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# Degradation of perchloroethylene aqueous solutions by sonochemical, electrochemical and sonoelectrochemical methods

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## ABSTRACT

In this work, we present a comparative analysis of the degradation of aqueous solutions of PCE by sonochemical, electrochemical and sonoelectrochemical treatment, pointing out the advantages and drawbacks of the different approaches, and also the synergic effects of the simultaneous applications of both energetic fields: ultrasound and electricity. Prior to these studies, not only were specific researches carried out in order to develop stable components (anodic materials) under high power ultrasound fields, but the experimental devices used during this study were also characterized. In summary, the sonochemical method presents serious deficiencies not only from an environmental point of view but also in its energetic requirements. The electrochemical method presents competitive costs and feasible technically processes (using optimized filter-press reactors), but it does not suit the environmental requirements. The sonoelectrochemical treatment has provided the best results from technical and environmental points of view but economical issues must be improved. Further research lines are suggested on the basis of the obtained results.

## INTRODUCTION

Chlorinated compounds have received special attention as pollutants due to their wide dissemination in the environment. Among them, perchloroethylene (PCE) is a widely used solvent in many areas of the industry and has been reported as a major intermediate in the degradation of other chlorinated compounds. The available conventional treatments are usually composed of a physicochemical step followed by a biological degradation. However, these methods have continuously presented deficiencies in treating some refractory compounds such as PCE because they are toxic for the microorganisms in the biological plant [1]. On the other hand, polluting companies are under legal pressure to degrade their own specific effluents prior to disposal, which is why we can find a wide range of emerging technologies trying to find a solution to this common problem. Chlorinated compounds have routinely been the subject of sonochemical analysis in order to check the polluted water remediation applications of this technology [2], but, to our knowledge, there has not been an extensive study of the sonochemical degradation of PCE aqueous solutions.

Other possibilities, such as the electrochemical degradation of waste waters, have not normally been used because the cheaper (but not useful) conventional treatments were widely disseminated. However, despite the general attractive advantages of the electrochemical technology such as: (i) it is applicable for a wide range of pollutants; (ii) it avoids the addition of chemicals using the electron as unique reactant; (iii) it is easily controlled by a PC; (iv) processes run under room temperature and atmospheric pressure; (v) it is easy to scale up; and (vi) it uses compact facilities [3], we do not find many electrochemical treatment studies of aqueous solutions of chlorinated compounds, especially aqueous PCE solutions. Sonoelectrochemistry means the application of ultrasound fields to electrochemical processes, and is an active research line in many different applications [4], specifically, in environmental remediation. However, the application to aqueous chlorinated compounds degradation is now emerging and only a few works can be found in the literature [5,6].

In this work, three approaches have been developed at laboratory scale, analyzing the viability of the processes from a technical, economical and environmental point of view, in spite of the fact that the sonochemical devices used were non-optimized laboratory systems and the sonoelectrochemical devices were sonochemical reactors adapted for sonoelectrochemical studies. Figures of merit, such as fractional conversion, current efficiency, mass balance error, selectivity (or speciation), degradation efficiency, degradation and energetic consumption, were defined and determined for the approaches used. This paper is not only an extracted review of part of our previous published work, but also presents new results on this subject.

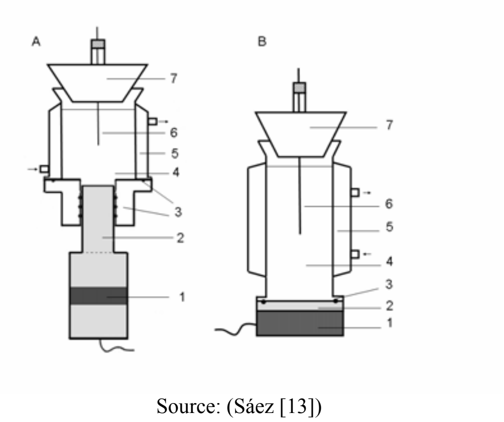
# EXPERIMENTAL SECTION

## Materials

Perchloroethylene (PCE), $C_2Cl_4$ 99.9% (Aldrich) trichloroethylene (TCE) (Aldrich) and dicloroethylene (DCE) (Aldrich), were used without further purification. Aqueous solutions were prepared with purified water obtained from a Milli-Q UV Plus system (18.2 MΩ cm resistivity). PCE was added to 500 mL of water and the solution was stirred overnight in a closed volumetric flask with a glass-covered magnetic bar to allow equilibration between the gas and liquid phases. The solution was not purged with any gas. Care was taken to minimize evaporation losses by using nearly-full volumetric flasks with tight-fitting ground-glass stoppers that were further sealed with a wrapping of Teflon tape.

## Experimental setup

Figure 1 shows a schematic diagram of the experimental setups used to sonicate the aqueous solutions of PCE at low (20 kHz) and high frequencies (380, 580, 850 and 1142 kHz). Figure 1(A) shows the 20 kHz, 100 W maximum power sonoreactor supplied by Undatim. This commercial sonoreactor, which has been fully characterized by the authors previously [7, 8], provides adjustable power. The equipment can operate at optimum frequency by means of an electronic device, which ensures that the maximum fixed power is transmitted to the reactor. Figure 1(B) presents a typical multifrequency system (MFLG) sonoreactor supplied by Meinhardt Ultraschalltechnik. The transducer is located at the bottom of the vessel and is connected to a high frequency supply. A cylindrical jacketed glass cell with 44 mm internal diameter and 270 mm height was used in these experiments.

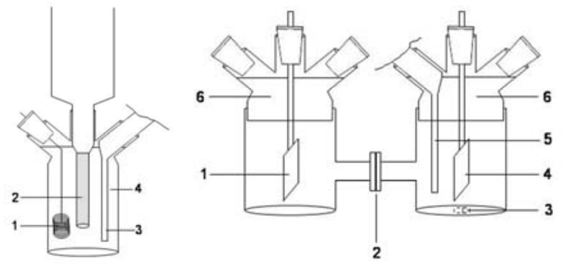


Source: (Sáez [13])

**Figure 1**. A) 20 kHz and B) multifrequency sonoreactors: (1) piezoelectric ceramic, (2) ultrasonic emitter, (3) O-ring joints, (4) solution, (5) glass cell, (6) thermocouple and sample taking, and (7) lid.

To avoid losses of PCE or reaction by-products by air-stripping, the ultrasound systems were kept closed with a cover attached to the sonoreactor. All systems were operated in continuous mode and the temperature inside the sonoreactors was kept constant at 20ºC. Power levels for the ultrasound systems were calculated using standard calorimetric methods [9, 10] and the presence of oxidative species was monitored by the terephthalic acid [11] and p-nitrophenol [12] methods. The results are given in reference [13].

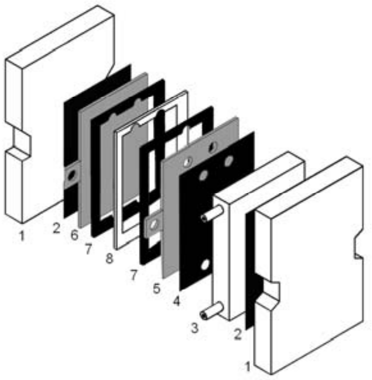
Due to the fact that the electrochemical treatment has been performed from voltammetric to pre-pilot scale, several experimental setups were used [14]. An Autolab PGSTAT30 station was used for the voltammetric analysis and also for the bulk electrolyses, in this case in galvanostatic mode. Figure 2 shows the typical voltammetric and the laboratory divided glass cell used. An AgCl/Ag/KCl(3M) electrode was used as the reference electrode in the polarization curve determination, and lead (4.5x2.5x0.3 cm) and lead dioxide (4x2.7x0.6 cm) plates were used as cathodes and anodes, respectively. A Nafion 450 cationic membrane was used to separate anolyte and catholyte solutions, of volume 150 mL each. The gas phase over the solution presented a volume of 166 mL. A Micro pH 2000 Crison pHmeter and a Crison conductivitymeter model 525 were used to measure the initial and final pH and conductivity of the solution.



Source: (Saéz [14])

**Figure 2**. Left: voltammetric cell (1) counterelectrode, (2) working electrode, (3) reference electrode, (4) working solution. Right: divided glass electrochemical cell (1) counterelectrode, (2) separator, (3) stir bar, (4) working electrode, (5) luggin capillary for the reference electrode, (6) top lid.

Electrochemical scale-up was carried out using a home-made electrochemical filter-press reactor, shown in Figure 3 [15]. The same electrode materials (lead as cathode and lead dioxide as anode) with the required dimensions were used.



Source: (Sáez [15])

**Figure 3**. Electrochemical filter-press reactor. (1) backplate, (2) backplate joint, (3) polypropylene block with flow channels, (4) electrode joint, (5) cathode, (6) anode, (7) compartment joint, (8) compartment.

Finally, the sonoelectrochemical studies so far (20 kHz) were carried out through sonoelectrolyses in galvanostatic mode using a Thandar precision DC power supply. Figure 4 shows the undivided sonoelectrochemical reactor at the laboratory scale used. This experimental setup is the 20 kHz sonochemical reactor used previously for the sonochemical treatment of PCE, which has been adapted for sonoelectrochemical trials in electrode-apart-transducer configuration. In this case, lead (4.5x2.5x0.3 cm) and lead dioxide (4x2.7x0.6 cm) plates were again used as cathodes and anodes, respectively. The volume of the working solution was 200 mL. The gas phase over the solution presented a volume of 130 mL.

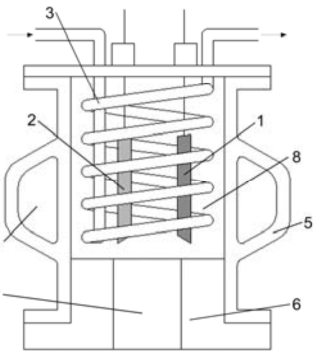


**Figure 4**. Sonoelectrochemical reactor. (1) working electrode, (2) counter electrode, (3) cooling spiral, (4) cooling jacket, (5) glass cell, (6) Teflon hold, (7) transducer ending, (8) working solution.

## Analytical methods

During the process for the aqueous phase, analyses were carried out by GC/MS (HP Technologies 6890N), GC/ECD (Varian GC 3800 microECD), CG/FID (HP 5890 Serie II), HPLC-UV (Agilent 1100 HPLC-UV) and ionic chromatography, IC, (690 Ion Chromatograph, Metrohm). Compounds in the gaseous phase were analyzed by GC/FID and GC/TCD.

At various times, aliquots were transferred from the reaction mixture in the sonoreactor, by a fine stainless steel or PTFE tube, into glass vials sealed with a PTFE/silicone septum-lined threaded cap.

At the end of the process, volatile compounds in the aqueous phase were analyzed using a DB 624 column (30 m x 0.25 mm I.D., 1.4 µm film thickness) connected with a Tekmar Dohrmann, 3100 Sample Concentrator Purge and Trap system. A 5973N Agilent mass spectrometer detector was used. The purge and trap step was carried out according to USEPA 624 protocol with the following temperature program: 40 ºC held for 10 min, then a ramp at 3 ºC/min to 200 ºC for 10 min. The sample volume was 20 mL. For determination of non-volatile trace compounds, 35ml aqueous samples were purged with nitrogen for 10 min to remove DCE, TCE and PCE in order to avoid interference with the analysis. NaCl, (8g) was added and dissolved by gentle shaking. The solutions were extracted with methyl *tert*-butyl ether (MTBE, 2mL) containing an internal standard. MTBE was removed for analysis by GC/ECD with 50% split injection.

GC/FID analyses for PCE, TCE, DCE and the determination of other organic compounds were carried out using a HP 5890 Serie II. An 80/100 carbograph 2 column of 2m x 2 mm was used with the following temperature program: 100 ºC held for 2 min, then a ramp at 5 ºC/min to 170ºC held for 10 min. The injector port and detector temperatures were 200 ºC and 225 ºC, respectively. The flow rate of nitrogen as carrier gas was 38 mL min$^{-1}$.

An Agilent 1100 HPLC-UV detector (210 nm) with a Hypersil ODS (C18) column (250 mm x 4 mm and particle diameter 5 µm) at 40ºC was used for confirmation the determination of PCE, TCE, DCE and other organic compounds. The mobile phase was a mixture of methanol/water (65/35, v/v) at a flow rate of 1 mL min$^{-1}$. A 20 µL inlet volume was used. The chloroacetic acids formed were analyzed at the same wavelength of 210 nm using a 20 mM $NaH_2PO_4$ aqueous solution, adjusted to pH 2.7 with $H_3PO_4$ as eluent at a flow rate of 1 mL min$^{-1}$. 60 µL (x2) samples were injected.

Chloride anions and other anionic species were monitored by IC. Samples of 1 mL were filtered through a 0.45 µm nylon filter, and 20 µL samples were injected into a Metrohm 690 Ion Chromatograph, equipped with a conductivity detector and an Ion-120 column, stable over the pH range. The eluent was a 4 mM sodium salicylate/salicylic acid aqueous solution, pH 7.8, at a flow rate of 1 mL min$^{-1}$.

Gaseous products in the headspace of the reactor were analyzed at the end of reaction using a HP 5890 Serie II gas chromatograph equipped with a FID detector (for column and experimental conditions vide supra). A TCD detector and a CTRI column were used for the analysis of $CO/CO_2$ and low molecular weight hydrocarbons ($CH_4$, $C_2H_2$, $C_2H_4$ and $C_2H_6$). The temperature program presented a fixed value of 35 ºC over 30 minutes. Injector port and detector temperatures were 120 ºC. Carrier: helium, 30 mL min$^{-1}$. 250 µL of gaseous headspace were taken at the beginning and the end of the reaction using a gas syringe and injected immediately. Calibration was realized with standard gaseous mixtures (Scott Specialty Gases) prior to the experiments.

The response of standards (PCE, TCE, DCE) held in sealed vials over a 24-hour time period was evaluated in order to determine how long samples could be stored prior to the analysis. The results showed a drop in response to approximately 75% of the start value after 12 hours, and to 40% after 24 hours. Therefore, all of the samples and standards were analyzed within three hours of sampling. Five standards were prepared each day for the initial calibration curve, and checked later on in the day, or when any questionable sample result was obtained. All compounds were confirmed unequivocally by comparison of retention times with the authentic standards, and their concentrations were determined from the calibration curves.

## Preliminary experiments and experimental system conditioning

For consistency of results, preliminary experiments and experimental system conditioning were carried out to establish the general behaviour of the system. (i) The temperature monitoring system was installed and checked to ensure strict control and minimize temperature fluctuation during sonication. This has allowed values to be fixed for the solubility, octanol-water partition coefficient, Henry constant, vapor pressure and other properties in our PCE + water system. The main physicochemical properties of this compound and derivatives are given in reference [13]. (ii) In spite of the glass, teflon and septum taps were used in chlorinated compound sonolysis [16,17], and the stability and compatibility of the chemicals with these reactor materials were also checked as an additional effort for the purpose of improving the mass balance, since low concentrations of the various species are involved. For this, solutions of PCE were prepared by stirring and maintained at 25ºC in volumetric flasks with (a) teflon or glass-covered magnetic bars and/or (b) glass or septum taps. Liquid and gas samples were sequentially withdrawn and analyzed for the possible combinations, and no more than 3% of the initial material was lost during the first 5 hours. These results are in agreement with the less than 5% volatilized loss of PCE during its sonochemical destruction observed by

Kang [18]. (iii) PCE is a volatile compound, so during the experiments the sonoreactor was carefully sealed, without the bubbling of any gas. After that, the equilibrium between gaseous and liquid phases (phase equilibrium) was checked experimentally. In spite of the fact that the headspaces should be as small as possible in order to avoid complications in the experiments [19], a headspace around ≈ 120 mL (to simulate further real situations) above the aqueous solution in our closed sonoreactor was used. Then, the starting material was dissolved in the sonochemical reactor and the gas and liquid concentrations were measured after the same period of time as used for the reaction. PCE partition was analyzed according to Henry's Law in respect of the gas and liquid volumes used [20], and a value of 30 % for the gas-liquid partition was obtained.

These experimental data were compared to, and found to be higher than, data given in the literature [21, 22], with a headspace lower than ours. Schwarzenbach et al. [20] reported the following equation to estimate the partitioning of organic chemicals due to Henry's law:

$$\text{fraction in water} = \frac{V_w}{K'_H V_g + V_w}$$

where $V_w$ represents the volume of the water phase, $V_g$ the volume of the gas phase, and $K'_H$ the dimensionless Henry's constant (0.73 for PCE). Using this equation, it was estimated that potentially 31% of PCE could be lost to the vapor headspace. This situation is not unusual [17] and was assumed due to the fact that it is stated [23] that in a closed system volatile solutes re-enter the treated solution and the observed losses are due to chemical reaction and not to volatilization. (iv) The pH of the solutions used was not adjusted. Buffers were not used to control the pH because many buffers are effective radical scavengers [24]. Studies were therefore carried out at the natural pH of the solutions (defined here as the pH of the solutions on dissolution of PCE in aqueous media), which was close to 5.

## RESULTS

In order to quantify the performance of the processes, the following performance parameters were defined for the three approaches: (i) fractional conversion (FC):

$$FC = \frac{[PCE]_{t=0} - [PCE]_{t=t}}{[PCE]_{t=0}} \times 100$$

(ii) degradation efficiency (DE):

$$DE = \frac{[Cl^-]_{t=t} - [Cl^-]_{t=0}}{4 \times [PCE]_{t=0}} \times 100$$

(iii) $Cl^-$ mass balance error (Cl-MBE), defined as

$$Cl-MBE = \left( 1 - \frac{\overset{P = \text{chlorinated compound}}{\sum (\text{mg of Cl in P})_{t=t}}}{(\text{mg of Cl in PCE})_{t=0}} \right) \times 100$$

(iv) selectivity or speciation, S, defined as:

$$S_i = \frac{\text{mol of the desired product i}}{\sum \text{mol of all compounds}}$$

together with other economical parameters such as (v) energetic consumption, EC, (kwh $m^{-3}$ treated) and (vi) degradation, D, ($m^3$ treated/($m^2$ day)) determined as a function of the operational variables. For electrochemical and sonoelectrochemical treatments, the current efficiency, CE, is also calculated. This parameter determines the percentage of the charge used in the desired reaction [3], and, in this case, we have calculated it from the chloride concentration measurements ($CE_{Cl^-}$) as a product of the C-Cl bond cleavage. Therefore, working at constant current, the current efficiency is defined as follows:

$$CE_{Cl^-} = \frac{[Cl^-]_{t=t_f} \times V \times 2 \times F}{I \times t} \times 100$$

in which V is the electrolyte volume (L), F is the Faraday constant (C $mol^{-1}$), I is the current (A), and t is the time (s).

### Sonochemical treatment (SCT)

In this work, not only 20 kHz but also higher frequencies (380, 580, 850 and 1142) were used for the treatment of the working solutions. The results obtained with 20 kHz showed a poor performance of the treatment. The influence of the power ultrasound is shown in Table 1.

**Table 1**. Experimental results obtained in the ultrasonic intensity series of the sonolysis of PCE, T =20 ºC, $[PCE]_0$= 452 µM, f= 20 kHz, aerated solution at natural pH.

| $I_a$(W $cm^{-2}$) | FC(%) | DE(%) | Cl-MBE% |
|---|---|---|---|
| 0.065 | 86 | 24 | 53 |
| 0.12 | 98 | 29 | 59 |
| 0.18 | 99 | 30 | 62 |
| 0.23 | 98 | 25 | 64 |
| 0.27 | 99 | 21 | 72 |

Source: (Sáez [13])

However, better results were obtained at higher frequencies, and a summary of the results of the sonochemical treatment is shown in Table 2.

**Table 2**. Experimental results obtained in the ultrasonic frequency series of the sonolysis of PCE, T =20 ºC, $[PCE]_0$= 925 μM, $I_a$= 1.436 W $cm^{-2}$, Π=0.061 W $cm^{-3}$, aerated solution at natural pH.

| f(kHz) | FC(%) | DE(%) | Cl-MBE% |
|---|---|---|---|
| 380 | 99 | 39 | 53 |
| 580 | 99 | 80 | 10 |
| 850 | 98 | 86 | 1 |
| 1142 | 98 | 43 | 43 |

Source: (Sáez [13])

The best results for PCE degradation or sonolysis (in terms of DE% and Cl-MBE) were obtained at 580 and 850 kHz, suggesting that these frequencies provide the highest cavitation efficiency. The first step of the mechanism is the degradation of PCE into other chloroethenes in the hot bubble interior, along with the production of $OH^{\cdot}$ radicals. Next, two parallel steps can interfere: pyrolysis of the remaining compounds, and oxidation by the $OH^{\cdot}$ radicals. The latter is predominant at low frequency, because in this case, contact with chloroethenes inside the cavitating bubbles is longer, leading to highly soluble oxygenated compounds, which were found to be, at least, chloroacetates. Conversely, at high frequencies, the pyrolysis of the chloroethenes inside the cavitation bubbles is prevalent, taking part in the degradation of the initial PCE and the formation of residual (at ppb level) 1C, 3C and 4C chlorinated compounds, which is supported by the larger DE% and Cl-MBE obtained in this case. The oxidation by $OH^{\cdot}$ radicals is lower at high frequencies because they are ejected into the solution and do not have time to form oxygenated compounds in the hot gas phase. This was checked with the sonochemical reactions carried out in the presence of t-ButOH, which scavenges the $OH^{\cdot}$ radicals in the liquid phase, therefore producing a higher DE and reducing the formation of oxygenated compounds compared to that in the absence of t-ButOH.

In particular we identified a problem in accounting for the mass balance before and after ultrasonic degradation. Therefore, we paid great attention to the determination of by-products and degradation products, and have identified a further class of products, a mixture of haloacetates, which, along with a wide range of by-products, 2C volatile and hydrophobic compounds such as TCE and DCE, now yields a mass balance > 97% in some conditions. However, other volatile and hydrophobic chlorinated compounds with 1C, 3C, 4C, and oxygenated chlorinated compounds such as trichloroacetaldehyde and other unidentified compounds, are also produced at ppb level as minor components.

From the applicative point of view, it should be noted that all these compounds, especially the water-soluble haloacetate ions, are of some intrinsic toxicity, so that the overall environmental benefit of insonation to destroy pollutants of this type remains debatable. However, if used in combination with a means of removing such ions from the solution, then a good level of water purification could be achieved.

## Electrochemical treatment (ECT)

The electrochemical treatment began with voltammetric analysis of PCE electroreduction [25, 26]. This study did not provide conclusive results about the electrocatalysis of the different materials under investigation, and therefore bulk electrolyses were also carried out. Three different approaches were used: cathodic, anodic and dual treatment. As a summary, Figure 5 shows the degradation percentage vs time for the three treatments using the system shown in Figure 2B. The anodic "degradation" has been included despite the fact that this treatment did not present a good performance. It is interesting to highlight that the degradation is higher in the dual treatment than in the cathodic treatment, even when there are more losses of chlorinated compound to the gas phase, and the PCE concentration decay appears very similar to the behavior presented in the cathodic treatment. The degradation in the dual treatment is not the sum of the cathodic and anodic contribution, so there is a synergistic effect. On the other hand, the evolution of major intermediates (TCE and DCE) presents similar behavior.

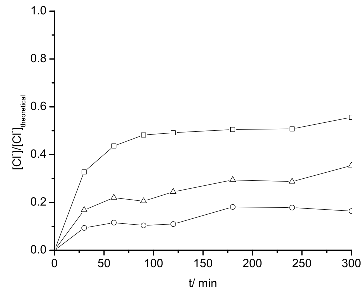


**Figure 5**. Degradation vs time for the three treatments: dual (□), cathodic (△) and anodic (○) degradation.

Source: (Sáez [14])

Several important conclusions have been obtained which support the further scale-up of the process:

*At potentials lower than the hydrogen evolution reaction onset, the initial compound can be totally degraded (lower than 7% of the initial product remaining) and $Cl^-$, DCE and TCE were found as chlorinated byproducts. The mass balance on total chlorine can now be closed so the process runs by a clean route: it does not follow a "soluble radical" mechanism, avoiding the production of more toxic, dangerous compounds or polymerization.

* The results show the need to use potentials lower than for the hydrogen evolution reaction, which means that the atomic hydrogen produced plays an important role in the reduction mechanism and low current efficiencies are obtained (lower than 2%).

* Chloroacetic anions have been clearly detected in the anodic treatment of PCE, which, along with the presence of $CHCl_3$ and $CCl_4$ compounds, suggests that the anodic degradation follows a slow and complex multipath route.

* The undivided configuration presents the highest degradation, around 50%, the cheapest investment (the membrane is one of the more expensive components), and the easiest handling (avoiding problems associated with membranes (fouling, replacement and overpressure)).

With this scenario, scale-up, using a practical filter-press reactor, as shown in Figure 3, was carried out. Figure 6 shows the normalized PCE concentration decay and the normalized TCE and DCE concentration evolutions for two- and three-dimensional carbon electrodes.

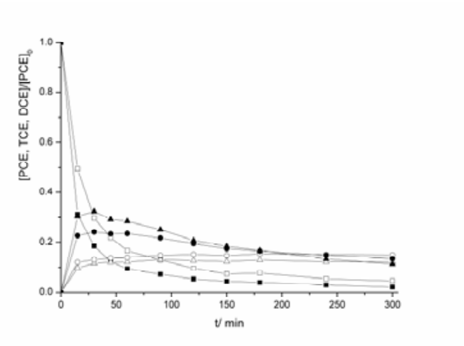


**Figure 6**. Evolution of the normalized PCE, TCE and DCE concentrations for 2D (☐, Δ,○) and 3D (■, ▲, ●) carbon electrodes. $[PCE]_0$= 150 μM, $Q_v$= 150L/h, anode $PbO_2$.
Source: (Sáez [15])

Electrochemical degradation presents a low speciation for the treatment of PCE, which lends simplicity to the process. However, even working with high volumetric flows or high electrode areas, the concentration of chlorinated compounds is not decreased at longer times. This tendency is shown for all the studied electrodes, indicating that there is no specific influence of the electrode material (similar results were obtained with copper and lead electrodes, figure not shown). Therefore, more environmentally friendly materials, such as carbon or copper (instead of lead), can be used as the cathode for this application.

Even though the results are not conclusive, the better performance of the three-dimensional electrode at shorter times, when the process seems to be under kinetic control, could support the relevance of indirect electron transfer by the adsorbed hydrogen.

From our results, it can not be concluded that the use of carbon felt is a good option for applied approaches (despite the shorter time needed) due to the higher EC. Two-dimensional electrodes, with an averaged cost close to 3 kWh $m^{-3}$ using the undivided configuration (which prevents any complication with the separation component (membranes)), provide the best option.

### 20 kHz sonoelectrochemical treatment (SECT)

Table 3 shows a summary of the results obtained using the sonoelectrochemical treatment, along with the results of the previous treatments.

Different effects have been described when an ultrasound field is applied simultaneously to an electrochemical process [27, 28], effects which have been observed in a large number of applications [4, 29]. Mass transport enhancement and, therefore, higher current efficiencies for processes under mass transport control are typical benefits observed [30]. Another described benefit is the surface activation [31], derived from cavitation at the electrode surface. In our case, we have shown previously that, working with two-dimensional electrodes [15], the degradation process of the PCE was, at least, partially controlled by mass transport conditions. Therefore, the enhancement of mass transport not only brings higher FC and current efficiencies (both increases due to the fact that even for a low concentration of starting material, a higher supply of this to the electrode surface is achieved) but also a higher speciation, probably due to the fact that the intermediates can mainly be removed from the electrode surface and suffer the sonochemical action of cavitation in the bulk solution. High mass transport conditions are also obtained with high volumetric flows or acoustic streaming [32], but it is routinely accepted that the cavitation events provide a stronger and more local increase of mass transport, especially at the surface of the electrode [33], which implies an extra agitation.

**Table 3**. Main results for bulk sonoelectrolysis at batch scale. Influence of the ultrasonic power. Comparison between sonoelectrochemical, electrochemical (data taken form reference [15]) and sonochemical (data taken from reference [13]) treatments

| **SECT** Π/ W $cm^{-3}$ | **FC** /% | **DE** /% | **Cl-MBE** /% | $\mathbf{S_{Cl^-}}$ | $\mathbf{CE_{Cl}}$ /% | **EC** /kWh $m^{-3}$ |
|---|---|---|---|---|---|---|
| 0.065 | 97 | 37 | 38 | 0.86 | 1.2 | 327 |
| 0.120 | 97 | 46 | 47 | 0.96 | 5 | 603 |
| 0.180 | 100 | 57 | 39 | 0.98 | 6 | 902 |
| 0.225 | 100 | 53 | 43 | 0.99 | 7 | 1128 |
| 0.270 | 100 | 56 | 41 | 0.99 | 8 | 1352 |
| **SCT** Π/ W $cm^{-3}$ | **FC** /% | **DE** /% | **Cl-MBE** /% | $\mathbf{S_{Cl^-}}$ | $\mathbf{CE_{Cl}}$ /% | **EC** /kWh $m^{-3}$ |
| 0.065 | 86 | 24 | 53 | 0.79 | --- | 325 |
| 0.120 | 98 | 29 | 59 | 0.88 | --- | 600 |
| 0.180 | 99 | 30 | 62 | 0.92 | --- | 900 |
| 0.225 | 98 | 25 | 64 | 0.90 | --- | 1125 |
| 0.270 | 99 | 21 | 72 | 0.91 | --- | 1350 |
| **ECT** $Q_v$/ L $h^{-1}$ | **FC** /% | **DE** /% | **Cl-MBE** /% | $\mathbf{S_{Cl^-}}$ | $\mathbf{CE_{Cl}}$ /% | **EC** /kWh $m^{-3}$ |
| 100 | 84 | 51 | 4 | 0.75 | 2 | 2.9 |
| 150 | 87 | 65 | 2 | 0.87 | 2.5 | 2.7 |
| 200 | 86 | 42 | 5 | 0.71 | 1 | 2.8 |
| 250 | 84 | 68 | 13 | 0.84 | 1 | 3.8 |

In the electrochemical degradation with divided configuration [14], we have proposed that the mechanism of the electroreduction (C-Cl cleavage) runs by means of a mechanism with some intermediates adsorbed onto the electrode. Working with an undivided configuration, the cleavage of the C=C and C-C bonds were suggested due to anodic process on the anode. Besides, the process seems to be partially controlled by the mass transport conditions [15], especially when the electrochemical process under these experimental conditions is carried out using two-dimensional electrodes. Due to the increase of the speciation when the ultrasound field is applied, it seems that the radical attack, coming from the cavitation events, becomes more relevant. This attack can be focused not only on the PCE, but also on the intermediates, such as TCE and DCE, due to the fact that we do not have enough evidence to ascribe the total elimination of these intermediates to their cavitationally enhanced mass transport and direct reduction onto the cathode. Besides, other aspects should not be unquestionably discarded as possible beneficial effects, such as the surface activation caused by the cavitation events. A dual mechanism for the reduction of chloroethenes, direct reduction vs mediated reduction by adsorbed hydrogen, has been routinely suggested [34], and the chemical activity of $H^{\cdot}$ radicals coming from water sonolysis has been reported previously [35]. Therefore, an increase of adsorbed hydrogen through the interaction between the $H^{\cdot}$ radicals and the electrode surface could partially improve this degradation by SECT.

## CONCLUSIONS

The combination of ultrasound and electrical fields provides a reaction environment for PCE aqueous solution treatment which greatly improves on the sonochemical and electrochemical treatments, providing an acceptable procedure from a technical point of view. Solutions with lower conductivities, simulating real waters, should complete the study of technical viability.

At a frequency of 20 kHz, the lower ultrasound intensity provides a smaller influence of the ultrasound field and, for ranges of higher ultrasound intensities, an increase of the ultrasound intensity does not exhibit a better performance of the process, so the influence is, in fact, related to the presence or absence of the ultrasound field.

The energetic consumption with the sonoelectrochemical treatment is lower than that presented by sonochemical treatment, due to the fact that the treatment time is significantly reduced. Sonoelectrochemical treatments using high frequencies, pulsed ultrasound strategies and/or flow sonoelectrochemical reactors should provide economically viable treatments.

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