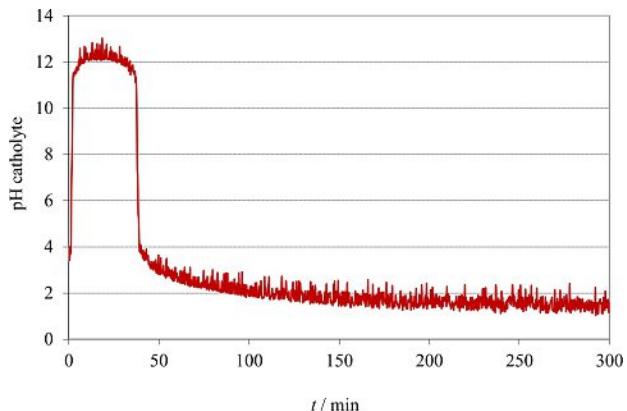


Figure 7. Catholyte pH variation during the electrolysis.

concentration promotes the onset of the hydrogen evolution parasitic reaction.

To analyze pH variation, Na_2SO_4 anolyte solution was replaced with NaOH 0.5 M. For these runs (Figure 6–3rd, 4th and 5th, not shown) the catholyte pH remained constant at 12 for the entire period of electrolysis and CHCl_3 conversion was above 98% for a longer period (Figure 6, 3rd run) with a high selectivity towards methane production. Unfortunately, the service life of the electrode underwent a drastic reduction, witnessed by a very low CHCl_3 conversion for the following run (Figure 6, 4th run). Hence, electrolysis had to be stopped after 80 minutes because of the degradation of the electrode polymeric component in contact with the alkaline solution. Testing again the same Ag-GDE, after the replacement of NaOH 0.5 M with Na_2SO_4 0.1 M as anolyte solution, the chloroform conversion further increased (>90%, see Figure 6, 6th run), but selectivity drastically reduced to 10% (by GC/FID peak area not shown), being dichloromethane the main dehalogenated product.

For some electrolyses, catholyte solution was sampled to monitor the chloride concentration through titration. By calculating, during the time period for which CHCl_3 conversion was constantly above 80% (from ca. 40 to 160 min for 1st and 2nd run in Figure 6), the mole of Cl^- production, the mole of CHCl_3 consumption and the mole of electrons passed, it was possible to obtain the mole of electrons used for mole of produced Cl^- in order to verify the reaction mechanism defined in Equation (1), the selectivity of the dehalogenation process and the current efficiency. All these data are collected in Table 1.

Table 1. Data of quantitative analysis on reagents and products for 1st and 2nd runs of Figure 6.

	E6 1st run	E6 2nd run
Period of time considered/min	120	120
% peak reduction	90	97
mol Cl^- /mol CHCl_3	2.81	1.45
moles of e^- passed	0.187	0.187
mol e^- /mol Cl^-	2.82	5.04
Current Yield [%]	71.0	39.7

Comparing Figure 6 with data reported in Table 1, some remarks can be drawn. Specifically, CHCl_3 conversion in the 1st run was lower than in the 2nd one; however, in 1st run, CHCl_3 was mainly converted in methane, since the ratio between moles of Cl^- produced and moles of CHCl_3 consumed was 2.81, nearly 3. Moreover, the ratio between moles of electrons passed and moles of Cl^- produced was 2.82 (should be 2 for the stoichiometry of [Eq. (1)]), thus indicating that more than 70% of current was used for the dehalogenation process to produce methane. In 2nd run, although CHCl_3 conversion was higher than 1st run, the electroreduction process produced mainly mono- and bi-halogenated compounds. Indeed, the ratio between moles of Cl^- and moles of CHCl_3 was 1.45, thus indicating a non-complete dehalogenation process. Moreover, the large value of moles of electrons and moles of Cl^- ratio, in 2nd run, corroborates the presence of a parasitic cathodic reaction that consumes current forming a by-product, i.e. mainly hydrogen.

In order to verify the electrocatalytic activity of silver-based GDE, a home-made bare-Vulcan (0% Ag) gas diffusion electrode, B-GDE, has been also tested with the same procedure applied for the Ag-GDE cathodes.

Figure 8 shows the GC/FID analysis carried out on exhausted gas coming from the electrolytic cell with B-GDE cathode. It is evident the small decrease of CHCl_3 peak area and the only presence of the mono dehalogenated product, CH_2Cl_2 ; both effects point to a scarce electrocatalytic activity of the B-GDE on the reaction under study. No methane was detected.

We must underline that the large decrease of CHCl_3 peak area during the first minutes is largely connected with the absorption of chloroform by the electrode carbon component. To prove this, cell was fed with $\text{N}_2 + \text{CHCl}_3$ mixture for 20 minutes, then only N_2 gas was fed to the cell and the potential was applied to the electrodes. Immediately, a Cl^- production was detected in catholyte solution, thus proving the presence of chloroform in the carbon electrode component for the previously absorption process.

2. Conclusions

The present work has demonstrated the feasibility of applying a commercially available Ag-GDE as electrocatalytic cathode in the dehalogenation process of CHCl_3 , a model molecule chosen to represent the volatile organic halides, a large family of substances whose toxicity constitute serious challenges in developing suitable detoxification methodologies. By means of CG/FID analysis of exhausting gas and Cl^- titration of catholyte solution, it has been proven that the main dehalogenated product is methane, with small amount of mono- and dichloromethane. Process can reach a current efficiency of more than 70% when a properly wetted electrode has been used. In fact, the interaction between solution and electrode, in terms of wettability of the cathode, has been demonstrated to play a key role for the effectiveness of electrocatalytic activity of the cathode: too dry or too flooded electrodes, although possibly leading to high CHCl_3 conversion, have shown very low selectivity, being dichloromethane the main product of the electrolysis, and low current efficiency.

Also, the catholyte pH can play a key role in the process current efficiency: for too acidic solution, it can promote the hydrogen evolution reaction at the cathode, thus reducing the rate of the dehalogenation process. On the other hand, the usage of alkali solution can reduce the service life of the electrode, for the possible interaction between NaOH and the plastic material constituting the diffuser of the GDE.

Finally, a carbonaceous support, containing Ag particles, can be used to absorb halorganic contaminants as a gas stream filter. When the filter is exhausted, it can be regenerated by using it as a cathode in an electrolytic cell.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: hydrodehalogenation • silver catalyst • polychloromethanes • gas diffusion electrode • electroreduction

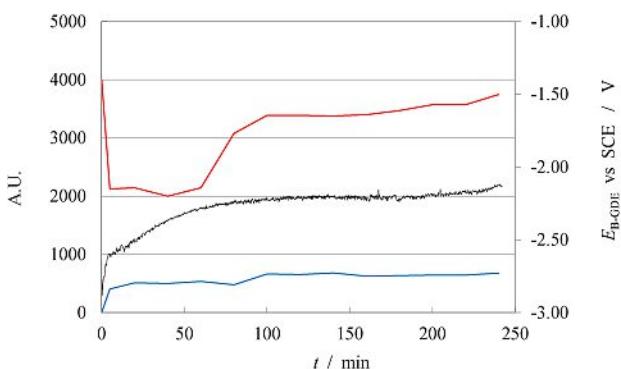


Figure 8. Left axis: gas chromatographic area, in Arbitrary Units, of gaseous outlet from the electrolytic cell: red line = CHCl_3 , blue line = CH_2Cl_2 ; right axis: B-GDE potential versus SCE.

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