A new electrochemically-based process for the removal of perchloroethylene from gaseous effluents

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Abstract

Removal of perchloroethylene using combined granular active carbon (GAC) adsorption and electrolysis is evaluated in this research. There is an interest in the regeneration of GAC using methanol solutions, because this process can obtain the almost complete desorption of the pollutant retained during the treatment of gaseous flows. In this work, the electrolysis of perchloroethylene (used not only as a hazardous pollutant but also as a model of organic pollutant) in methanol media containing sodium chloride and sodium hydroxide is evaluated and results are compared to those obtained during the electrolysis of this pollutant in aqueous media. Results demonstrate the feasibility of this treatment technology, which does not only remove the raw molecule but it is also capable to remove all the intermediates detected by GC-ECD, allowing the possibility of the reuse of the methanol solution for further regeneration steps.

Keywords

Perchloroethylene, gas treatment, electrochemical oxidation, GAC adsorption

Highlights

- Perchoroethylene can be removed from methanol solutions by electrolysis with BDD
- NaCl or NaOH can be used to increase the conductivity of the methanol solution
- All reaction intermediates are oxidized during the electrolytic tests
- Adding sodium hydroxide to methanol seems to produce a faster removal of intermediates
- Total removal of perchloroethylene from aqueous and methanol media is attained

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1. Introduction

In previous work of our group, it was found [1-3] that during the treatment of wastes or soils contaminated with volatile pollutants a very important fraction of the pollution contained in the soil can be transferred to atmosphere, shifting the environmental concern from soil to atmosphere. In fact, at large scales, volatilization was found to be the primary removal mechanisms during the electrochemically-assisted treatment of soil, for instance using conventional thermal treatment [4].

In order to avoid this hazardous source of air pollution, adsorption GAC particles is one of the reference technologies [5-7], because it allows retaining the pollutant in a very efficient and fast way. However, after the use of GAC, it should be regenerated and one possible and promising way to regenerate this adsorbent consists of the desorption of the adsorbed molecule using methanol, because this non-thermal GAC treatment may reduce the loses of GAC which are produced during the conventional thermal treatments. Then, once the GAC has been regenerated, the methanol solution waste has to be treated in order to remove the pollutant and the key problem is that, to the knowledge of the authors, up to now no oxidative technology has been tested for this application.

Hence, to propose a complete treatment technology in the remediation of soils polluted with volatile species, regeneration of this GAC particles may become a very important stage in many electrochemically-assisted soil remediation treatments and this work focuses on the treatment of liquids used to desorb the pollutant from GAC using electrolysis with diamond anodes.

In the last two decades, electrolysis of wastewater has undergone an important transformation with the use of diamond anodes [8-10]. The wide electrochemical window of these electrodes helps to improve the efficiency of the electrolysis by preventing the water discharge and promoting the generation of many oxidants, among which hydroxyl radicals are the most important [11, 12], although not the unique oxidants produced.

In this context, the new concept of regeneration of GAC particles is based on the previous results obtained unintentionally during the assessment of the degradation of health-related molecules (particularly progesterone and triclosan) using electrolysis with diamond anodes. Because of the low solubility of these molecules, electrolysis were carried out in methanol media in order to get valuable mechanistic information and it was found that the molecule undergoes degradation with a negligible degradation of the methanol [13-15]. These results were also found in a more recent work in the literature although in the case it was not methanol electrolyte but aqueous electrolyte with methanol [16]

Thus, except for a short communication of our group with outstanding results focused on clopyralid [17], to the knowledge of authors, no further studies were carried out about the electrochemical degradation of hazardous organics in methanol, because up to know we did not think of an application like the one presented in that work. For this reason, taking into account those surprising results, this work is focused on the treatment of methanol polluted with perchloroethylene, a chlorinated hydrocarbon pollutant with a very high volatility and whose removal has a great importance from the viewpoint of environment [18-22], because its occurrence is related to may industrial activities, in particular to those related to the cleaning of metallic pieces. It is aimed to compare results obtained by electrolysis in methanol supporting electrolyte with those obtained during the treatment of an aqueous solution of perchloroethylene of the same concentration and to pre-evaluate the process in terms of cost-efficiency. This will help to complete the first objectives in a more ambitious project that help to obtain the complete development of an electrochemical technology, which can be integrated in the treatment of gaseous effluents polluted with chlorinated hydrocarbons, by combining adsorption with electrolysis in a common treatment.

2. Materials and methods

2.1. Chemicals and reagents

Perchloroethylene ($C_2Cl_{4,}$>99%) and Hexane HPLC grade were obtained from Sigma Aldrich (Madrid, Spain) and used for GC-ECD and GC-MS. Granular Active Carbon (GAC), (Chemviron, Feluy, Belgium) was used as received. Methanol was obtained from VWR and was used as dissolvent for electrolysis. Sodium chloride and sodium hydroxide were analytical grade (Sigma Aldrich, Spain). Helium and nitrogen (Al Air Liquide España, S.A) were used in gas chromatography and helium was filtered by a Hydrocarbon Cartridge Filter (Thermo Fisher Scientific) previous to its use. Double deionized water (Millipore Milli-Q System, resistivity: 18.2 MΩ cm at 25ºC) was used to prepare soil washing fluid.

2.2. Analytical techniques

To determine perchloroethylene concentration in the liquid phase, an L–L extraction process was used before the analytical analysis. Methanol samples (2.0 mL) were analysed following extraction with hexane (2.0 mL) for 2 min using a vortex stirrer and 10 minutes with a centrifugal pump at 4000 rpm for the separation of the phases. Then hexane phase was transferred to a GC vial. All samples extracted from electrolyzed solution were filtered with 0.22 μm nylon filters before analysis. The removal of perchloroethylene was quantified by Gas Chromatography Electron Capture Detector (GC-ECD) (Thermo Fisher Scientific) using analytical column using a TG-5MS capillary column (30 m × 0.25 mm 0.25 mm), 63 Ni micro-electron capture detector, a split/splitless injector and ChromCard Software. Under the conditions used, the quantification limit of the GC- ECD was 0.1 mg dm^{-3}. The flow rate of gas He was 1.0 mL min^{-1}. The temperature of the oven was programmed as follows: kept at 50ºC for 1 minute increased to 140ºC at 10ºC min^{-1} followed by another ramp at 10ºC min^{-1} to reach 260ºC followed by 2 minutes hold. The temperature of the injector was 260 ºC. For the determination of degradation by-products originated in the electrolysis treatment a gas chromatography with a mass detector (GC-MS) was used (Thermo Fisher Scientific DSQ II) using Capillary, HP-5MS column with length and diameter of 30 m and 0.25 mm respectively. The concentration of oxidants species was determined iodometrically according to Kolthoff & Carr [23] and Standard methods [24].

2.3. Adsorption tests

The adsorption capacity of the GAC was tested with a solution of 100 mg dm^{-3} of perchloroethylene in methanol and milli- Q water as solvents. These solutions were mixed with different quantities of GAC from 0.5 to 5 g L^{-1} to obtain the different isotherms. The experiment was carried out in closed glass bottles of 100 mL placed in an incubating orbital shaker (VWR) with a stirring speed of 180 rpm for 24 hours to guarantee the thermodynamic equilibrium. A similar procedure is used in the desorption tests, in which polluted 2 g of GAC are mixed with 30 mL of solvent (water or methanol). No carbon losses were observed.

2.4. Electrochemical oxidation of synthetic solutions

Synthetic solutions were prepared with 100 mg L^{-1} of the pollutant and 50 mmol L^{-1} of electrolyte (NaCl and NaOH) in methanol and water (1 L) to determine the removal efficiency of perchloroethylene. The electrolysis were carried out in a bench-scale electrochemical setup described elsewhere [25], containing 600 mL of solution and circulated through the cell using a peristaltic pump at flow rate of 60 L h^{-1}. The anode was a 78 cm^2 BDD film (Adamant Technologies, Switzerland), (500 ppm of B, 2.25 μm thickness) and p- type Si as support and a stainless steel of similar size was the cathode. The inter-electrode gap was 1.6 mm. The electric current was provided by a Delta Electronika ES030-10 power supply (0-30V, 0-10A). Current density applied in galvanostatic mode was in the range of 20- 30 mA cm^{-2} according with typical values studied in previous works [26]. Prior to use, the electrode was polarized for 10 min in a 0.035 mol L^{-1} Na_2SO_4 solution at 15 mA cm^{-2} to remove any impurities from its surface. Samples (20 mL) were collected in the glass tank and temperature was kept constant by means of a thermo-regulated water bath.

3. Results & Discussion

Effectiveness of GAC in the retention of pollutants does not only depend on the adsorption equilibrium of the particular pollutant onto the GAC but also on its volatility. This can be clearly seen in Figure 1, where it is compared (in a discontinuous-operated system) the retention of perchloroethylene (PCE) (P^0= 18.5 mmHg at 25ºC) and clopyralid (P^0= 1.10^{-5} mmHg at 25ºC), into a column containing 7 trays filled each of them with 20 g of GAC and connected to a tank with 1L with 100 mg L^{-1} of these pollutants. The test lasted after 24 hours. While the volatilization of clopyralid is almost negligible and after the experimental time fixed for the test most of it remains in the tank, PCE is completely depleted from this tank and it is retained in the three first trays of the column. It is important to point out that because of the discontinuous operation mode, the trays in which the pollutant is retained could shift towards the end of the column, as once depleted the pollutant in the container no more pollutant is passed through the column.

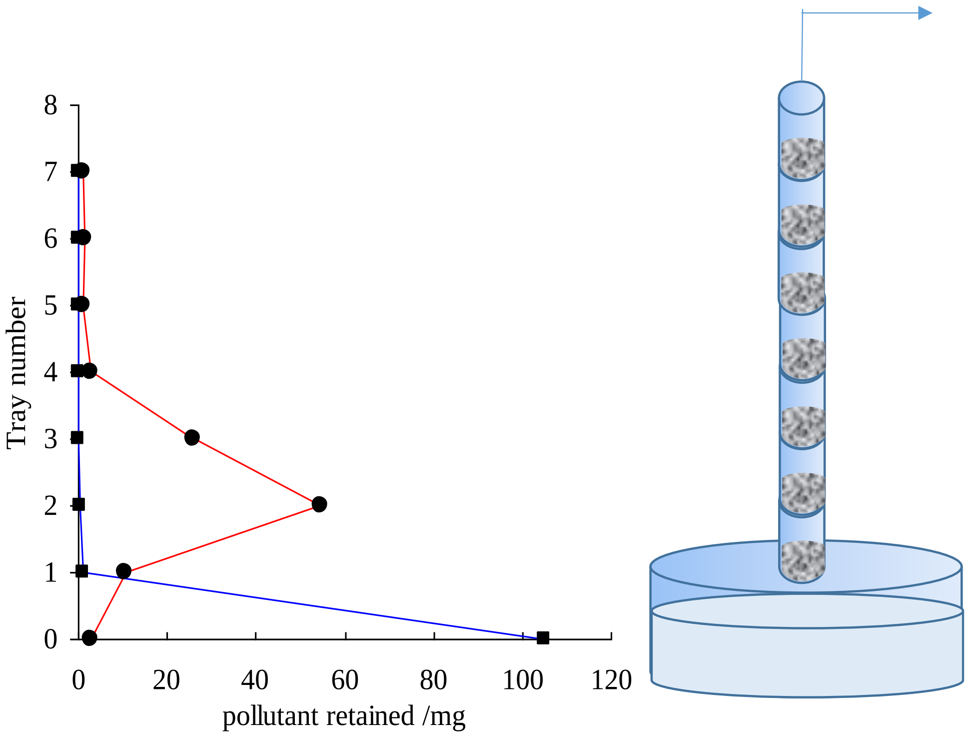

Figure 1. Adsorption of 100 mg dm^{-3} of PCE (●) and clopyralid (■) in a tray column with 140 g of GAC particles divided in 7 trays after 24 hours.

In order to recover the organic pollutant retained in the GAC, desorption with water and methanol is evaluated. As seen in Part a of the Figure 2, where the isotherms of perchloroethlyene in aqueous and methanol solutions are shown, there are very strong differences between them. The retention capability of GAC is almost two log-units higher when using water as compared to methanol, and this becomes a clear advantage for the regeneration of GAC into the organic compound instead of water, as it is a common practice in Analytical Chemistry labs.

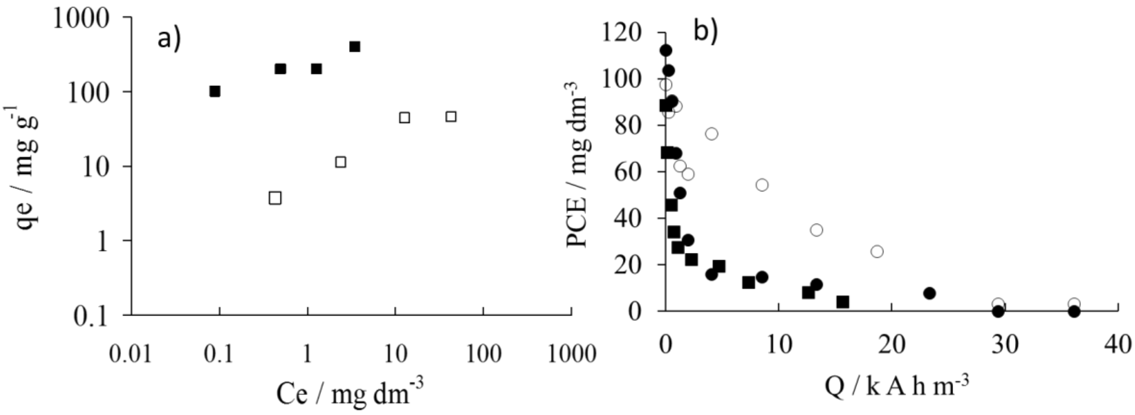

Figure 2. a) Adsorption isotherms of perchloroethylene in water (■) and methanol (□) using the same initial concentration of PCE and an increasing ratio of GAC particles. b) PCE removal vs. electric charge passed (Q) during electrolysis of a synthetic solution of 100 mg L^{-1} of PCE in water with 3000 mg L^{-1} NaCl (■), methanol with 3000 mg L^{-1} of NaCl (●) and methanol with 2000 mg L^{-1} of NaOH (○).

Part b of Figure 2 focuses on the electrolysis of synthetic solutions of 100 mg dm^{-3} of perchloroethylene in methanol. For comparison purpose, the removal of perchloroethylene in aqueous media is also shown. In this case, sodium chloride is added to increase conductivity of the solution. As PCE is a strongly chlorinated molecule, this is not a major handicap because no additional production of hazardous species is expected. In the case of using methanol as supporting electrolyte, there are two cases of study: sodium chloride and sodium hydroxide (both added in the same molar concentration). It can be seen that there are almost no differences between the electrolysis in aqueous and methanol media when both contain the same concentration of sodium chloride and that both are more efficient than the degradation in methanol with high concentrations of sodium hydroxide. Anyway, what is it really interesting is that PCE can be removed in supporting electrolytes consisting of methanol and that the efficiency of the process is suitable to try to develop a process based on the electrolysis of this pollutant in this non-aqueous media, where the concentration obtained will be much higher after a desorption process.

In order to confirm this feasibility of the electrolysis in non-aqueous media, an important piece of information can be obtained by a very simple voltammetric study. Figure 3 shows cyclic voltammograms (Electric intensity vs applied voltage) of diamond coatings (used as working electrodes) on three different solutions: methanol, methanol with 2000 mg L^{-1}of NaOH and this later electrolyte with 100 mg L^{-1} of perchloroethylene.

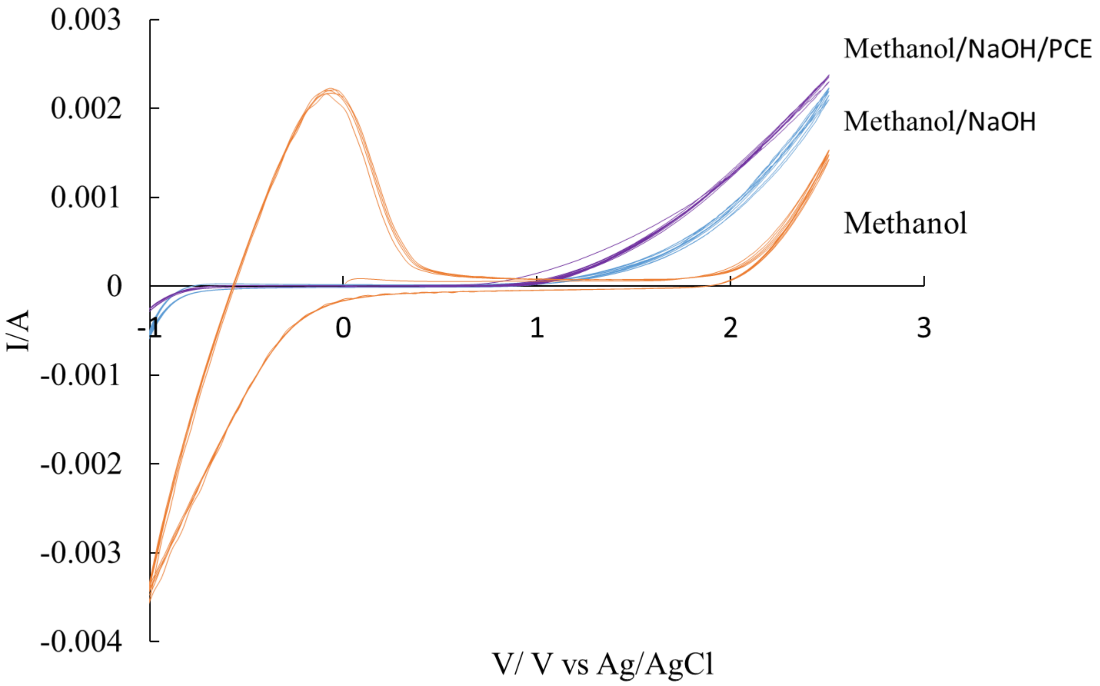

Figure 3. Cyclic voltammograms (5 cycles) of p-Si/BDD electrodes on CH$_3$OH (orange line), CH$_3$OH/NaOH (blue line) and CH$_3$OH/NaOH/PCE (purple line) solutions. Auxiliary electrode: Pt; Reference electrode: Ag/AgCl. Scan rate: 50 mV s^{-1}.

The first important observation is the extremely large electrochemical window of diamond anodes in methanol supporting electrolytes, which is quite similar to that observed in voltammograms in aqueous media [27]. It can also be pointed out a significant difference between the voltammogram obtained in pure methanol and in CH_3OH/NaOH. The peak observed in the first case can be explained in term of the oxidation of protons to hydrogen and it is very similar to that obtained to calculate the electrochemically active surface area in studies about PEMFC [28]. This is confirmed by its complete disappearance when NaOH is added and the concentration of protons becomes negligible. This clearly indicates that there is no decomposition of methanol in a very wide electrochemical window. It is also important to remark that the voltammograms in alkaline media started to rise at lower positive cell voltages, suggesting a higher reactivity in those conditions. In fact, this increase may correspond to the formation of hydroxyl radicals from the hydroxyl ions added to increase the conductivity [29]. Likewise, the higher intensities measured when perchlorothylene is contained in the electrolyte demonstrated that this compound can undergo transformations directly on the diamond surface. Hence, all these data are indicative of the good prospects of the methanol supporting electrolyte for the oxidation of PCE.

Another very interesting information about the removal mechanisms of PCE is given by the intermediates formed during the bulk electrolysis. They were monitored by GC- MS chromatography and results are shown in Figure 4. As seen in both media the three same primary intermediates were observed (there were other peaks but less important and without a clear trend, suggesting that they correspond to extremely low concentrated intermediates). Regarding the three peaks, analysis with GC determine that corresponds to dehalogenated compounds generated during the oxidation of PCE. The hydrogenation process that presumably occurs may remove the double bond and generate dehalogenated compounds as chloromethyl dichloroacetate and chloroethyl dichloroacetic acid. This behavior has previously reported in bibliography with dehalogenated intermediates as trichloroethylene and dichloroethylene. Both are compounds very close to PCE but they were obtained with softer oxidation conditions using ultrasound waves [30]. Additionally, our degradation pathway could include the pentachlroethylene as it was commented elsewhere [31], because of the reaction with the chloride radical with PCE, however due to its low concentration it was not detected with GC-MS. However, it is important to state that the compounds detected behave as intermediates and they are oxidized during the treatment, what it is a very important outcome, because it clearly indicates the technical feasibility of this technology. However, the electrolysis in methanol/sodium hydroxide media seems to be more efficient as the total removal of the raw organic and its degradation intermediates is attained during the electrolysis time, obtaining pure methanol as final product. Hence, anodic oxidation with diamond anodes in methanol media seems to behave as a good technology for the removal of PCE from methanol solutions.

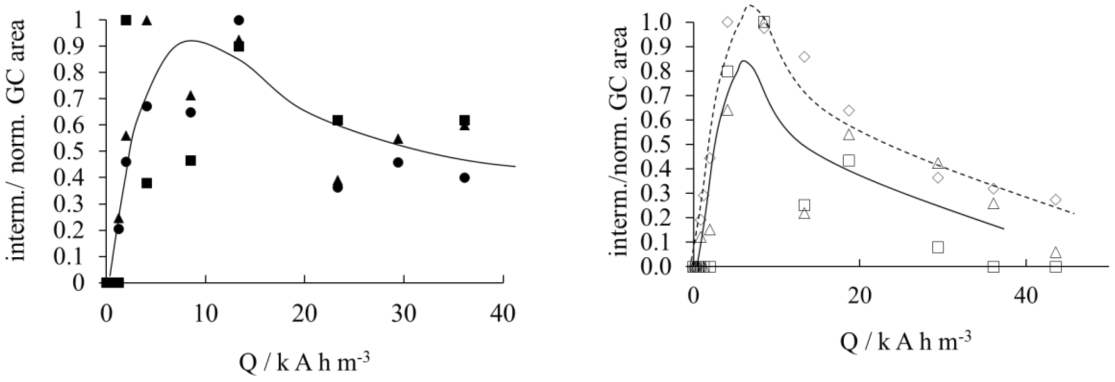

Figure 4. Intermediates detected vs. electric charge passed (Q) during the electrolysis of the two methanol solutions containing 100 mg L^{-1} of perchloroethylene in 3000 mg L^{-1} sodium chloride (full points) and 2000 mg L^{-1} sodium hydroxide (empty points). 2,2-dimethoxibutane (●); chloromethyl dichloroacetate (■); chloroethyl dichloroacetic (▲).

Figure 5 shows the amount of oxidants produced in the electrolyte during the electrolysis with the applied electric charge. As it can be seen, there is a different pattern in the three supporting electrolyte. Thus, in the alkaline methanol, almost no oxidants (capable to oxidize iodine) are produced or, if they are produced, they are rapidly consumed (this agrees with the faster oxidizability of the three intermediates found). Opposite, when sodium chloride is contained in the electrolyte, there is an important concentration of oxidants, whose time course depends on the media (methanol or water). In methanol, the concentration is much lower and it increases continuously during the treatment. Conversely, in water there is a maximum in the concentration from which it is observed a decay.

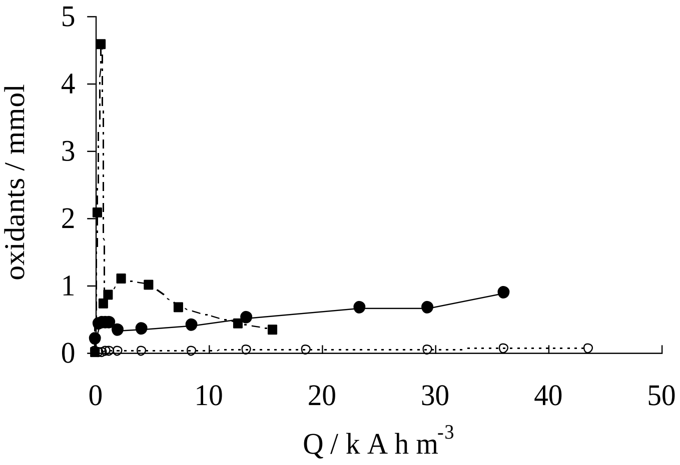

Figure 5. Oxidants formed vs. electric charge passed during the electrolysis of 100 mg L^{-1} PCE in water with 3000 ppm NaCl ■, methanol with 3000 ppm NaCl ● and methanol with 2000 ppm NaOH ○ . j: 250 A m^{-2}.

In order to explain these differences, the speciation of chlorine in the two electrolysis in which sodium chloride was contained as supporting electrolyte has to be taken into account. Thus, one very important observation is the almost absence in the production of chlorates and perchlorates during the electrolysis in methanol (Figure 6), which opposites the results obtained in aqueous media and that points out the relevance of the hydroxyl radicals in the formation of chlorinated oxoanions indicated in previous works of our group [32]. Nowadays, one of the major handicaps for the full-scale implementation of the anodic oxidation technology in the treatment of organic wastes is the production of high-oxidation state chlorine oxoanions and methanol seems to be a promising way to avoid this handicap [9, 33].

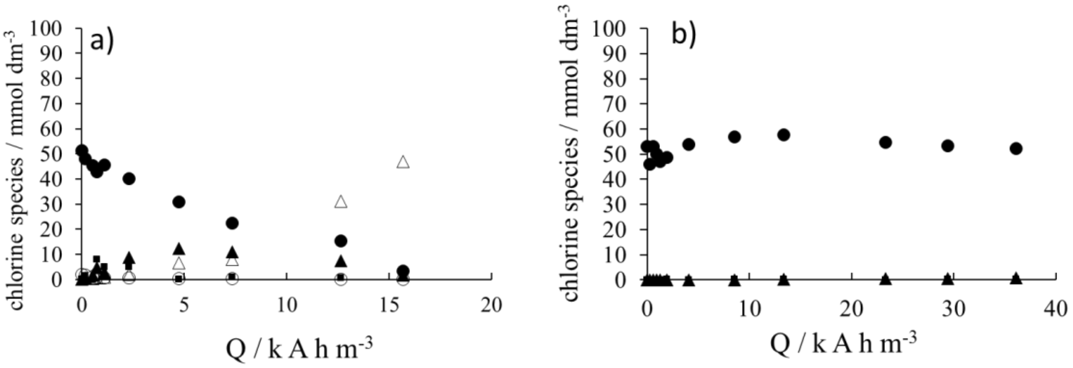

Figure 6. a) Chlorine species detected vs. electric charge passed during the electrolysis of aqueous solution with 3000 mg L^{-1} of sodium chloride b) Chlorine species vs. electric charge passed detected during the electrolysis of methanol solution with 3000 mg L^{-1} of sodium chloride. j: 250 A m^{-2}. ●chloride■ hypochlorite ▲chlorate and △ perchlorate.

Another important point to be considered for the economic feasibility is the cell voltage. Power consumption (W) depends on the intensity (I) and cell voltage (V) according to eq. 1.

$$W = I \cdot V \qquad (1)$$

In turn, cell voltage depends on the equilibrium potential, overpotentials applied and on the ohmic loses of the cell, which depend on the contribution of the electrolyte, electrode and other components of the cell. Figure 7 compares the ionic conductivity of the three electrolytes tested and the cell voltages monitored during the electrolysis. As expected the ionic conductivity is much higher in the case of water than in the two methanol solutions, indicating that the contribution of the ohmic loses associated to the electrolyte should be lower in this case. However, as observed in part b, the cell voltage is nearly the same, because the main contribution to ohmic loses in using anodic oxidation with boron doped diamond is produced by the low conductivity of the anode material.

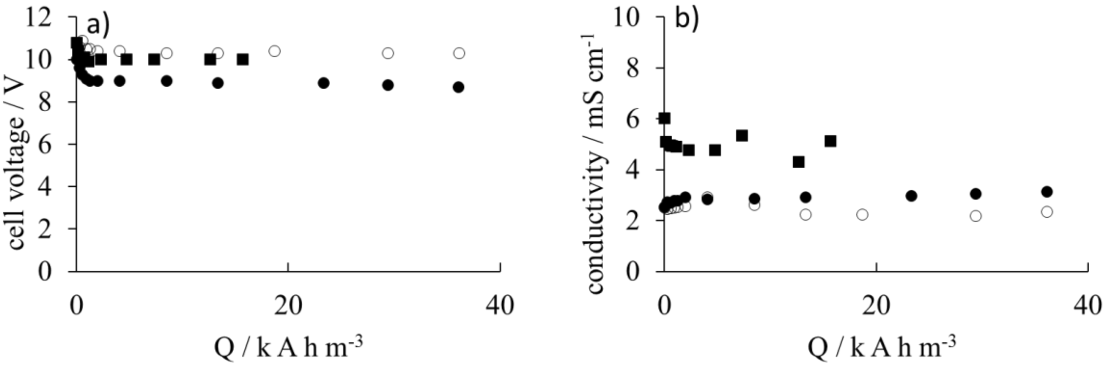

Figure 7. Evolution of cell voltage (a) and conductivity (b) during the electrolysis with BDD anodes of aqueous solution with 3000 mg L^{-1} of NaCl (■), methanol with 3000 mg L^{-1} of NaCl (●) and methanol with 2000 mg L^{-1} NaOH (○).

Hence, from the energy consumption point of view, it seems that, initially, there are no economic restriction in the use of this technology, because it does not increase the power consumed as compared to the electrolysis in water. Taking into account the higher concentration of the pollutant which can be extracted from the GAC and the direct relation of the current efficiency with the concentration, a lower amount of applied electric charge is expected to be required when using this novel technological approach.

4. Conclusions

Perchloroethylene can be removed from methanol solutions by electrolysis with diamond anodes. The electrochemical technology does not only eliminate the raw pollutant but it is also capable to oxidize all the intermediates produced. Both, sodium hydroxide and sodium chloride can be used to increase the conductivity of the electrolyte and improve the feasibility of the electrochemical treatment technology, being more efficient the use of sodium hydroxide, because it produces a faster depletion of the primary intermediates. These results point out the relevance of a new technology, which can be efficiently coupled with GAC adsorption for the treatment of gaseous effluents polluted with volatile chlorinated hydrocarbons.

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