20 kHz sonoelectrochemical degradation of perchloroethylene in sodium sulfate aqueous media: Influence of the operational variables in batch mode

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ABSTRACT

A preliminary study of the 20 kHz sonoelectrochemical degradation of perchloroethylene in aqueous sodium sulfate has been carried out using controlled current density degradation sonoelectrolyses in batch mode. An important improvement in the viability of the sonochemical process is achieved when the electrochemistry is implemented, but the improvement of the electrochemical treatment is lower when the 20 kHz ultrasound field is simultaneously used. A fractional conversion of 100% and degradation efficiency around 55% are obtained independently of the ultrasound power used. The current efficiency is also enhanced compared to the electrochemical treatment and a higher speciation is also detected; the main volatile compounds produced in the electrochemical and sonochemical treatment, trichloroethylene and dichloroethylene, are not only totally degraded, but also at shorter times than in the sonochemical or electrochemical treatments.

1. Introduction

Chlorinated compounds have been revealed as a strong recalcitrant group of pollutants, found in all kinds of water sources [1]. As a consequence of the poor efficiency of the biological methods for the degradation of chlorinated compounds, a large number of alternative technologies have emerged and been developed in the last decade. These include not only simple procedures such as catalytic hydrogenation [2], metal alloys in dilute aqueous alkaline solutions [3] or other techniques such as photochemistry [4], sonochemistry [5] and also electrochemistry [6], but also combined treatments such as reductive dehalogenation and biodegradation [7], which are being considered as possible methods for the degradation of chlorinated organocompounds.

Sonoelectrochemistry means the application of ultrasound fields to electrochemical processes, and is an active research line in many different applications [8]; specifically, in environmental remediation we can find peer-reviewed papers since the 1990s. Recently, there have been reports not only of combined multi-techniques for the destruction of organic pollutants in water [9,10], which show the wide range of possible com-

binations of sonoelectrochemistry with other technologies, but also of the applications of sonoelectrochemistry for non-chemical treatments [11] or for the mediated synthesis of disinfectant agents, such as hypochlorite [12]. However, the most common approach in the sonoelectrochemical treatment (SECT) is direct sonoelectrolysis in the configuration named "electrode-apart-transducer" [13]. With this kind of experimental set-up, Trabelsi et al. [14] analyzed the sonoelectro-oxidation of aqueous solutions of phenol + 0.5 g L^{-1} NaCl, and compared the results with those obtained by sonochemical (SCT) and electrochemical (ECT) treatments used separately. Both 20 and 540 kHz frequencies and a constant current density of 6.8 mA cm^{-2} were used during the sonoelectrolyses, with nickel foam as the cathode and platinized titanium grid as the anode. Higher fractional conversions were obtained at both frequencies, but shorter times were needed at high frequency. The authors revealed that the process becomes unrealistic at low frequency due to the formation of toxic compounds such as quinones, but higher frequency did not yield toxic aromatic compounds, with only acetic and chloroacrylic acids detected. Better effects in the combined technology, sono-electrochemistry, were detected in contrast with the sonolytical and electrochemical route. The sonoelectro-oxidation of pollutants has been further used in the degradation of dye effluents such as Sandolan Yellow [15], Procion Blue [16], and Meldova Blue [17], of pesticides such as 2,4-dihydroxybenzoic acid [18], 2,4-

dichlorophenol [19], and of additives such as thiosulfate [20] and cyanides [21].

Sonoelectroreduction is the other route, which has been used for environmental applications. The recovery of silver from photographic processing solutions [22], and the degradation of pollutants present in water, such as chlorinated organocompounds [23,24] are examples of processes studied. Perchloroethylene (PCE) is a widely used solvent in many areas of industry and has been reported as a major intermediate in the degradation of other chlorinated compounds. In our laboratory we are analyzing the degradation of this compound using different approaches: (i) by electrochemical treatments with not only fundamental [25,26] but also applied [27,28] studies; (ii) sonochemical treatments [29] and now (iii) sonoelectrochemical treatments, as in the present study.

2. Experimental section

2.1. Materials

Perchloroethylene, C_2Cl_4, 99.9% (Aldrich) was used without any further purification. Aqueous solutions were prepared with purified water obtained from a Milli-Q UV Plus system (18.2 MΩ cm resistivity). Na_2SO_4 was dissolved to give a concentration of 0.05 M, with the solutions subsequently purged with Argon. PCE was then added and the solution stirred in a closed volumetric flask with a glass-covered magnetic bar. The solutions were left overnight with slow stirring to dissolve and equilibrate. Care was taken to minimize the effects of evaporation losses by using nearly full volumetric flasks with tight-fitting ground-glass stoppers that were further sealed with Teflon tape. The initial concentration of PCE was in the range of 60–452 μM.

2.2. Experimental set-up

Bulk sonoelectrolyses were carried out in galvanostatic mode using a Thandar precision DC power supply. Fig. 1 shows the undivided sonoelectrochemical reactor at the laboratory scale used. This experimental set-up is the 20 kHz sonochemical reactor previously
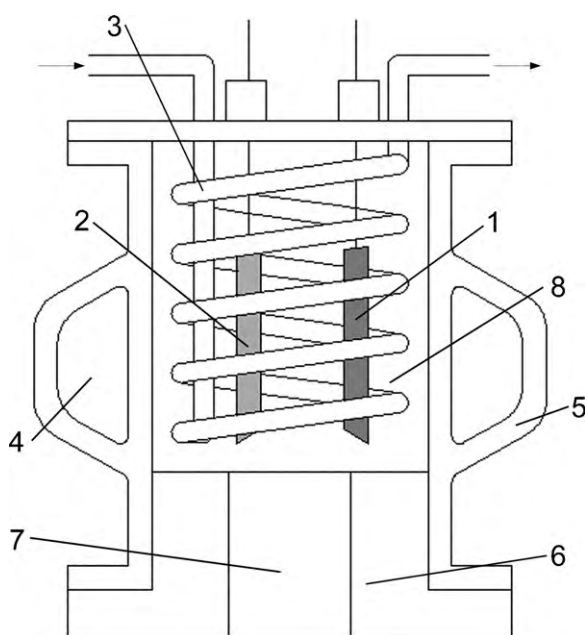
Fig. 1. Sonochemical reactor adapted as sonoelectrochemical reactor. (1) Working electrode, (2) counter electrode, (3) cooling spiral, (4) cooling jacket, (5) glass cell, (6) Teflon hold, (7) transducer ending, and (8) working solution.

used for the sonochemical treatment of PCE [29] and characterized [30,31], which has been adapted for sonoelectrochemical trials in electrode-apart-transducer configuration. Lead (4.5 cm × 2.5 cm × 0.3 cm) and lead dioxide (4 cm × 2.7 cm × 0.6 cm) plates were used as cathodes and anodes, respectively. Lead was chosen as the working electrode for this approach because of its high overpotential for the reduction of water [32], in spite of the theoretical drawbacks from an environmental point of view. No erosion of this material was observed during the sonoelectrochemical experiments. The volume of the working solution was 200 mL. The gas phase over the solution presented a volume of 130 mL. A Micro pH 2000 Crison pHmeter and a Crison conductimeter model 525 were used to measure the initial and final pH and conductivity of the solution. The pH and conductivity changed from the initial values (6.0 and 7.3 mS cm^{-1}) to the final values (3.4 and 8.6 mS cm^{-1}).

2.3. Analysis

For the aqueous phase, analyses were carried out by GC/MS (HP Technologies 6890N), GC/ECD (Varian GC 3800 microECD), GC/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. Detailed information about the temperature programmes used can be found in previous papers of the authors [27,28]. Due to the fact that the pH was also higher than 3.5 during the sonoelectrolyses, chlorine evolution was disregarded.

3. Results and discussion

Even using a specific sonoelectrochemical reactor for which geometry aspects are already established, in sonoelectrolysis a large number of operational variables have to be fixed. So, in addition to the chemical operational variables, such as concentration of the starting material, solvent, pH, conductivity, convection conditions and temperature, and the pure electrochemical operational variables, such as electrode materials, current density or electrode potential, we also have to establish the specific ultrasound operational variables, such as working frequency and ultrasound power. Therefore, an extensive study of a sonoelectrochemical process should imply a huge number of experimental trials, which is beyond the scope of this paper. In this study, we will analyze the combination of a high power 20 kHz ultrasound field with the conditions previously reported for the electrochemical degradation of PCE electrolysis [27], and the influence of the ultrasound power as an operational variable. Two different trials were conducted: (i) sonoelectrolyses in which samples were taken at different times along the process, and (ii) sonoelectrolyses in which samples were only taken at the beginning and at the end of the process. No differences in the results were detected in these two methods.

We have carried out PCE sonoelectrolysis experiments at different ultrasound intensities of 1.84, 3.39, 5.09, 6.36 and 7.64 W cm^{-2} (i. e. 0.065, 0.120, 0.180, 0.225 and 0.270 W cm^{-3}), with $T = 20\,°C$, 60 ppm (362 μM), and the value of the working current density, j_w, fixed at 3.5 mA cm^{-2}. Fig. 2A shows the normalized concentration decay and Fig. 2B shows the current efficiency for the ultrasonic intensity series. The current efficiency determines the percentage of the charge used in the desired reaction [33], and, in this case, we have calculated it from the chloride concentration measurements (CE_{Cl^-}) as a product of the C–Cl bond cleavage. Along the manuscript, the [Cl$^-$] should be really assumed as the sum of all inorganic chlorinated compounds (Cl$^-$ and ClO$_3^-$). Therefore, working at constant current, the current efficiency is defined as follows:

$$CE_{Cl^-} = \frac{[Cl^-]_{t=t_f} \times V \times 2 \times F}{I \times t} \times 100 \tag{1}$$
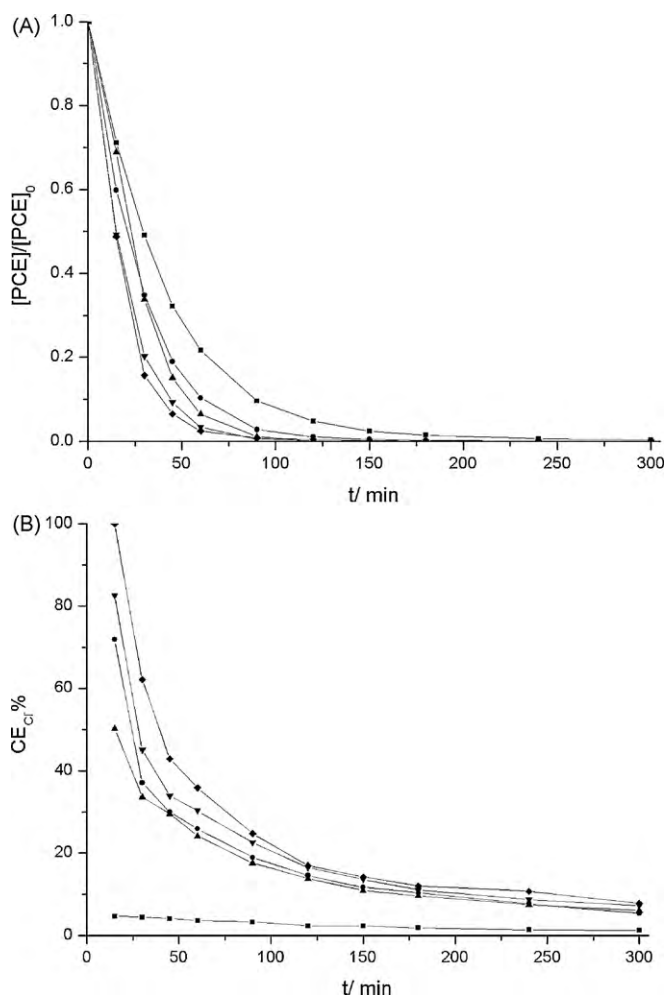
Fig. 2. (A) The normalized concentration decay of PCE and (B) the current efficiency for the ultrasonic intensity series: ■ 1.84, ● 3.39, ▲ 5.09, ▼ 6.36, ♦ 7.64 W cm^{-2}. f = 20 kHz, 3.5 mA cm^{-2}, 20 °C.

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). A clear influence of the increasing ultrasound intensity was shown with an increase in the rate of disappearance of PCE and also in the CE$_{Cl^-}$. Despite the special behavior detected for the lower ultrasound intensity, for which the CE$_{Cl^-}$ is quite low, it is important to point the exponential decay for any studied ultrasound intensity. It is also important to highlight the fact that the reasonable values of CE$_{Cl^-}$ obtained (>25% for chlorinated compounds), are maintained during the first hour of treatment, in comparison with those obtained during the electrochemical route (not higher than 8% in the best situation).

In order to quantify the performance of the process, the following performance parameters were defined:

(i) Fractional conversion (FC):

$$FC = \frac{[PCE]_{t=0} - [PCE]_{t=t}}{[PCE]_{t=0}} \times 100 \qquad (2)$$

(ii) Degradation efficiency (DE):

$$DE = \frac{[Cl^-]_{t=t} - [Cl^-]_{t=0}}{4 \times [PCE]_{t=0}} \times 100 \qquad (3)$$

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

$$Cl\text{-}MBE = \left(1 - \frac{\displaystyle\sum^{P=\text{chlorinated compound}} (\text{mg of Cl in P})_{t=t}}{(\text{mg of Cl in PCE})_{t=0}} \right) \times 100 \qquad (4)$$

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

$$S_i = \frac{\text{mol of the desired product } i}{\sum \text{mol of all compounds}} \qquad (5)$$

with other economical parameters such as (vi) energetic consumption, EC, (kWh m^{-3} treated) and (vii) degradation, D, (m^3 treated/(m^2 day)) determined as a function of the operational variables.

Investigating the influence of the presence of the ultrasound field in the electrochemical degradation more closely, the main intermediates detected during the previous electrochemical studies [27,28], trichloroethylene (TCE) and dichloroethylene (DCE), were followed during the reactions. Fig. 3 shows the evolution of PCE, TCE and DCE and the appearance of chloride and chlorate anions for all studied ultrasonic intensities. In an averaged analysis for all ultrasound intensities, all of these volatile compounds were totally degraded in the first 2.5 h of the process, in contrast to the electrochemical route, for which, even at high volumetric flows, steady state remaining concentrations of TCE and DCE (higher than 10% of the initial concentration of PCE for each one) were routinely detected even after 5 h of treatment.

The evolution of DE (not shown) with time can be envisaged from the evolution of [Cl$^-$] and [ClO$_3^-$] in Fig. 3. This evolution also corroborates the idea that the degradation proceeds mainly during the first hour, reaching DE values higher than 40% in this first period. No detectable differences are envisaged for most ultrasonic intensities, but the lowest one, 1.84 W cm^{-2}, showed a lower DE.

In order to quantify the performance of the process, different performance parameters, such as fractional conversion, FC, energetic costs, EC, (kWh m^{-3} treated) or degradation, D, (m^3 treated/(m^2 day)), along with DE and Cl-MBE have also been determined as a function of the ultrasonic intensity, I_a. All these results will be a first approximation of the technical and environmental viability of the process. Table 1 shows the main results after 2.5 h of processing and at the end of these experiments, and also the best results obtained by the ECT electrochemical [28] and SCT sonochemical [29] treatments. First, it is important to highlight that the US + ECT simultaneous combination implies synergic effects rather than the addition of these effects. On one hand, SCT is clearly improved when electrolysis is simultaneously carried out: FC, DE, Cl-MBE and S_{Cl^-} improve without a significant enhancement of EC. Besides, the number of different volatile compounds is lower, with only CH$_2$Cl$_2$ and CHCl$_3$ at ppb level detected at the lowest ultrasound intensities. On the other hand, the addition of an ultrasonic field to the ECT, albeit beneficial, has a less evident impact, and merits a deeper analysis. With SECT, FC is practically 100% at any ultrasonic intensity, and DE is around 55% regardless of the ultrasound intensity used. It is also important to point out that the Cl-MBE increases due to the fact that, as in reference [29], we have not taken into account soluble chlorinated compounds, such as chloroacetic acids. These kinds of compounds have previously been reported by the authors as an important group of byproducts, poorly formed during the ECT of PCE aqueous solution [27] and especially during the SCT at high power and low frequencies (20 kHz) [29]. However, from an applied point of view, the param-
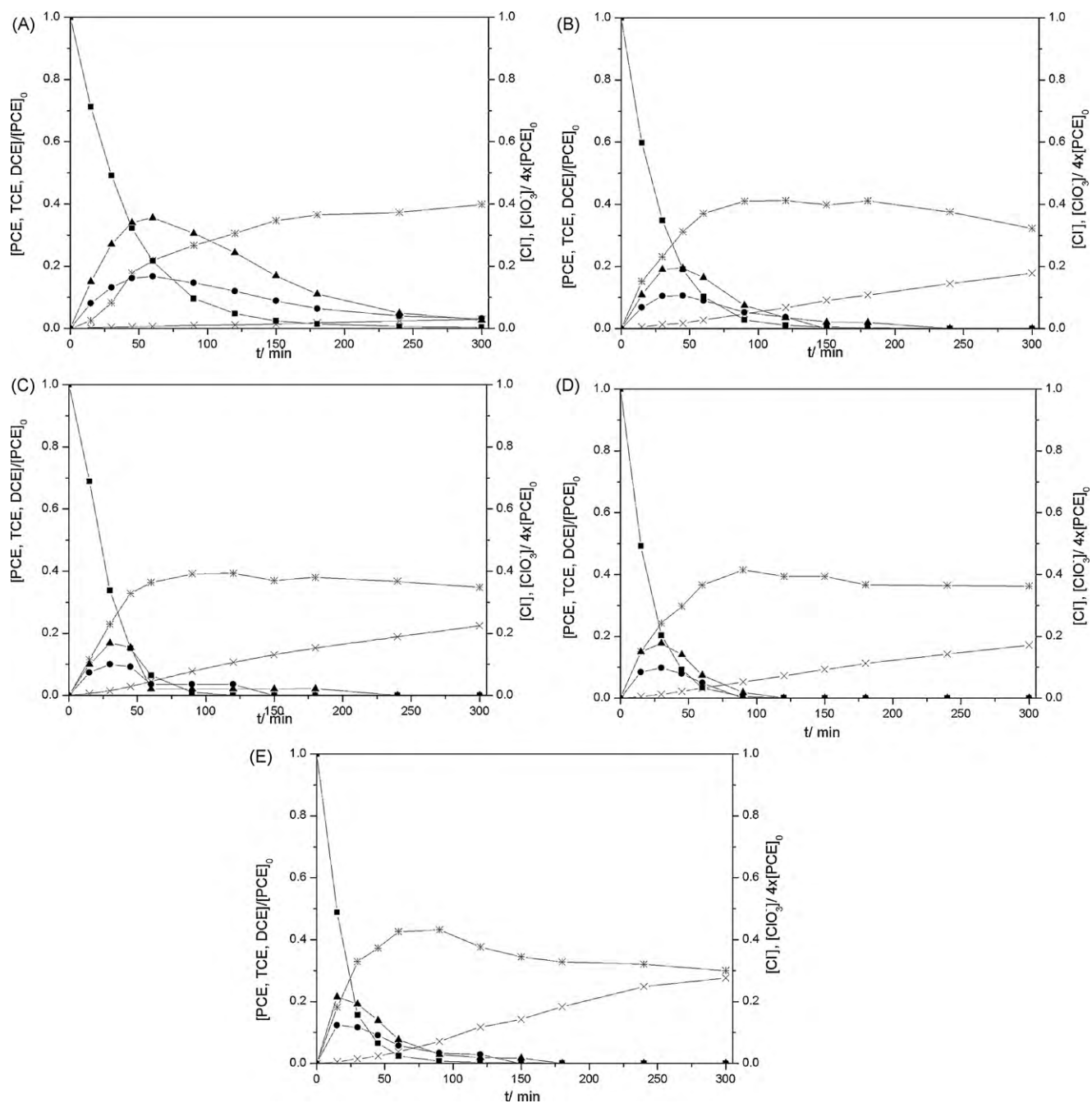
Fig. 3. Normalized concentration evolution vs time: ■ PCE, ▲ TCE ● DCE, *Cl$^-$ and *ClO$_3^-$ at different ultrasonic intensities (A) 1.84; (B) 3.39; (C) 5.09; (D) 6.36 and (E) 7.64 W cm^{-2}. f = 20 kHz, 3.5 mA cm^{-2}, 20 °C.

eters which must be optimized are the FC and, especially, the DE (which gives us a clear idea about the removal of chlorinated toxicity), and the EC, which is the main drawback of the SCT and SECT. In relation to this aspect, different developments [34–36] and strategy studies [37–39] are providing promising results to overcome this drawback. The main contribution of the presence of the ultrasound field during the ECT is not only the total degradation of the main volatile compounds (PCE, TCE and DCE), but also the decrease of the effective reaction time. The CE$_{Cl^-}$ is also higher in the presence of ultrasound. A longer time in sonoelectrolyses (from 150 to 300 min) improves the Cl-MBE but decreases the CE$_{Cl^-}$.

Different effects have been described when an ultrasound field is applied simultaneously to an electrochemical process [40,41], effects which have been observed in a large number of applica-

tions [8,13]. Mass transport enhancement and, therefore, higher current efficiencies for processes under mass transport control are typical benefits observed [42]. Another described benefit is the surface activation [43], derived from cavitation at the electrode surface. In our case, we have previously shown that, working with two-dimensional electrodes [28], 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

Table 1

Main results for bulk sonoelectrolysis at batch scale. Influence of the ultrasonic power. Undivided configuration. Comparison between sonoelectrochemical, electrochemical (data taken from Ref. [28]) and sonochemical (data taken from reference [29]) treatments.

	FC/%	DE/%	Cl-MBE/%	S_{Cl^-}	CE_{Cl^-}/%	EC/kWh m^{-3}	Reaction time/min
SECT (this study) I_a/W cm^{-2}–Π/W cm^{-3}						US + ECT	
1.84–0.065	95	30	52	0.83	2.3	163 + 1.17	150
	97	37	38	0.86	1.2	325 + 2.46	300
3.39–0.120	96	46	45	0.97	12	300 + 1.22	150
	97	46	47	0.96	5	600 + 2.51	300
5.09–0.180	96	50	50	1.00	11	450 + 1.17	150
	100	57	39	0.98	6	900 + 2.46	300
6.36–0.225	97	49	48	0.99	13	563 + 1.13	150
	100	53	43	0.99	7	1125 + 2.21	300
7.64–0.270	97	50	46	0.98	14	675 + 1.20	150
	100	56	41	0.99	8	1350 + 2.32	300
SCT [29] I_a/W cm^{-2}–Π/W cm^{-3}							
1.84–0.065	86	24	53	0.79	–	325	300
3.39–0.120	98	29	59	0.88	–	600	300
5.09–0.180	99	30	62	0.92	–	900	300
6.36–0.225	98	25	64	0.90	–	1125	300
7.64–0.270	99	21	72	0.91	–	1350	300
ECT [28] Q_v/L h^{-1}							
100	84	51	4	0.75	2	2.9	300
150	87	65	2	0.87	2.5	2.7	300
200	86	42	5	0.71	1	2.8	300
250	84	68	13	0.84	1	3.8	300

mass transport conditions are also obtained with high volumetric flows or acoustic streaming [44], 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 [45], which implies an extra agitation.

In the electrochemical degradation with divided configuration [27], 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 [28], 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 [46], and the chemical activity of H• radicals coming from water sonolysis has been reported previously [47]. Therefore, an increase of adsorbed hydrogen by the interaction between the H• radicals and the electrode surface could partially improve this degradation by SECT. Further work related to this aspect is in progress.

Another aspect to keep in mind when we compare our SCT and SECT is the fact that, as a consequence of the application of the electrical field, we have also added sodium sulfate to the aqueous solution of PCE to provide a minimum electrical conductivity (concentration as low as 0.05 M). We point out this fact because some authors have reported the addition of an electrolyte for the enhancement of the sonochemical treatment of pollutants [48–50] and, therefore, a possible contribution from this must, in principle, be considered. Seymour and Gupta [48] reported enhancements of reaction rates (6-fold for chlorobenzene, 7-fold for p-ethylphenol and 3-fold for phenol oxidation), which are proportional to the diethyl ether–water partitioning coefficient of the pollutants. It appeared that the majority of oxidation reactions occur in the bubble-bulk interface region. The addition of salt increases the ionic strength of the aqueous phase, which drives the organic pollutants toward the bubble-bulk interface. This conclusion was reached with concentrations of 0, 0.17, 0.67 and 1.38 M. The same authors, in addition to the partitioning enhancement, also pointed out that salt decreases the vapor pressure and increases the surface tension. These latter two factors will help in promoting a more violent collapse of the bubble. Further study needs to be carried out in order to understand the salt effect in terms of the influence on surface tension and vapor pressure. However, the same authors estimated that the 1.38 M concentration should decrease vapor pressure by only 8% and increase surface tension by only 5%. Hence it is quite possible that the surface tension and vapor pressure effects may be negligible in comparison to the partitioning effect. Another interesting influence is the decrease in the surface tension due to the presence of excess hydrophobic molecules at the interface. The surface tension affects the nucleation process [51] and the cavitational threshold. Other effects ascribed to the presence of electrolyte are the decrease in the gas solubility, its non-coalescing action [49] and persistence of the bubbles after insonication [50]. With this wide scenario, the disentangling of the benefits from application of the electrical field and from the presence of the background electrolyte merits a deeper analysis in further work.

4. 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, but for ranges of higher ultrasound intensities, the increase of the ultrasound intensity does not exhibit a better performance.

The energetic consumption with 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.

Acknowledgements

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List of symbols and abbreviations

CE: counter electrode acting as anode, also current efficiency
CE_{Cl}: current efficiency calculated from chloride concentration measurements
Cl-MBE: mass balance error following chlorine atoms, %
D: degradation, m^3 treated/(m^2 day)
DCE: dichloroethylene
DE: degradation grade, %
EC: energetic consumption, $kWh\,m^{-3}$
ECT: electrochemical treatment

F: Faraday constant, $96,485\,C\,mol^{-1}$
FC: fractional conversion, %
GC/ECD: gas chromatography with electron capture detector
GC-FID: gas chromatography with flame ionization detector
GC/MS: gas chromatography with mass selective detector
GC/TCD: gas chromatography with thermal conductivity detector
HPLC–UV: High performance liquid chromatography with ultraviolet detector
I: current, A
IC: ion-exchange chromatography
j_w: working current density in galvanostatic electrolyses
PCE: perchloroethylene
S: selectivity
S_{Cl^-}: selectivity of chloride anion
SCT: sonochemical treatment
SECT: sonoelectrochemical treatment
t: time, s
TCE: trichloroethylene