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Electrolytic synthesis of chloroacetic acids in a filter-press reactor from polychloromethanes

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ABSTRACT

Electrochemical carboxylation of carbon tetrachloride and chloroform to synthesize chloroacetic acids in mild conditions has been investigated by galvanostatic electrolyses using a homemade electrochemical filter-press reactor. Undivided filter-press reactor consisting of a planar Zn cathode and a planar Al sacrificial anode has been shown to be an optimal electrochemical device for the electrocarboxylation reaction. The influence of some operative parameters, such as current density and concentration of supporting electrolyte, on the efficiency and selectivity of the synthetic process has been investigated. Highly current efficiencies and target products yields (both of them>85%) were achieved in all cases, whereas byproducts formation was minimal.

1. Introduction

In recent years, changes in environmental policies and strategies for the treatment of chemical industrial waste, has fuelled interest in the development of environmental friendly processes, mainly focused on the removal or conversion of pollutants. In this way, electrochemical technology offers several advantages for the treatment of wastes, over conventional homogeneous methods in terms of environmental compatibility, security, versatility and energy efficiency [1].

Polychloromethanes such as carbon tetrachloride and chloroform are considered one of the most restricted pollutants because of their high toxicity, volatility and carcinogenic properties [2]. Hence, the employ of carbon tetrachloride and chloroform have decreased significantly, being their main use as organic solvents. Nevertheless, nowadays, these compounds are still generated indirectly in two processes: the industrial synthesis of polychloromethanes and the disinfection of drinking water with chlorine [3,4].

A number of technologies have been developed to the conversion of these compounds either for a further reuse or disposal, with limited success [5–16]. The exploratory results reported for the majority of these methods show the generation of useless and/or equally toxic products.

In this paper, we propose a new electrochemical process based on the electrocarboxylation of carbon tetrachloride and chloroform as a first step in the development of a new strategy for the elimination and conversion of these pollutants into chloroacetic acids, which are profitable products with a wide range of applications [17].

Early studies have been devoted to the electrocarboxylation of organic compounds as a powerful tool for electroorganic synthesis of carboxylated products, even at semiindustrial-scale [18–23]. Recently, the electrochemical carboxylation has been used as a method focused on the reductive dehalogenation of some organic halides, mainly aromatic derivatives [24–28]. However, the carboxylation of aliphatic compounds in a continuous flow electrochemical reactor, has not yet been explored. In previous works, the experimental conditions for the electrochemical carboxylation of polychloromethanes, to obtain chloroacetic acids, have been optimized in a small-scale continuous-stirred batch electrochemical cell [29,30]. Herein, we describe the results on the electrochemical carboxylation of carbon tetrachloride and chloroform using a homemade laboratory-scale filter-press reactor as a first step in the development of a pre-industrial process.

2. Experimental

2.1. Chemicals and electrodes

Carbon tetrachloride and chloroform (Sigma-Aldrich, 99.9%, HPLC grade) were used as received. Acetonitrile (ACN) (HPLC grade from Sigma-Aldrich) and tetrabutylammonium perchlorate (TBPA) (from Fluka >98%) were used without further purification. All the chemicals used for the preparation of standard solutions for GC analysis were of analytical reagent grade. The electrolytic solutions were saturated with

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high-purity CO_2 (Abello Linde, Spain). The electrode materials used were zinc and aluminium foils (both from Goodfellow, 99.90%, 100 × 100 mm, thickness = 1 and 2 mm). All potentials were measured against a commercial Ag/AgCl/NaCl sat. reference electrode (from Metrohm). The contact between the reference electrode and the electrolytic solution was done by using a Luggin capillary tube inserted into the wall of the electrolyte frame.

2.2. Galvanostatic electrolyses experiments

Electrolyses of polychloromethanes in the presence of CO_2 were carried out under galvanostatic conditions, at room temperature, in a homemade undivided filter-press reactor with a geometric electrode area of 64 cm^2 using a Thandar TS3023S DC power supply. Mass transport and hydrodynamic behavior of this reactor has been characterized and the mass transport coefficient has been calculated as a function of electrolyte flow rate. The calculated mass transport correlation for the reactor with planar electrodes and empty channel was found comparable to similar commercial electrochemical reactors reported in the literature. Zn cathode and an Al anode were employed, with an interelectrode gap of 12 mm. The reactor was built up in a simple design and easy assembly in which the consumable anodes could be easily replaced. 750 mL of 0.1 M TBPA + 0.1 M polychloromethane in ACN was used as electrolytic solution. Solutions were pumped at a constant flow rate of 96 L h^{-1}, using a centrifugal pump IWAKI mod. MD-15-FX-220 N. The experiments were stopped when the theoretical charge required for complete polychloromethanes reduction was passed, considering a charge consumption of $2e^-$ per molecule. CO_2 was continuously bubbled through the electrolytic solution.

In order to control the evolution of some operative parameters on the efficiency and selectivity of the process, the electrolysis solution was sampled (1 mL) during the process. The quantification process via GC, isolation of chloroacetic acids and recovery of the supporting electrolyte have been previously described [29,30].

3. Results and discussion

3.1. Electrochemical carboxylation of carbon tetrachloride in a filter-press reactor

Some results for the galvanostatic electrolyses of carbon tetrachloride in the presence of CO_2 are gathered in Table 1. A summary of the influence of current density and supporting electrolyte concentration is shown. Thus, the values of current efficiency and trichloroacetate (TCA) yield were both over 87% (entries 1–4 in Table 1). In addition, chloroform and dichloroacetate (DCA) byproduct formation was low. Other possible byproducts such as hexachloroethane and oxalate were not detected.

Table 1
Electrocarboxylation of 0.1 M Cl_4C in ACN + 0.1 M TBAP.

Entry	Current density ($mA\ cm^{-2}$)	Current efficiency[a] (%)	Product yield[b] (%)			E_F[e] (V)
			Cl_3CH	TCA	DCA	
1	6	91	6	85	8	−2.27
2	8	89	5	90	11	−2.32
3	10	87	5	87	15	−2.40
4	12	86	5	85	14	−2.49
5[c]	12	86	4	87	8	−2.54
6[d]	12	76	7	77	18	−2.67

[a] (Charge used to reduce the reactant/total charge) × 100.
[b] (Moles of product/moles of reactant consumed) × 100.
[c] [TBAP] = 0.05 M.
[d] [TBAP] = 0.03 M.
[e] Final cathode potential vs. Ag/AgCl/NaCl sat.

Current efficiency and product yield are affected by supporting electrolyte concentration. In this way, at low TBAP concentration, a decrease of the current efficiency and TCA product yield was observed (entries 5, 6 in Table 1). These effects can be explained by the lowering of the conductivity of the electrolytic solution. Nonetheless, a successful electrosynthesis of TCA can be achieved even under the lowest conductivity condition used (entry 6 in Table 1).

The evolution of current efficiency was monitored during the electrolyses. As can be seen in Fig. 1, at the beginning of the electrolyses, current efficiency values over 95% were reached. Subsequently, a linear slightly diminution of this parameter was observed indicating a kinetic control of the reaction as can be expected by the decrease of the carbon tetrachloride concentration, lowering the limiting current. In addition, the trend observed in this Fig. 1 point out that the mass transport, in our reactor, is rather efficient since high current efficiencies are reached.

3.2. Electrochemical carboxylation of chloroform in a filter-press reactor

In order to check the versatility of the reactor, the electrochemical carboxylation of chloroform has been investigated. Thus, the electrolysis in the presence of CO_2 has been developed with the same filter-press reactor. Table 2 collects the main results obtained in these experiments. In all cases, current efficiencies and DCA (target product of chloroform carboxylation) yields are over 90% and 70%, respectively. Moreover, some byproducts such as dichloromethane (DCM), trichloroacetate (TCA) and monochloroacetate were also formed. The presence of TCA as byproduct can be explained as a consequence of the self-protonation side reaction described in a previous work [30]. Other possible byproducts such as tetrachloroethane and oxalate were not detected. Therefore, we can state that it is also possible to carry out an efficient and selective electrochemical carboxylation of chloroform.

On the other hand, the same abovementioned behavior in the profile of current efficiency and product amount during the carbon tetrachloride electrolysis was observed, indicating that the mass transport in the reactor was also adequate for the chloroform carboxylation.

On the basis of these promising results, we encourage to develop further in the scaling up of this process. In this way, some requirements must be considered for large scale production, related to the recovery of the solvent, cell geometry, operating conditions and process costs [18].

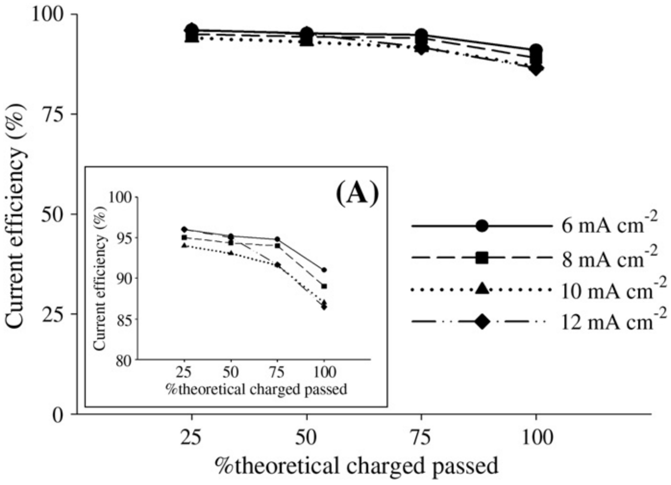

Fig. 1. Evolution of the current efficiency during the electrolyses of 0.1 M Cl_4C in CO_2 saturated solution containing ACN + 0.1 M TBAP. (A) Closer view.

Table 2
Electrocarboxylation of 0.1 M Cl_3CH in ACN + 0.05 M TBAP.

Entry	Current density (mA cm^{-2})	Current efficiency (%)	Product yield (%)			E_F (V)
			DCA	TCA	DCM	
1	6	89	69	18	3	−2.05
2	8	91	68	15	5	−2.40
3	10	92	77	11	5	−2.75
4	12	84	70	11	9	−2.96

4. Conclusions

A homemade filter-press electrochemical reactor has been designed and constructed to synthesise chloroacetic acids based on the electrocarboxylation of carbon tetrachloride and chloroform as a first step in the development of a pre-industrial process for the elimination and conversion of these polychloromethanes. It has been demonstrated that the electrochemical carboxylation of carbon tetrachloride and chloroform to synthesize the chloroacetic acids is feasible, rendering excellent current efficiencies and high carboxylated product yields. These outcomes point out that the electrochemical carboxylation of polychloromethanes appears as a promising strategy for the industrial recycling of chlorinated pollutants.

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References

[1] D. Plecther, Electrochemistry for a Cleaner Environment, The Electrosynthesis Company Inc., New York, 1992.
[2] E.P.A. (Environmental Protection Agency), Office of Air qualityin, http://www.epa.gov/ttn/atw/hlthef/carbonte.html.
[3] F.H. Kraybill, J. Am. Water Works Assoc. 370 (1981).
[4] M.N. Ram, E.J. Calabresse, R.F. Christman, Organic Carcinogens in Drinking Water, John Wiley & Sons, New York, 1986.
[5] C.R. Mullin, D.J. Perettie, Patent U.S. 4.105.702, (1978).
[6] K. Myazaki, Y. Mizushima, S. Kawahara, Jpn. Kokai Tokkyo Koho JP 08127548 A2, 1996.
[7] B.M. Penetrante, M.C. Hsiao, J.N. Bardsley, B.T. Merritt, G.E. Vogtlin, A. Kuthi, C.P. Burkhart, J.R. Bayless, Sources Sci. Technol. 6 (1997) 251.
[8] J. Wang, P. Blowers, J. Farrell, Environ. Sci. Technol. 38 (5) (2004) 1576.
[9] T. Li, J. Farrell, Environ. Sci. Technol. 34 (2000) 173.
[10] V.M. Molina, D. González-Arjona, E. Roldán, M. Domínguez, Collect. Czech. Chem. Commun. 67 (2002) 279.
[11] V.M. Molina, V. Montiel, M. Domínguez, A. Aldaz, Electrochem. Commun. 5 (2003) 246.
[12] J. He, A. Eduardo-Sáez, W.P. Ela, E.A. Betterton, R.G. Arnold, Ind. Eng. Chem. Res. 43 (2004) 913.
[13] J. He, W.P. Ela, E.A. Betterton, R.G. Arnold, A. Eduardo-Sáez, Ind. Eng. Chem. Res. 43 (2004) 7965.
[14] W.-Y. By Xu, T.-Y. Gao, J. Environ. Sci. 19 (2007) 792.
[15] Y. Jiao, D. Wu, H. Ma, C. Qiu, J. Zhang, L. Ma, Electrochem. Commun. 10 (2008) 1474.
[16] C. Durante, A.A. Isse, G. Sandona, A. Gennaro, Appl. Catal. B Environ. 88 (2009) 479.
[17] E.D. Morris, J.C. Bost, Kirk-Olmer Encyclopedia of Chemical Technology, Vol. 1, John Wiley & Sons, New York, 2001.
[18] J. Chaussard, M. Troupel, Y. Robin, G. Jacob, J.P. Juhasz, J. Appl. Electrochem. 19 (1989) 345.
[19] J. Chaussard, J.C. Folest, J.Y. Nedelec, J. Perichon, S. Sibille, M. Troupel, Synthesis 5 (1990) 369.
[20] N.S. Murcia, D.G. Peters, J. Electroanal. Chem. 326 (1992) 69.
[21] A.K. Data, P.A. Maroon, C.J.H. King, J.H. Wagenknecht, J. Appl. Electrochem. 28 (1998) 569.
[22] C.M. Sánchez-Sánchez, V. Montiel, D.A. Tryk, A. Aldaz, A. Fujishima, Pure Appl. Chem. 7 (2001) 1917.
[23] C.M. Sánchez–Sánchez, E. Expósito, B. Batanero, V. Montiel, F. Barba, A. Aldaz, Trends in electrochemistry and corrosion at the beginning of the 21st century, Publicaciones de la Universidad de Barcelona, 2004, p. 431.
[24] D. Golinske, J. Voss, G. Adiwidjaja, Collect. Czech. Chem. Commun. 65 (2000) 862.
[25] A.A. Isse, A. Gennaro, J. Electrochem. Soc. 149 (2002) D113.
[26] A.A. Isse, A. Gennaro, Chem. Commun. (2002) 2798.
[27] R.R. Raju, S.K. Mohan, S.J. Reddy, Tetrahedron Lett. 44 (2003) 4133.
[28] D.F. Niu, L.P. Xiao, A.J. Zhang, G.R. Zhang, Q.Y. Tan, J.X. Lu, Tetrahedron 64 (2008) 10517.
[29] J.L. Olloqui-Sariego, V.M. Molina, D. González-Arjona, E. Roldán, M. Domínguez, J. Electrochem. Soc. 155 (2008) E157.
[30] J.L. Olloqui-Sariego, V.M. Molina, D. González-Arjona, E. Roldán, M. Domínguez, J. Electrochem. Soc. 157 (2010) E64.