Sonoelectrochemical degradation of perchloroethylene: the influence of ultrasonic variables, and the identification of products

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Sonochemistry is a technique that offers promise for pollutant degradation, but earlier studies on various chlorinated substrates do not give a definitive view of the effectiveness of this methodology. We now report a thorough study of ultrasonic operational variables upon perchloroethylene (PCE) degradation in water (variables include ultrasonic frequency, power and system geometry as well as substrate con-centration) and we attempt to close the mass balance where feasible. We obtained fractional conversions of >97% showing very effective loss of pollutant starting material, and give mechanistic proposals for the reaction pathway based on cavitational phenomena inducing pyrolytic and free radical processes. We note major products of Cl^- and CO_2/CO, and also trichloroethylene (TCE) and dichloroethylene (DCE) at ppm concentrations as reported earlier. The formation at very low (ppb) concentration of small halocom-pounds ($CHCl_3$, CCl_4) and also of higher-mass species, such as pentachloropropene, hexachloroethane, is noteworthy. But of particular importance in our work is the discovery of significant quantities of chloro-acetate derivatives at ppm concentrations. Although these compounds have been described as by-prod-ucts with other techniques such as radiolysis or photochemistry, this is the first time that these products have been identified in the sonochemical treatment of PCE; this allows a much more effective account of the mass balance and may explain earlier inconsistencies. This reaction system is now better identified, but a corollary is that, because these haloacetates are themselves species of some toxicity, the use of ultrasound here may not sufficiently diminish wastewater toxicity.

1. Introduction

Chlorinated compounds have routinely been subjects of sonochemical analysis in order to check the polluted water remediation applications of this technology [1]. Among them, hydrophobic and volatile chlorinated organic compounds, such as CCl_4 [2–4], trihalomethanes [5], chlorobenzene [6–9] and TCE [10–12], have attracted significant attention, and it has been routinely accepted that they are degraded in the interior of cavitation bubbles by pyrolysis or in the interfacial region of a cavitation bubble, rather than in the aqueous solution. Petrier et al. [13] compared the sonochemical degradation of chlorobenzenes and chlorophenols as examples of hydrophobic and hydrophilic compounds. They suggested that when the substrates are mixed, chlorobenzene is degraded inside the bubble before chlorophenols. They explained these findings by the different volatilities of the two species and by the fact that in the bubble, chlorobenzene degradation overwhelms the $OH^{\cdot}$ formation process. Thus, they found that the degradation of chlorobenzene was total, giving CO_2 and HCl, whereas chlorophenols are degraded into formic acid, oxalic acid and CO_2. However, this simple mechanism can present several interactions with other operational variables, such as the dissolved gas. Drijvers et al. [7] have detected different intermediates depending on whether the saturating gas is air or argon. For air-saturated

Abbreviations: t-ButOH, tert-butanol; Cl-MBE, mass balance error following chlorine atoms (%); DCAA, dichloroacetic acid; DCAAD, dichloroacetaldehyde; DCE, dichloroethylene; DE, degradation efficiency (%); FC, fractional conversion (%); FID, flame ionization detector; G, product yield (mol J^{-1}); GC/ECD, gas chromatography with electron capture detector; GC/MS, gas chromatography with mass spectroscopy detector; HPLC–UV, high performance liquid chromatography with ultraviolet detector; IC, ion-exchange chromatography; K_{ow}, octanol–water partition constant; MCAA, monochloroacetic acid; MCAAD, monochloroacetaldehyde; MTBE, methyl tert-butyl ether; PCE, perchloroethylene; PTFE, Teflon; TCA, trichloroethane; TCAA, trichloroacetic acid; TCAAD, trichloroacetaldehyde; TCD, thermal conductivity detector; TCE, trichloroethylene.

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solutions, it is possible to detect oxygenated compounds due to the interaction between the organic radicals formed in the interior of the cavitating bubble and oxygen, rather than direct degradation by $OH^{\cdot}$ radicals. However, few authors have previously suggested such a complex mechanism in sonochemical treatments, and further research is needed.

An aspect related to the previous one is the analysis of the mass balance in the sonochemical degradation and the speciation at the end of the reaction. Both aspects are also directly related to the real detoxification of wastewater by sonochemical methods. A literature review shows that few authors comment on the mass balance, due to the difficulty in identifying all the species [6,13,14] involved in complicated chemical kinetics and a wide distribution of products [15]. With chlorinated organic compounds, two different atoms can be followed: C and Cl. The latter is easier to monitor from an analytical point of view. However, even when choosing Cl as the target element, some authors [3] have admitted that the mass balance after sonolysis can be as low as 50% [16] and frequently >70% [2,3,14]. Therefore, the question of the fate of the chlorine atoms in the degradation process remains.

Although 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, [2–4,10,17] to our knowledge, there has been no extensive study addressing the sonochemical degradation of this compound. Colussi et al. [18] and Bhatnagar and Cheung [19] related kinetics to the ultrasonic frequency (20 kHz) and vapor pressure of the compound. This latter work showed: (i) pH and temperature have little effect upon the destruction rate of the compound and the vapor pressure does not correlate with the destruction rate of 2C compounds such as PCE; (ii) nonspecificity of the process with a percentage of destruction higher than 72%; (iii) PCE can be degraded by pyrolysis accompanied by radical oxidation; and (iv) no other chlorinated products in the sonolysis of PCE were found by GC/MS analysis. Inazu et al. [20] analyzed the influence of the dissolved gas on the degradation grade, which is close to 80% at 200 kHz, following the chemical yields for chloride anions and carbon monoxide and/or carbon dioxide. They concluded that the main reactions are thermal decomposition or combustion in cavitation bubbles, rather than reactions involving $OH^{\cdot}$ radicals or H atoms. Clark et al. [21] studied the influence of the initial concentration on the kinetics and found no influence for concentrations above 75 ppm PCE. They reduced the concentration to less than 0.9 ppm. No TCE or DCE as by-products were formed at concentrations above the detectable limits in solution (<0.01 ppm). PCE has also been detected and ultrasonically degraded in natural ground water at concentrations in the range of μg/L [22]. The effect of initial concentration, steady state temperature and frequency were investigated, but a thorough account of quantitative data on by-product analysis, reaction mass balance and a systematic study of the influence of the operational variables have not been given. The aim of our work is to address these issues.

2. Experimental section

2.1. Materials

Perchloroethylene, C_2Cl_4 99.9% (Aldrich), was used without further purification. Aqueous solutions were prepared with purified water obtained from a Milli-Q UV Plus system (18.2 MΩ cm resistivity). The solvent was not purged with any inert gas, and, therefore, remained air-equilibrated. 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. Care was taken to minimize evaporation losses by using nearly-full volumetric flasks with tight-fitting ground-glass stoppers, which were further sealed with a wrapping of Teflon tape. The initial values for pH and conductivity were 5 and 1 μS cm^{-1}.

2.2. Experimental setup

Fig. 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). Three different sonoreactors were used. Fig. 1(a) shows the 20 kHz, 100 W maximum power, sonoreactor supplied by Undatim, previously characterized by the authors [23,24]. Fig. 1(b) presents a typical multifrequency system (MFLG), sonoreactor supplied by Meinhardt Ultraschalltechnik. Two similar systems were used (one per laboratory), each one with specific features of maximum power frequencies.

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 20 °C. Power levels for the ultrasound systems were calculated using standard calorimetric methods [25,26] and the presence of oxidative species was monitored by the Fricke [27] and p-nitrophenol [28] methods. The results are given in Table 1. A Micro pH 2000 Crison pH meter and a Crison conductimeter model 525 were used to measure the pH and conductivity of the solution.

2.3. Analytical methods

Aliquots were routinely withdrawn at various times from the reaction mixture in the sonoreactor by a fine stainless steel PTFE tube into 2.5 mL glass vials and sealed with a PTFE/silicone septum-lined threaded cap.

PCE and the main by-products in the aqueous phase were monitored using a high performance liquid chromatograph. An Agilent 1100 HPLC–UV detector set to a wavelength of 210 nm with a Hypersil ODS (C18) column was used. The eluent was a mixture methanol/water (65/35, v/v) for PCE, TCE and DCE analyses, and a 20 mM NaH_2PO_4 aqueous solution, adjusted to pH 2.7 with H_3PO_4, was used as eluent in the determination of chloroacetic acids.

Qualitative analyses were carried out by GC/MS to determine all the possible volatile products formed at the end of the reaction. An HP Technologies 6890N gas chromatograph was used with a DB 624 column connected with a Tekmar Dohrmann, 3100 Sample Concentrator Purge and Trap system, and a 5973N Agilent mass spectrometer detector was used. The purge and trap step was carried out according to the USEPA 624 method. The temperature program was 40 °C for 10 min then a ramp at 3 °C min^{-1} to 200 °C for 10 min.

For the determination of nonvolatile chlorinated compounds, aqueous samples were purged with nitrogen to eliminate volatile compounds prior to the analysis, and the extraction was carried out with methyl *tert*-butyl ether (MTBE) containing an internal standard. The extract was analyzed by GC/ECD (Varian GC 3800 microECD) with a DB-5 MS fused-silica capillary column. The temperature program was 40 °C for 12 min then a ramp at 15 °C min^{-1} to 150 °C for 8 min followed by other ramp at 10 °C min^{-1} to 200 °C. The injector port and detector temperatures were 200 and 290 °C, respectively. The flow rate was 1 mL min^{-1} for He and 25 mL min^{-1} for N_2. Using this procedure, trichloroacetaldehyde (TCAAD) and monochloroacetaldehyde (MCAAD) could be detected, but some of the peaks found in the chromatogram were not identified.

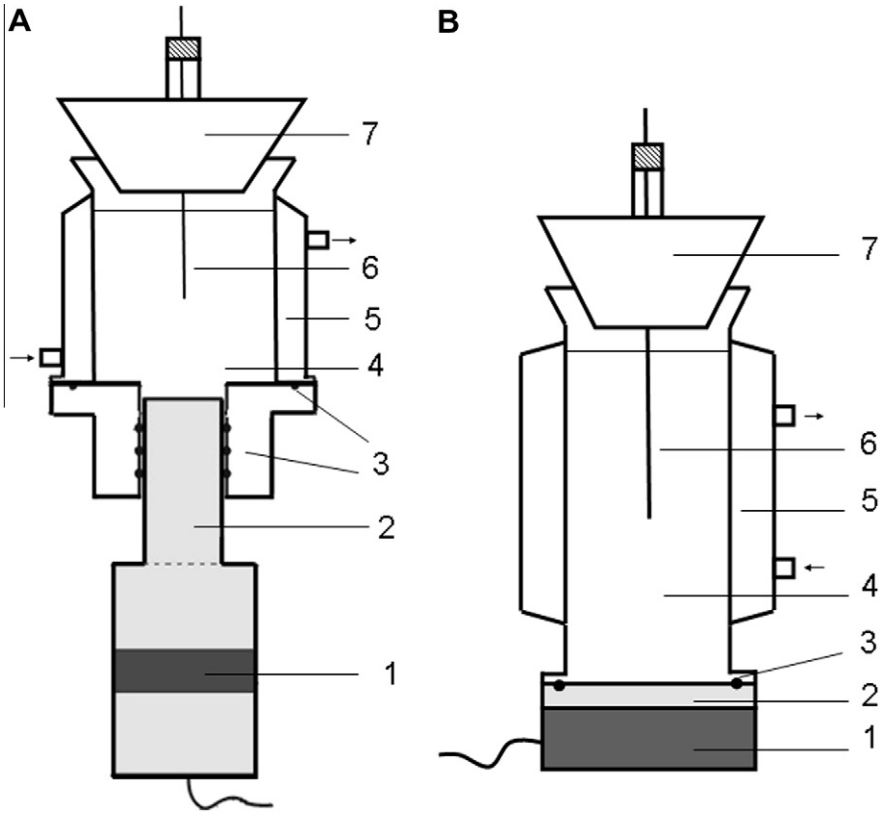

Fig. 1. (A) 20 kHz and (B) multifrequency sonoreactors: (1) piezoelectric ceramic (2) ultrasonic emitter, (3) O-ring joints, (4) solution, (5) glass cell, (6) thermocouple and sample taking and (7) lid.

Table 1
Characterization of the sonoreactors used.

Frequency (kHz)	I_a (W cm^{-2})	Π (W cm^{-3})	[$^{\cdot}$OH] (μM min^{-1})	G (10^{-11} mol J^{-1})
20	1.84	0.07	0.158[a]	9.40
	3.39	0.12	0.452[a]	15.69
	5.09	0.18	0.594[a]	13.75
	6.36	0.23	0.557[a]	10.09
	7.64	0.27	0.609[a]	9.40
380	1.436	0.061	0.923[b]	25.22
580	1.436	0.061	2.081[b]	56.86
850	1.436	0.061	0.977[b]	26.69
1142	1.436	0.061	0.855[b]	23.36
850	0.094	0.004	0.105[b]	43.75
	0.424	0.018	0.287[b]	26.57
	1.436	0.061	0.977[b]	26.69
	2.778	0.118	–	–

[a] Hydroxyl radical production calculated using Fricke dosimeter.
[b] Hydroxyl radical production calculated using nitrophenol dosimeter.

Chloride anions and other anionic species were monitored by ionic chromatography (IC). Samples were filtered through a 0.45 μm nylon filter and were injected into a Metrohm 690 Ion Chromatograph, equipped with a conductivity detector and an Ion-120 column. The eluent was a 4 mM sodium salicylate/salicylic acid aqueous solution.

Gaseous products (PCE, TCE, DCE) in the headspace of the reactor were analyzed at the end of the reaction using HP 5890 Serie II gas chromatograph equipped with an FID detector using an 80/100 carbograph column. The temperature program was an initial value of 100 °C for 2 min then a ramp at 5 °C min^{-1} to 170 °C for 10 min. The inject temperature was 200 °C and the detector temperature was 225 °C. Nitrogen was the carrier gas with a flow rate of 38 mL min^{-1}. The same gas chromatograph, equipped now with a TCD detector and a CTRI column, was 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 °C for 30 min. The inject and detector temperatures were 120 °C. Helium was the carrier gas with a flow rate of 30 mL min^{-1}. Calibration was carried out 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 h period was evaluated 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 h, and to 40% after 24 h. Therefore all of the samples were analyzed immediately after collection. 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.

3. Results

In order to ensure consistency of results and to establish the general behavior of the system, (i) the temperature monitoring system; (ii) the stability and compatibility of materials and chemicals (no more than 3% of the initial material was adventitiously lost during the first 5 h in accordance with the literature [29]) and (iii) the watertightness and equilibrium between gaseous and liquid phases were experimentally checked. The experimental value of 30% of gas–liquid partition was in agreement with the 31% PCE partition obtained with Henry's law in respect of the gas and liquid volumes used [30]. This situation is neither unusual [10] nor problematic because it is assumed [3] that in a closed system volatile solutes reenter the treated solution and the observed losses are due to chemical reaction rather than volatilization.

Besides, the pH of the solutions used was not adjusted. All these preliminary experiments permitted the experimental system conditioning.

3.1. Sonolysis of aerated aqueous solution of PCE at low frequency

3.1.1. Initial concentration effects at 20 kHz

We have carried out PCE sonolysis experiments at different initial concentrations of 101, 383 and 618 μM, reflecting the narrow window of solubility for this substrate. Other variables were kept constant at the following values: 20 kHz frequency, ultrasonic intensity 6.36 W cm^{-2}, power density 0.23 W cm^{-3} and solution volume 200 mL. Fig. 2 shows the normalized concentration for three different initial concentrations of PCE. A clear superposition can be seen, showing the required reproducibility in our analysis in spite of the problematic system under study. In order to quantify the performance of the process, the fractional conversion (FC), defined as

$$\mathrm{FC} = \frac{[\mathrm{PCE}]_{t=0} - [\mathrm{PCE}]_{t=t_f}}{[\mathrm{PCE}]_{t=0}} \times 100 \quad (1)$$

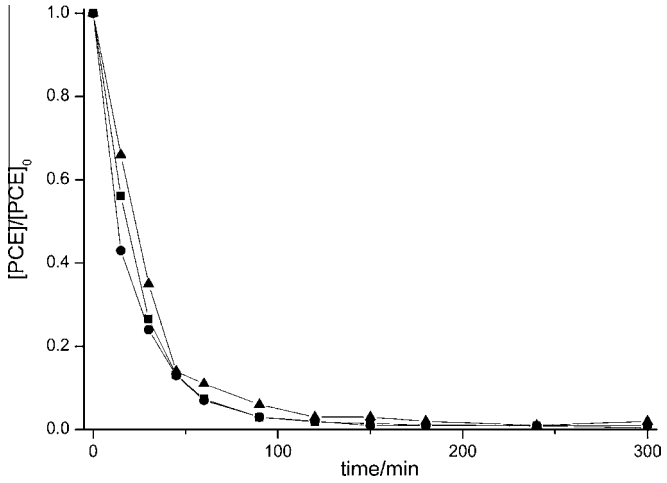

Fig. 2. PCE normalized concentration decay for different initial concentrations: (●) 101, (■) 383 and (▲) 618 μM PCE. Frequency 20 kHz, ultrasonic intensity 6.36 W cm^{-2}, T 20 °C.

the degradation efficiency (DE), defined as

$$\mathrm{DE} = \frac{[\mathrm{Cl}^-]_{t=t_f} - [\mathrm{Cl}^-]_{t=0}}{4 \times [\mathrm{PCE}]_{t=0}} \times 100 \quad (2)$$

and the Cl^- mass balance error (Cl-MBE), defined as

$$\mathrm{Cl-MBE} = \left(1 - \frac{\sum^{\text{P=chlorinated compound}} (\text{mg of Cl in P})_{t=t_f}}{(\text{mg of Cl in PCE})_{t=0}}\right) \times 100 \quad (3)$$

were routinely determined for each experiment. Table 2 shows the main results with the final products detected at the end of these experiments and those found in literature. In this table, we have also included the values of product yield, G (mol J^{-1}), as defined in Ref. [27]. However, these previous works were mainly focused on kinetic studies on the sonochemical degradation of PCE without giving detailed mass balances or calculations of degradation efficiency. These authors suggested total degradation based on non-detection of other chlorinated compounds [19] or based on previous literature [21]. Our fractional conversions were close to those expected by other authors under similar experimental conditions and, like Clark et al. [21], we also detected TCE and DCE as major by-products. According to the pyrolytic nature of the degradation mechanism for volatile compounds repeatedly suggested in the literature [12], GC analyses proved to be able to detect not only simple chlorinated organic compounds (1C: carbon tetrachloride and chloroform) but also more complex chlorinated organic compounds (2C: pentachloroethane, hexachloroethane, 3C: tetrachloropropene, 1,1,2,3,3,3-hexachloropropene and 4C: 1,1,2,3,4,4-hexachlorobutadiene) at ppb levels. The formation of these breakdown products confirmed the radical-pyrolytic nature of the sonolytic degradation mechanism. The degradation efficiency values obtained in our experiments were lower than we should expect from literature. The Cl-MBE values were much higher than expected and only in agreement with specific comments in literature with other volatile chlorinated compounds [16]. It is important to highlight that even despite the fact that the PCE reaction kinetic seems to be unaffected by the initial concentration (Fig. 2), the DE decreased and the Cl-MBE increased as the initial concentration of PCE was increased.

3.1.2. Ultrasonic intensity effects at 20 kHz

Table 3 shows our typical experimental results obtained at the end of the sonolysis in the 20 kHz ultrasonic intensity series. These

Table 2
Comparison of the experimental results obtained in the initial concentration series for the sonolysis of PCE at 20 kHz, I_a = 6.36 W cm^{-2}, II = 0.23 W cm^{-3}, T = 20 °C, aerated solution, pH_i natural, with those found in literature in similar experimental conditions.

C (μM)	FC (%)	DE (%)	Cl-MBE (%)	Final products C (μM) other operational variables	G (10^{-11} mol J^{-1})	References
482	100	100	–	Not detected (n.d.) pH_f = 3.5, T = 20–25 °C I_a = 157 W cm^{-2}, II = 0.1 W cm^{-3}	–	[19]
151, 301, 452, 602, 904	>99	–	–	Only TCE and DCE < 0.1 T > 33 °C, II = 0.3 W cm^{-3}	–	[21]
101	86	48	35	PCE 14 TCE (n.d.) DCE (n.d.) Cl–1C Cl–3C, Cl–4C < 6	– – – –	This work
383	96	42	52	PCE 17 TCE (n.d.) DCE (n.d.) Cl–1C, Cl–3C, Cl–4C < 6	– – – –	This work
618	98	25	64	PCE 13 TCE 35 DCE 41 Cl–C, Cl–C, Cl–4C < 6	– 0.85 1 –	This work

Table 3
Comparison of the experimental results obtained in the ultrasonic intensity series of the sonolysis of PCE at 20 kHz, T = 20 °C, $[PCE]_0$ = 452 μM, aerated solution, pH_i natural, with those found in literature in similar experimental conditions, $pH_f \approx 3$ for all experiments.

Π (W cm^{-3}) I_a (W cm^{-2})	χ_f (μS cm^{-1})	FC (%)	DE (%)	Cl-MBE (%)	Final products C (μM) other operational variables	G (10^{-11} mol J^{-1})	References
0.1 157	–	100	100	–	Not detected (n.d.) $[PCE]_0$ = 482 pH_f = 3.5, T = 20–25 °C	–	[19]
0.3 –	–	>99	–	–	Only TCE and DCE < 0.1 $[PCE]_0$ = 151, 301, 452, 602, 904 T > 33 °C	–	[21]
0.065 1.84	200	86	24	53	PCE 58 TCE 25 DCE 29 Cl–1C, Cl–3C, Cl–4C < 6	– 2.0 2.3 –	This work
0.12 3.39	342	98	29	59	PCE 6 TCE 23 DCE 47 Cl–1C, Cl–3C, Cl–4C < 6	– 1.1 2.2 –	This work
0.18 5.09	374	99	30	62	PCE 6 TCE 30 DCE 36 Cl–1C, Cl–3C, Cl–4C < 6	– 0.9 1.1 –	This work
0.23 6.36	415	98	25	64	PCE 13 TCE 35 DCE 41 Cl–1C, Cl–3C, Cl–4C < 6	– 0.8 1.0 –	This work
0.27 7.64	508	99	21	72	PCE 6 TCE 27 DCE 41 Cl–1C, Cl–3C, Cl–4C < 6	– 0.6 0.8 –	This work

results have been compared to results found in the literature. A sharp decrease in PCE concentration with sonication time was observed for all ultrasonic intensities studied. This decrease is higher as ultrasonic intensity increases until high values of ultrasonic intensity are reached, where small differences are seen (between 5.09 and 7.64 W cm^{-2}). Again, fractional conversion is close to 100%, suggesting that all PCE is degraded. The main final products are again TCE and DCE, with 1C, 3C and 4C chlorinated compounds at ppb level. The values of G for the degradation by-products are very low compared with those obtained by radiolysis [36] and also lower than those obtained for OH· radicals produced by ultrasound. In addition, these low values decrease as the ultrasound intensity increases, in agreement with the idea that as the power increases, OH-radical production is favored. At this relatively high initial concentration of 452 μM, the DE is barely affected by ultrasonic intensity. In addition, Cl-MBE and conductivity values increase as the ultrasonic intensity increases. This conductivity enhancement cannot be related to the final pH, because its value is an averaged constant in spite of the ultrasonic intensity used. Thus, constant degradation efficiency (reflecting a constant level of chloride ions) as ultrasound power is varied implies that the increase in conductivity is due to the appearance of other undetected ions, the formation rate of which is enhanced by the ultrasonic intensity.

Due to the low values of DE and high values of Cl-MBE, and in spite of the routinely reported assumption that volatile compounds are mainly degraded by pyrolysis inside a cavitation bubble, a new strategy of analytical procedure was developed, aimed at looking for additional ionic species. Several experiments were carried out at 6.36 W cm^{-2} of ultrasonic intensity and at an initial concentration of around 140 μM. In this case, the final pH and conductivity were 3.2 and 200 μS cm^{-1}, respectively. FC was close to 99% and DCE was also detected. Using this analytical strategy, new oxygenated by-products were identified, including trichloroacetic (TCAA) and dichloroacetic (DCAA) acids. These by-products have not been previously reported to occur in the sonochemical degradation of PCE. It is very important to point out that, in addition to the chloride anion, 12% of the starting material is converted to TCAA, which becomes the second main final product among the detected compounds, and 3% of DCAA is also detected. Now, taking into account all chlorinated compounds detected, volatile (PCE and DCE) and nonvolatile (Cl^-, TCAA and DCAA), the Cl-MBE decreased to an averaged value of 24%. From now on, we therefore take into account the formation of haloacetate ions in the experiments presented in the remaining part of this paper.

3.2. Sonolysis of aerated aqueous solution of PCE at high frequencies

3.2.1. Ultrasonic frequency effects

Table 4 summarizes the main results of the ultrasonic frequency series. In this case we did not introduce the few results found in literature, addressing only the presence of final products as TCE and DCE < 0.1 μM and FC and DE around 100% [18,19,21]. In all our reactions, FC was higher than 98% and DE reaches a maximum ranging from 580 to 850 kHz. The optimum frequency value has been reported by other authors for sonochemical reactions of other chlorinated organic compounds [2], depending upon the mechanism of the sonochemical reaction. It is also important to note that the mass balance error follows an opposite tendency to the degradation efficiency. The Cl-MBE reaches a minimum value close to zero ranging from 580 to 850 kHz, being higher at 380 and 1142 kHz. This is related to the absence of TCE and to the production of lower levels of DCAA and monochloroacetic acid (MCAA). Now, the values of G are higher than at low frequencies, pointing to a better use of the irradiated energy. While the G values for pyrolytic compounds (TCE, DCE) are independent of the frequency, the G values for the OH-radical by-products follow a similar tendency to that shown by OH· radicals, but shifted to higher frequencies (maximum OH· production at 580 kHz and maximum OH-radical by-products at 850 kHz). A double-optimum behavior

Table 4
Experimental results obtained in the ultrasonic frequency series of the sonolysis of PCE, T = 20 °C, $[PCE]_0$ = 925 μM, I_a = 1.436 W cm^{-2}, Π = 0.061 W cm^{-3}, aerated solution at natural pH.

f (kHz)	pH$_f$	χ_f (μS cm^{-1})	FC (%)	DE (%)	Cl-MBE (%)	Final products C (μM)	G (10^{-11} mol J^{-1})
380	2.72	1004	99.28	38.54	52.9	PCE 6	–
						TCE 15	1.7
						DCE 21	2.4
						TCAA 36	4.1
						DCAA 31	3.5
						MCAA 42	4.6
						Traces of TCAAD	–
580	3.20	754	99.02	80.83	10.1	PCE 8	–
						TCE (n.d.)	–
						DCE 25	2.9
						TCAA 60	6.8
						DCAA 9	1.0
						MCAA 17	1.9
						Traces of TCAAD	–
850	3.06	848	98.35	86.49	1.4	PCE 12	–
						TCE (n.d.)	–
						DCE 21	2.4
						TCAA 129	14.7
						DCAA 8	0.9
						MCAA 0	–
						Traces of TCAAD	–
1142	2.80	772	98.04	43.12	42.8	PCE 18	–
						TCE 13	1.5
						DCE 21	2.4
						TCAA 92	10.5
						DCAA 31	3.5
						MCAA 21	2.4
						Traces of TCAAD	–

has also been reported in the literature by Zhang et al. [31] who, analyzing the degradation of PCBs, which are hydrophobic and nonvolatile compounds, concluded that the OH· attack contributed substantially to the enhanced sonochemical rates at 358 kHz, but that the chloride recovery was optimal at 1071 kHz.

3.2.2. Initial concentration effects at 850 kHz

The main results giving Cl-MBE at the end of the ultrasonic treatment and distribution of products are summarized in Table 5. It is important to highlight that not only was DCE detected, according to the pyrolytic mechanism for degradation of volatile compounds, but also TCAA, DCAA and MCAA. The G values for pyrolytic compounds (DCE) are now again independent of the initial concentration, but the G values for the OH-radical by-products increase with the initial concentration of PCE. The DE increases as the initial concentration increases with values close to 90%. But here, in spite of these higher initial concentrations in this set of experiments, the DE is higher than that found in 20 kHz experiments. On the other hand, upon increasing the initial concentration, the level of TCAA increases. The Cl-MBE decreases from the typical value around 30% to become negligible at high concentrations. Under these conditions, the levels of DCAA and

Table 5
Experimental results obtained in the initial concentration series of the sonolysis of PCE at 850 kHz, T = 20 °C, I_a = 1.436 W cm^{-2}, Π = 0.061 W cm^{-3}, aerated solution at natural pH.

C (μM)	pH$_f$	χ_f (μS cm^{-1})	FC (%)	DE (%)	Cl-MBE (%)	Final products C (μM)	G (10^{-11} mol J^{-1})
313	3.88	334	97.32	64.27	26.3	PCE 8	–
						TCE (n.d.)	–
						DCE (n.d.)	–
						TCAA 28	3.2
						DCAA (n.d.)	–
						MCAA (n.d.)	–
						Traces of TCAAD	–
362	3.07	443	96.74	73.90	7.3	PCE 12	–
						TCE (n.d.)	–
						DCE 21	2.4
						TCAA 43	4.9
						DCAA 23	2.6
						MCAA 12	1.4
						Traces of TCAAD	–
925	3.06	848	98.35	86.49	1.4	PCE 12	–
						TCE (n.d.)	–
						DCE 21	2.4
						TCAA 129	14.7
						DCAA 8	0.9
						MCAA (n.d.)	–
						Traces of TCAAD	–

MCAA are also low. This clearly means that higher frequencies favor the total degradation of PCE in a cleaner route.

3.2.3. Ultrasonic intensity effects at 850 kHz

The typical results obtained in the ultrasonic intensity series at low initial constant concentration were as follows: increase of the FC (from 68% up to 98%), of the DE (from 26% to 48%), of the electrical conductivity, and a Cl-MBE close to 30% independently of the increasing ultrasonic power used in the range studied. High values of DE at 850 kHz are obtained compared to those obtained at 20 kHz even for low initial concentrations. Higher ultrasonic intensities yield a lower DE, so a maximum value is obtained. This "passivation effect" (a simple increase of ultrasonic power does not necessarily improve the efficiency of a sonochemical reaction) has been previously reported in the literature [32,33].

3.3. Final sonolyses of aerated aqueous solution of PCE. Comparison between 20 kHz and 850 kHz

A detailed comparison was carried out at 20 and 850 kHz. It is important to note that the pH decreases irrespective of the different ultrasonic frequencies and volumes used. However, conductivity increases at higher frequencies and higher ultrasonic intensities, suggesting that ionic compounds – chloride and later some of them identified as chloroacetic acids – were formed during the sonolysis. The presence of these oxygenated compounds suggests possible product formation via oxidation of PCE or its first-formed derivatives. As a summary of our findings, the remarkable results are: Cl-MBE was lower at 20 kHz when important levels of TCAA and DCAA were taken into account and no presence of TCE was observed. Cl-MBE was close to zero at 850 kHz at higher concentrations, but was around 30% at lower concentrations. Another important aspect for attention is the formation of NO_3^-/NO_2^-, which occurs in aerated solutions at 20 kHz but not at 850 kHz, suggesting a clear frequency effect on the mechanism.

In the literature, there are non-conclusive results about the chemical reactivities of the systems OH·/PCE and OH·/TCE in the aqueous and gas phases. Either TCAA [34,35] or DCAA (in the absence of TCAA) [36] have been proposed as major products from OH·/PCE and OH·/TCE aqueous systems [37]. For the OH·/TCE aqueous system, dichloroacetaldehyde (DCAAD) and TCAAD have also been reported [37]. In the gas phase, trichloroacetyl and dichloroacetyl chlorides have been proposed as products of the reaction of PCE and TCE with hydroxyl radicals [38]. Additional products, such as phosgene and CCl_4 for PCE and $CHCl_3$ for TCE, have been also reported together with chlorinated carbonyl compounds [39]. Therefore, experimental checking in our own systems was carried out, firstly using the chemical Fenton reaction, which is based on H_2O_2 decomposition to OH· radicals, catalyzed by the addition of trace Fe (II) in acidic medium [40]. For PCE, the major product detected was chloride and traces of TCAA. After 180 min the FC was 65%, the DE was close to 62% and the Cl-MBE was 3%. For TCE, the FC was 80% and only a trace of chlorinated acid was detected. Secondly, a PCE 850 kHz reaction was carried out in the presence of tert-butanol (t-ButOH). This compound is a radical scavenger widely used in sonochemical studies on pollutant degradation to help elucidate reaction mechanisms [41,42]. Under these experimental conditions, 50 mM t-ButOH vs. 0.2 mM PCE, the degradation was confirmed from the increase in the chloride concentration in the solution, with a DE close to 83%, but neither TCAA nor DCCA were detected after 5 h of treatment at 850 kHz and 2.09 W cm^{-2}. The absence of oxygenated by-products when t-ButOH is present in the solution supports the suggestion that hydroxyl radicals are involved in the degradation of PCE or intermediates in solution, giving TCAA and DCAA. However, the DE is also increased, which suggests that the pyrolytic route also takes place. Glaze and Kang [43] reported rate constants for the aqueous reactions of the OH· radical with some compounds, highlighting the fact that the kinetics with TCE or t-ButOH are twice as fast as for PCE. According to these constants, hydroxyl radicals will mainly react with t-ButOH and the reaction with at least PCE will be inhibited, which is confirmed by our experimental results.

4. Discussion

Our study has detected a wide range of compounds and the reaction scenario seems to be quite different from simpler ones previously proposed. At the beginning, it is clear that only PCE is present, a compound with high log K_{ow} (K_{ow}: octanol–water partition constant), high Henry constant and relatively high vapor pressure. Therefore, a pyrolytic degradation inside the bubble or near the interphase should be expected at the early stages. We obtain the highest DE at high frequency, where a clean reaction (low levels of TCE, DCE and chlorinated oxygenated compounds) and total pyrolytic degradation to Cl^- is favored. This is in agreement with the theory that at high frequencies, a greater number of gas nuclei can reach resonance size more quickly than at lower frequencies [2]. On the other hand, we have detected chloroacetic acids at ppm level. In Ref. [36], the degradation of PCE by OH-radicals, radiolytically generated in oxygen-free aqueous solution, produces tetrachlorosuccinic acid and chloride ions as primary products, and also dichloroacetic acid. The former decomposes into trichloroacrylic acid and carbon dioxide. The same authors, now using photolysis of air-saturated aqueous solution of PCE, reported chloride ions, carbon dioxide, trichloroacetic acid, dichloroacetic acid and hypochlorite as major products [44]. In the same work, the authors mention that trichloroacetic acid is not formed in the absence of oxygen. Moreover, its formation is suppressed either by the addition of hydrogen donors (such as tert-butanol) or by carbonate/bicarbonate ions. In any case, the quantum yield of dichloroacetic acid remains unaffected by oxygen and hydrogen donors. In addition, in this reference it is also suggested that the trichlorovinyl radical formed from the homolytic breakdown of a C–Cl bond in the PCE can be scavenged by hydrogen donors such as alcohols (giving TCE), in competition with the oxygen attack for the formation of the trichlorovinylperoxyl radical. All these findings have been obtained using γ-radiolysis, UV-photolyis or high-energy electrons produced by electron-beam technologies, with reaction scenarios quite different from the one observed in sonochemical reactions (high temperatures and pressures and radical generation). Related to the OH· radical concentration, the availability of radicals in solution will be different depending on the methodology used to generate them. For example, it has been reported [27] that OH· radical production per unit energy provided by ultrasound is only about 0.1% of that achieved by γ-radiolysis or high-energy electrons. In the case of sonochemical reactions, the reaction may occur in different reaction areas (inside the bubble, at the interphase and in solution), so that the feasible reactions and degradation products could be different from those occurring with other OH· radical generation methods. Keeping in mind the volatile character of PCE, the explanation for the presence of chloroacetic acids implies the reaction of air-solvent radicals with the chloroethenes in the gas phase or in the interphase, rather than in aqueous solutions (as in the case of photolysis or γ-radiolysis). It has been previously suggested that volatile compounds first react with sonolytic radicals inside the bubble or in the interphase, and that these reaction locations are favored at lower frequencies.

Hua and Hoffmann [45] studied the influence of the frequency and dissolved gas during the production of hydrogen peroxide by sonolysis. The highest production of hydrogen peroxide and OH· radicals was observed for Kr-saturated solution at 500 kHz, and

the lowest for He-saturated solution at 20 kHz. The authors suggested that the increased efficiency of H_2O_2 and OH· production at higher irradiation frequencies may be due to the fact that, at higher frequencies, the collapse time of the bubble is shorter and hydroxyl radicals are ejected out of the bubble before they can recombine in the gas phase. The same conclusions were proposed by Wayment and Casadonte [46], who found higher reaction rates with argon-saturated solutions at 20 kHz for the sonochemical oxidation of potassium iodide. Petrier et al. [47], in contrast with the results of previous researchers, found higher rates in oxygen-saturated solutions. Wayment and Casadonte [46], working with alachlor, have found that the oxidative reaction with hydroxyl radicals appears to occur in the bubble and in the interfacial region rather than in the bulk, and, as such, a higher rate of ejection of OH· from the bubble interior may lead to the decrease in the observed rate. So it is possible to think that the main route for the production of chloroacetic acids is the reaction of OH· radicals with PCE and/or TCE in the gas phase or interphase. Among those acids, TCAA is mainly present and TCE is routinely absent when the process presents the lowest Cl-MBE, close to zero. OH· reactivity with TCE is faster than with PCE when both are in the gas phase [48], and we find it also to be the case in the aqueous phase [43]. It is therefore reasonable to think that the level of TCE is low for two reasons: (i) the pyrolytic route is favored and (ii) TCE reacts with the OH· and forms DCAA, i.e. it acts as scavenger for the OH· radicals formed. TCE presents a lower Henry Law constant than PCE and, as Weavers suggested [49], OH· attack becomes increasingly more dominant. In agreement with this author, our experimental results show that the highly hydrophobic compounds PCE and TCE react most rapidly at high frequencies. Besides, the 850 kHz sonolysis of PCE in the presence of t-ButOH, with a high DE close to 83%, does not yield detectable chloroacetic acids, supporting not only the assumption that the reaction between TCE (and in minor percentage PCE) and OH·/air radicals, which takes place inside or at the interphase of the bubble, is not the main route of degradation, but also that the degradation by OH· radicals in the bulk solution poorly contributes to the formation of chloroacetic acids. This is in agreement with the conclusions reported by Mark et al. [27], who questioned the use of the sonochemical degradation (on the basis of OH-radical reaction in the bulk solution) in the destruction of water pollutants. These conclusions were obtained from the monitoring of species (radicals or active by-products) in solution, using as dosimeters chemicals whose fugacity is so low that they are not drawn into the oscillating bubble. From our results, it is clear that the poor OH· radical reaction with PCE/TCE in aqueous solution is inhibited by the presence of t-ButOH and that the pyrolytic route is also favored. It has been found that chloroacetic acids are not degraded to a practically relevant level either by ultrasonic fields (high and low frequencies) or by the Fenton reaction. Therefore, avoiding the formation of chloroacetic acids will increase the DE. Unfortunately, there is little information in the literature related to this specific PCE sonochemical degradation scenario. Clark et al. [21] analyzed PCE degradation in aqueous solution and in aqueous solution with ethanol as co-solvent. They concluded that pyrolysis was the more dominant degradation mechanism in this experiment.

Our results about the influence of the initial concentration at low (20 kHz, Table 2) and high frequencies (850 kHz, Table 5) are also of interest. When increasing the initial PCE concentration, at 20 kHz, the DE decreased and the Cl^- mass balance got worse, whereas at 850 kHz, the DE increased and the Cl^- mass balance was improved. In both cases, as the initial concentration increases the quantity of the volatile PCE entering the bubble during the expansion phase also increases. According to our reaction scenario, at low frequency PCE is scavenging OH· radicals, yielding oxygenated compounds whose concentrations increase with the initial PCE concentration, thus yielding low DE and poor mass balance. Conversely, at high frequency, the pyrolytic route is favored and OH· radicals could be ejected more efficiently into the solution before they have time to recombine or to attack other molecules in the cavitation bubble [47]. In this case, almost all the PCE entering the bubble is converted into chloride ions, thus enhancing the DE and the mass balance for higher initial PCE concentration. Even in this case, a small amount of oxygenated compounds was still found, also increasing with the initial concentration of PCE.

Other experimental findings are in agreement with our proposition. We have detected NO_3^-/NO_2^- at 20 kHz but not at 850 kHz, in relation with the use of aerated solutions. It has been reported [50,51] that nitrite ions are the primary products of sonolysis of air-equilibrated water with the generation of nitrate resulting from onward oxidation of nitrite [9]. In our case, there is no detection of NO_3^-/NO_2^- at 850 kHz, and this can be also explained due to the fact that the other volatile compound, i.e. N_2, proceeds following the same fate as PCE and derivatives: a stronger interaction with OH·/air radicals at 20 kHz compared to 850 kHz. From our results, the high presence of TCE and DCE at low frequency compared to high frequency remains to be explained. This issue is linked with the precise mechanism occurring in the bubble, which may involve complex interplay between heating by adiabatic compression and endothermic reactions.

The mass balance and speciation are the main subjects of our study and deserve specific discussion. The sonochemical degradation of PCE at high frequencies resulted in higher DE than at low frequencies, with a typical value higher than 60%, which follows a multipath mechanism providing Cl^- and CO_2/CO as major products. We have also detected not only non-oxygenated compounds, reported routinely in the literature by other workers, but also oxygenated chlorinated compounds (such as chloroacetic acids, which are a second group of major products, and chloroacetaldehydes). When high power density and concentrations and ultrasonic frequencies around 580–850 kHz are used the mass balance is closed. For other experimental conditions, especially for frequencies different from 580 to 850 kHz, or for low concentrations, the chlorine mass balance is not closed and 25% of chlorinated compounds remain undetected. In a further effort, we treated PCE solutions with high frequency ultrasound, and used GC/MS and GC/ECD to analyze now the nonvolatile chlorinated compounds in the reaction mixture. We sought the products suggested in the literature from the TiO_2-mediated photodegradation of PCE and TCE [37]. We conclude that at 850 kHz and when high ultrasonic intensities were used, a low speciation of nonvolatile chlorinated reaction compounds was obtained.

Unfortunately, few examples of extensive mass balance analyses can be found in the literature. Francony and Pétrier [52] have developed specific methods in order to analyze the mass balance in the degradation of CCl_4 with experimental systems (20 and 500 kHz) quite similar to ours. In aqueous solution and during the first hour C_2Cl_4 and C_2Cl_6 are the main products along with small amounts of chlorinated 1C, 2C, 3C and 4C compounds. The same compounds are identified in the gas phase in addition to chlorocyclopropenes. The authors pointed out that the total amount of all these reaction products was very low and only C_2Cl_4 could be quantified with HPLC. All these chlorinated products were degraded to chloride anion and not just volatilized during irradiation. Since compounds with high molecular weight ($C > 4$) were no longer detected, they supposed that chlorinated organic species degraded into smaller molecules rather than polymerizing into longer chains. Gaddam and Cheung [16] followed the chlorine balance in the degradation of 1,1,1,-trichloroethane (1,1,1-TCA) and only Cl^-, OCl^-, HOCl and unreacted 1,1,1-TCA were detected. Other authors have analyzed the intermediates of the sonochemical degradation of TCE [10], concluding that TCE is not degraded in

the bulk solution by the action of OH· radicals. The reaction mechanism proceeds by elimination of HCl from TCE followed by radical formation and oligomerization, yielding dichloroacetylene (C_2Cl_2) as major intermediate, PCE and other compounds such as chlorobutadienes in very low concentrations. The range of potential products being formed is quite wide. As we have mentioned before, for example, looking at different reaction environments (compared to the sonochemical one) such as those provided by radiolysis, tetrachlorosuccinic acid, trichloroacrylic acid and oxalic acid have been reported as by-products of the reaction of the OH-radical with PCE in oxygen-free aqueous solutions [36]. All these reports are in agreement with our results at high frequencies and offer an explanation for our experimental values obtained for the Cl-MBE at 20 kHz, where oxygenated chlorinated compounds were not taken into account.

Due to the fact that there is a dramatic change in the OH· radical yields in the frequency range studied [27], the disentangling of the pyrolytic from the radical attack routes can be attempted by analyzing the ratio of thermolytic and OH·-induced products. Fortunately, reactions with a closed mass balance can be used for this analysis and we have firstly used those reactions with a Cl-MBE lower than 10%. For these low error reactions, from the quantity of free Cl^- anions detected and assuming that the pyrolytic route provides TCE and DCE as intermediates and CO_2 and Cl^- as final products, more than 70% of the degraded PCE at higher frequencies follows the pyrolytic route. As we have mentioned before, TCAA, DCAA and MCAA are not sonochemically degraded, so we may consider them as OH·-induced products. For those reactions with Cl-MBE higher than 10%, the conclusions are only tentative. Even assuming that all the free Cl^- anions detected come from the pyrolytic route and taking into account that the analytical techniques used detect a large number of non-hydroxylated compounds, only percentages lower than 50% can be related to the pyrolytic route, particularly at low frequencies (20 kHz). Therefore, low frequencies present a high percentage of the OH·-induced products reaction route. Finally, in the previous tables, we have included the product yields, G, in terms of mol J^{-1}, which can be used for analyzing the energy requirements for a potential application of sonochemistry and radiolysis and for comparing them. However, this analysis is beyond the scope of the present work.

As a final remark, we would like to note that the above conclusions strongly rely on one hand on the location of the hydroxyl radicals, and on the other hand on the collapse strength. The arguments used were based on classical cavitation literature, invoking concepts of resonant bubbles, and slower and milder collapse at low frequency compared to high frequency. We suggest that the present results could be reconsidered in the light of more modern cavitation theory, not necessarily invalidating the present conclusions. First, recent experimental and theoretical results [53,54] question the presence of resonant bubbles in strong cavitation fields. Moreover, such bubbles, if any, would be less chemically active than much smaller near Blake-threshold bubbles [55]. Besides, Storey and Szeri [56,57] showed that at low frequency, water vapor and hydroxyl radicals are confined in the center of the bubble during the collapse by a diffusional barrier, which is one of the issues of the present paper. Preliminary calculations based on the reduced model of the latter authors show that this is no longer the case at high frequency, the collapse of a given bubble being smoother at 850 kHz than at 20 kHz. Work is in progress.

5. Conclusions

The comparison between the results at low and high frequencies provides a clearer idea about the reaction scenario:

(1) First, 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· radicals. Next, two parallel steps can interfere: pyrolysis of the remaining compounds, and oxidation by the OH· radicals. The latter is predominant at low frequency, because in this case, the contact with chloroethenes inside the cavitating bubbles is longer, leading to highly soluble oxygenated compounds, which were found to be mainly 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) of 1C, 3C and 4C chlorinated compounds, which is supported by the larger DE% and Cl-MBE obtained in this case. The oxidation by OH· 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· radicals in the liquid phase, therefore producing a higher DE and reducing the formation of oxygenated compounds compared to in the absence of t-ButOH.

(2) We emphasize that our results are in agreement when tested in different reaction arrangements (in two different laboratories), providing a good reproducibility in what can be sometimes seen as a difficult reaction methodology for this paradigm. In addition, we have identified that ultrasonic frequency is the most important operational variable.

(3) In particular we identified a problem in accounting for the mass balance before and after ultrasonic degradation. We therefore paid great attention to this aspect, 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. Further work, focused on the determination of intermediates in order to propose a more detailed mechanism, is in progress.

(4) From the applicative point of view, it should be noted that all these compounds, and especially 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. Therefore, hybrid technologies should be proposed.

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References

[1] J. González-García, V. Sáez, I. Tudela, M.I. Díez-García, M.D. Esclapez, O. Louisnard, Sonochemical treatment of water polluted by chlorinated organocompounds. A review, Water 2 (2010) 28–74.

[2] H.M. Hung, M.R. Hoffmann, Kinetics and mechanism of the sonolytic degradation of chlorinated hydrocarbons: frequency effects, J. Phys. Chem. A 103 (1999) 2734–2739.

[3] I. Hua, M.R. Hoffmann, Kinetics and mechanism of the sonolytic degradation of CCl_4: intermediates and byproducts, Environ. Sci. Technol. 30 (1996) 864–871.

[4] B.H. Jennings, S.N. Townsend, The sonochemical reactions of tetrachloride and chloroform in aqueous suspension in an inert atmosphere, J. Phys. Chem. 65 (1961) 1574–1579.

[5] H. Shemer, N. Narkis, Sonochemical removal of trihalomethanes from aqueous solutions, Ultrason. Sonochem. 12 (2005) 495–499.

[6] P. Kruus, R.C. Burk, M.H. Entezari, R. Otson, Sonication of aqueous solutions of chlorobenzene, Ultrason. Sonochem. 4 (1997) 229–233.

[7] D. Drijvers, H. Van Langenhove, K. Vervaet, Sonolysis of chlorobenzene in aqueous solution: organic intermediates, Ultrason. Sonochem. 5 (1998) 13–19.

[8] D. Drijvers, H. Van Langenhove, V. Herrygers, Sonolysis of fluoro-, chloro-, bromo- and iodobenzene: a comparative study, Ultrason. Sonochem. 7 (2000) 87–95.

[9] Y. Jiang, C. Pétrier, T.D. Waite, Kinetics and mechanisms of ultrasonic degradation of volatile chlorinated aromatics in aqueous solutions, Ultrason. Sonochem. 9 (2002) 317–323.

[10] D. Drijvers, R. De Baets, A. De Visscher, H. Van Langenhove, Sonolysis of trichloroethylene in aqueous solution: volatile organic intermediates, Ultrason. Sonochem. 3 (1996) S83–S90.

[11] D. Drijvers, H. Van Langenhove, L.N.T. Kim, L. Bray, Sonolysis of an aqueous mixture of trichloroethylene and chlorobenzene, Ultrason. Sonochem. 6 (1999) 115–121.

[12] J. Dewulf, H. Van Langenhove, A. De Visscher, S. Sabbe, Ultrasonic degradation of trichloroethylene and chlorobenzene at micromolar concentrations: kinetics and modelling, Ultrason. Sonochem. 8 (2001) 143–150.

[13] C. Petrier, Y. Jiang, M.-F. Lamy, Ultrasound and environment: sonochemical destruction of chloroaromatic derivatives, Environ. Sci. Technol. 32 (1998) 1316–1318.

[14] G. Zhang, I. Hua, Cavitation chemistry of polychlorinated biphenyls: decomposition mechanisms and rates, Environ. Sci. Technol. 34 (2000) 1529–1534.

[15] V. Griffing, The chemical effects of ultrasonics, J. Chem. Phys. 20 (1952) 939–942.

[16] K. Gaddam, H.-M. Cheung, Effects of pressure, temperature, and pH on the sonochemical destruction of 1,1,1-trichloroethane in dilute aqueous solution, Ultrason. Sonochem. 8 (2001) 103–109.

[17] L.A. Spurlock, S.B. Reifsneider, Chemistry of ultrasound. I. Reconsideration of first principles and the applications to a dialkyl sulfide, J. Am. Chem. Soc. 92 (1970) 6112–6117.

[18] A.J. Colussi, H.-M. Hung, M.R. Hoffmann, Sonochemical degradation rates of volatile solutes, J. Phys. Chem. A 103 (1999) 2696–2699.

[19] A. Bhatnagar, H.M. Cheung, Sonochemical destruction of chlorinated C_1 and C_2 volatile organic compounds in dilute aqueous solution, Environ. Sci. Technol. 28 (1994) 1481–1486.

[20] K. Inazu, Y. Nagata, Y. Maeda, Decomposition of chlorinated hydrocarbons in aqueous solutions by ultrasonic irradiation, Chem. Lett. 22 (1993) 57–60.

[21] C.J. Clark II, M.D. Annable, P.S. Rao, Evaluation of sonochemical destruction of PCE in situ flushing waste fluids, J. Environ. Eng. 126 (2000) 1033–1038.

[22] O. Krüger, Th.L. Schulze, D. Peters, Sonochemical treatment of natural ground water at different high frequencies: preliminary results, Ultrason. Sonochem. 6 (1999) 123–128.

[23] V. Sáez, A. Frías-Ferrer, J. Iniesta, J. González-García, A. Aldaz, E. Riera, Chacterization of a 20 kHz sonoreactor. Part I: analysis of mechanical effects by classical and numerical methods, Ultrason. Sonochem. 12 (2005) 59–65.

[24] V. Sáez, A. Frías-Ferrer, J. Iniesta, J. González-García, A. Aldaz, E. Riera, Characterization of a 20 kHz sonoreactor. Part II: analysis of chemical effects by classical and electrochemical methods, Ultrason. Sonochem. 12 (2005) 67–72.

[25] M.A. Margulis, A.N. Mal'tsev, A relative colorimetric method for the determination of ultrasound power, Russ. J. Phys. Chem. 43 (1969) 592–595.

[26] M.A. Margulis, I.M. Margulis, Calorimetric method for measurement of acoustic power absorbed in a volume of a liquid, Ultrason. Sonochem. 10 (2003) 343–345.

[27] G. Mark, A. Tauber, R. Laupert, H.-P. Schuchmann, D. Schulz, A. Mues, C. Von Sonntag, OH-radical formation by ultrasound in aqueous solution – part II: terephthalate and Fricke dosimetry and the influence of various conditions on the sonolytic yield, Ultrason. Sonochem. 5 (1998) 41–52.

[28] A. Kotronarou, G. Mills, M.R. Hoffmann, Ultrasonic irradiation of p-nitrophenol in aqueous solution, J. Phys. Chem. 95 (1991) 3630–3638.

[29] J.W. Kang, K.H. Lee, C.I. Koh, S.N. Nam, The kinetics of the sonochemical process for the destruction of aliphatic and aromatic hydrocarbons, J. Chem. Eng. 18 (2001) 336–341.

[30] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental Organic Chemistry, Wiley, New York, 1993.

[31] G. Zhang, I. Hua, Cavitation chemistry of polychlorinated byphenyls: decomposition mechanisms and rates, Environ. Sci. Technol. 34 (2000) 1529–1534.

[32] C.M. Sehgal, S.Y. Wang, Threshold intensities and kinetics of sonoreaction of thymine in aqueous solutions at low ultrasonic intensities, J. Am. Chem. Soc. 103 (1981) 6606–6611.

[33] M. Gutierrez, A. Henglein, Chemical action of pulsed ultrasound: observation of an unprecedented intensity effect, J. Phys. Chem. 94 (1990) 3625–3628.

[34] K.C. Bailey, W.S.E. Hickson, The formation of trichloroacetic acid from perchloroethylene by atmospheric oxidation, J. Chem. Soc. (1941) 145.

[35] C. von Sonntag, P. Dowideit, X. Fang, R. Mertens, X. Pan, M.N. Schuchmann, H.-P. Schuchmann, The fate of peroxyl radicals in aqueous solution, Water Sci. Technol. 35 (1997) 9–15.

[36] R. Mertens, C. Von Sonntag, Reaction of the OH radical with tetrachloroethene and trichloroacetaldehyde (hydrate) in oxygen-free aqueous solution, J. Chem. Soc. Perkin Trans. 2 (1994) 2181–2185.

[37] W.H. Glaze, J.F. Kenneke, J.L. Ferry, Chlorinated byproducts from the titanium oxide-mediated photodegradation of trichloroethylene, tetrachloroethylene in water, Environ. Sci. Technol. 27 (1993) 177–184.

[38] K.S. Wiltshire, M.J. Almond, P.C.H. Mitchell, Reactions of hydroxyl radicals with trichloroethene and tetrachloroethene in argon matrices at 12 K, Phys. Chem. Chem. Phys. 6 (2004) 58–63.

[39] N. Itoh, S. Kutsuna, T. Ibusuki, A product study of the OH radical initiated oxidation of perchloroethylene and trichloroethylene, Chemosphere 28 (1994) 2029–2040.

[40] J. Ma, W. Song, C. Chen, W. Ma, J. Zhao, Y. Tang, Fenton degradation of organic compounds promoted by dyes under visible irradiation, Environ. Sci. Technol. 39 (2005) 5810–5815.

[41] Y. Nagata, M. Nakagawa, Y. Mizukoshi, B. Yim, Y. Maeda, Sonochemical degradation of chlorophenols in water, Ultrason. Sonochem. 7 (2000) 115–120.

[42] A. Tauber, M. Mark, H.P. Schuchmann, C. Sontag, Sonolysis of *tert*-butyl alcohol in aqueous solution, J. Chem. Soc. Perkin Trans. 2 (1999) 1129–1135.

[43] W.H. Glaze, J.-W. Kang, Advanced oxidation processes. Description of a kinetic model for the oxidation of hazardous materials in aqueous media with ozone and hydrogen peroxide in a semibatch reactor, Ind. Chem. Eng. Res. 28 (1989) 1573–1580.

[44] R. Mertens, C. von Sonntag, Photolysis ($\lambda = 254$ nm) of tetrachloroethene in aqueous solutions, J. Photochem. Photobiol. A: Chem. 85 (1995) 1–9.

[45] I. Hua, M.R. Hoffmann, Optimization of ultrasonic irradiation as an advanced oxidation technology, Environ. Sci. Technol. 31 (1997) 2237–2243.

[46] D.G. Wayment, D.J. Casadonte Jr., Frequency effect on the sonochemical remediation of alachlor, Ultrason. Sonochem. 9 (2002) 251–257.

[47] C. Petrier, A. Jeunet, J.-L. Luche, G. Reverdy, Unexpected frequency effects on the rate of oxidative processes induced by ultrasound, J. Am. Chem. Soc. 114 (1992) 3148–3150.

[48] R. Atkinson, Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, Chem. Rev. 86 (1986) 69–201.

[49] L.K. Weavers, F.H. Ling, M.R. Hoffmann, Aromatic compound degradation in water using a combination of sonolysis and ozonolysis, Environ. Sci. Technol. 32 (1998) 2727–2733.

[50] E.J. Hart, A. Henglein, Sonolytic decomposition of nitrous oxide in aqueous solution, J. Phys. Chem. 90 (1986) 5992–5995.

[51] E.L. Mead, R.G. Sutherland, R.E. Verral, The effect of ultrasound on water in the presence of dissolved gases, Can. J. Chem. 54 (1976) 1114–1120.

[52] A. Francony, C. Pétrier, Sonochemical degradation of carbon tetrachloride in aqueous solution at two frequencies: 20 kHz and 500 kHz, Ultrason. Sonochem. 3 (1996) S77–S82.

[53] R. Mettin, Bubble and particle dynamics, in: A.A. Doinikov (Ed.), Acoustic Fields: Modern Trends and Applications, 2005, pp. 1–36.

[54] R. Mettin, in: T. Kurz, U. Parlitz, U. Kaatze (Eds.), Oscillations, Waves and Interactions, 2007, pp. 171–198.

[55] K. Yasui, T. Tuziuti, J. Lee, T. Kozuka, A. Towata, Y. Iida, The range of ambient radius for an active bubble in sonoluminescence and sonochemical reactions, J. Chem. Phys. 128 (2008) 184705-1–184705-12.

[56] B.D. Storey, A.J. Szeri, Water vapour, sonoluminescence and sonochemistry, Proc. Royal Soc. London A 456 (2000) 1685–1709.

[57] B.D. Storey, A.J. Szeri, A reduced model of cavitation physics for use in sonochemistry, Proc. Royal Soc. London A 457 (2001) 1685–1700.