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Sonochemical degradation of perchloroethylene

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Abstract

An extensive study of the sonochemical degradation of the perchloroethylene (PCE) in water has been carried out. The influence of the initial concentration, ultrasonic intensity and frequency on the speciation and degradation efficiency has been analyzed. Required preliminary work has been carried out analysing the analytical procedures, partition of the organic chemicals due to the volatility (Henry constant) and other experimental aspects to configure the experiment series. The sonochemical degradation runs by a radical mechanism which yields a very wide range of chlorinated compounds in very low concentrations. Special attention has been paid to the mass balance comparing the results from several analytical techniques. As a conclusion, the sonochemical degradation by itself is not an efficient treatment to diminish the toxicity of the waste water.

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Keywords: chlorinated compounds; degradation; perchloroethylene; sonochemistry; treatment.

1. Introduction

In spite of the fact that perchloroethylene is a widely used solvent in many areas of the industry and has been reported as major intermediate in the degradation of other chlorinated compounds [1], to our knowledge, there is not an extensive study about the sonochemical degradation of this compound. Hoffmann et al. [2] related the kinetics to the ultrasonic frequency and vapour pressure of the compound. Temperature and pH were found to have little effect on the destruction rate of the compound [3] and the vapour pressure does not correlate to the destruction rate for C₂ compounds such PCE. Besides, no specificity of the process with a percent destruction higher than 72% was found.

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The same authors suggest a degradation mechanism by pyrolysis along with radical oxidation. GC/MS analyses of the samples showed no other chlorinated products in the sonolysis of PCE. The influence of the gas dissolved in the degradation grade has been studied at 200 kHz [4]. The degradation grade was determined following the chemical yields in chloride anion and carbon monoxide and/or carbon dioxide and was close to 80%. They concluded that the main reactions were thermal decomposition or combustion in cavitation bubbles and no reactions by OH[•] radicals or H atoms. Clayton J. Clark II [5] studied the influence of the initial concentration on the kinetics of the process. However, they do not indicate the frequency used. No influence for concentration above 75 ppm was reported. They reduced the concentration below 0.9 ppm and the presence of trichloroethylene and dichloroethylene as by-products were, if did, below detectable limits in solution (< 0.01 mg/L). PCE has also been detected and ultrasonically degraded in natural ground water at concentration in the range of µg/L [6]. The few results reported seem to be contradictory and a systematic study is required. The effect of reaction variables such as initial concentration, steady state temperature and frequency has been investigated.

2. Experimental

2.1. Analyses

2.1.1. Solution analyses

Aliquots were routinely withdrawn at initial and final times of the reaction from the sonoreactor by a fine stainless steel PTFE tube into 2.5 mL glass vials, sealed with a PTFE/silicone septum-lined threaded cap. From these glass vials, samples of the aqueous solution were injected into a HP 5890 Serie II gas chromatograph equipped with a FID detector. A Hewlett-Packard GC/MS (G1800A GCD) associated with HP 7695 purge-and-trap system following the USEPA 624 method was also used in the identification of degradation by-products. Alternatively to the gas chromatograph monitoring, HPLC analysis was also routinely carried out for the analysis of the C₂Cl₄ and other by-products using an Agilent 1100 HPLC-UV detector. Chloride and other anionic species were monitored too with an Ion-exchange chromatograph (IC), 690 Ion Chromatograph, Metrohm, equipped with a conductivity detector.

2.1.2. Gas phase analyses

The gas phase was analyzed with the same gas chromatograph HP 5890 Serie II gas chromatograph using the FID detector and additionally a TCD detector for the analysis of CO/CO₂ and low molecular weight hydrocarbons (CH₄, C₂H₂, C₂H₄ and C₂H₆).

2.2. Sonochemical reactions

Sonochemical reactions were carried out at 380, 580, 850 and 1142 kHz in a Meinhardt MFLG system, calorimetrically calibrated. The temperature was kept constant at 293K in the 500 mL glass reactor. The reaction time was 4 hours.

Due to the fact that PCE is a volatile compound, the experiments were carried out in the sonoreactor carefully sealed, without bubbling any gas. The main physicochemical properties of the compound are presented in Table 1. Besides, required preliminary experiments were carried out trying to establish the general behaviour of the system. In a first step, the equilibrium between gaseous and liquid phases (phase equilibrium) has been experimentally checked. Therefore, initial compound was dissolved in the sonochemical reactor and the gas and liquid concentration was measured after the same reaction time than before. PCE partition was analyzed with agreement

with the Henry Law and the gas and liquid volume used [7]. Stability and compatibility of the chemicals with the reactor materials were also checked as an additional effort with the purpose of improving the mass balance. Results are shown in Table 2.

Table 1. Physicochemical properties of PCE

Chemical name	Empirical formula	Melting point/ ^o C	Boiling point/ ^o C	Density g mL ⁻¹	Solubility mg L ⁻¹	Log K _{ow}	Vapour pressure/torr	Henry law constant/ atm m ³ mol ⁻¹
Tetrachloroethylene	CCl ₂ =CCl ₂	-19	121	1.63	150	2.5	18.47	0.018

Table 2. Partitioning of PCE

V _{gas} / mL	V _{liq} / mL	K _H / atm m ³ mol ⁻¹	% compound _{liq}	% compound _{gas}
120	200	0.0177	70	30

3. Results

During all initial concentrations, power and frequency series, a wide range of chlorinated compounds were detected. It is important to mention that the initial pH, whose natural value is close to 5.7 falls to around 3 for any frequency, concentration and power used, and the conductivity increases from 1 to 300-1000 $\mu\text{S cm}^{-1}$ (averaged values) depending on the experimental conditions. The fractional conversion (FC), defined as

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

was always higher than 97%, indicating that almost all initial product was degraded. Besides, the major by-product analytically determined was Cl⁻ (88%), stoichiometrically balanced with CO₂/CO when the mass balance is closed. Trichloroethylene (TCE) and dichloroethylene (DCE), typical products related to the pyrolytic mechanism inside of the cavitating bubbles, were detected at the end of the reaction at ppm level. At ppb levels, chloroform, carbon tetrachloride and chlorinated compounds with more than two carbons were detected. Besides, the presence of pentachloroethane, hexachloroethane and pentachloropropene implies the formation not only of C-H bonds but also C-C bonds.

However, typical compounds coming from the OH[•] radical attack (hydroxylated compounds) have also been detected, such as trichloroacetic (TCAA), dichloroacetic (DCAA) and monochloroacetic (MCAA) acids. They have been the major components detected at ppm level after Cl⁻. Their final presence was around 10% of the initial product, being trichloroacetic acid the main contributor.

3.1. Initial concentration effect.

PCE sonolysis experiments were carried out at different initial concentrations 156, 59 and 52 ppm, ranging the narrow window of solubility. Other variables were kept constant with the following values: power density 0.061 W cm⁻³, (it means ultrasonic intensity 1.436 W cm⁻²), temperature 293K, solution volume 500 mL, and ultrasound frequency 850 kHz. Fig. 1 shows the degradation efficiency, DE, (or degradation grade) defined as

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

Fig. 1 shows a high degradation efficiency, higher than 60%, for any initial concentration, increasing with the initial concentration. Influence of the initial concentration on the kinetics of the process has also been reported in literature. Some authors have found no influence, according to the volatile nature [8] of PCE and the pyrolytic degradation mechanism, but other authors have found dependence, decreasing the rate constant as initial concentration increases [9].

On the other hand, when the initial concentration decreases, the level of DCAA and MCAA increases at the end of the reaction. In these cases, the mass balance is not closed, with a Cl-mass balance error, Cl-MBE, defined as

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

This error increases with a maximum value of around 30%.

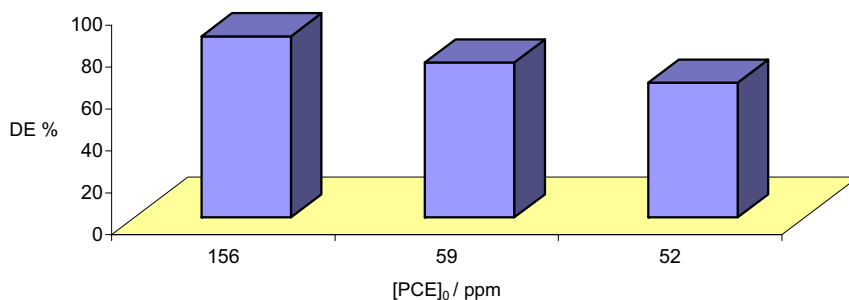


Fig.1 Degradation efficiency vs. initial concentration of PCE at sonochemical reactions carried out at 850 kHz, 0.061 W cm⁻³.

3.2. Ultrasonic intensity / power density effect.

Fig.2 shows the degradation efficiency at different ultrasonic intensities: 0.094, 0.424, and 1.436 W cm⁻², corresponding to power densities of 0.004, 0.018, and 0.061 W cm⁻³ respectively, for sonochemical reactions carried out with solutions of 50 ppm and at 850 kHz.

In this case, the fractional conversion increases as the ultrasonic intensity increases, ranging from 68 to 98%. According with this low kinetics, the degradation grade increases with the insonated power. High values of degradation grade are obtained even for low initial concentrations. Other aspect which has to be taken into account is that the error in the Cl-mass balance has been closed to 30% independently of the power ultrasound but it is related to the presence of DCAA and MCAA.

Higher ultrasonic intensities than those shown in figure 2 have provided lower degradation grade, so a maximum value could be expected. This behaviour has been reported in literature [10] in homogeneous sonochemical reactions, called as “passivation effects”. Further work is in progress in this aspect.

3.3. Frequency effect.

Fig. 3 shows the degradation efficiency at different ultrasonic frequencies: 380, 580, 850 and 1142 kHz at sonochemical reactions carried out for solutions of 150 ppm and a power density of 0.061 W cm^{-3} . In all these reactions, the fractional conversion was higher than 98%. As it can be seen, the degradation efficiency presents a maximum at frequencies in the range between 580 and 850 kHz. This maximum has been reported by other authors in sonochemical reactions of chlorinated organocompounds [1], conclusions based on the nature of the mechanism of the sonochemical reaction. However, it is also important to note that the mass balance error follows an opposite tendency than the degradation efficiency. The mass balance error presents a minimum around 580 and 850 kHz, being higher at 380 and 1142 kHz and it is again related with high levels of DCAA and MCAA.

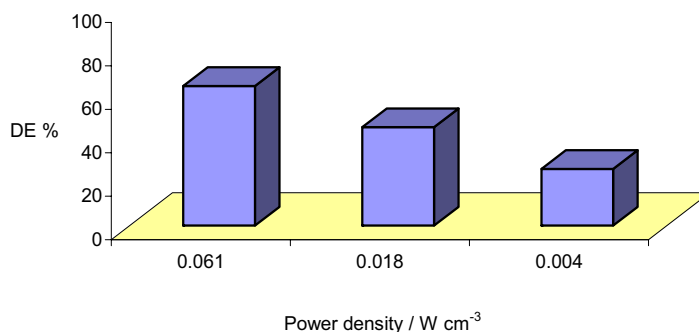


Fig.2 Degradation efficiency vs. power density at sonochemical reactions carried out at 850 kHz, 50 ppm., 0.061 W cm^{-3} , 0.018 W cm^{-3} , (3) 0.004 W cm^{-3} .

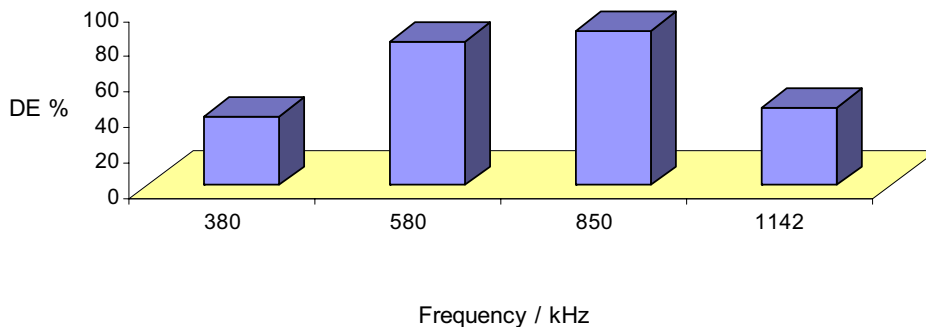


Fig.3 Degradation efficiency vs. ultrasonic frequency at sonochemical reactions carried out at 0.061 W cm^{-3} , 150 ppm.

4. Conclusions

The sonochemical degradation of PCE at high frequencies presents a high degradation efficiency, with a typical value higher than 60%.

The sonochemical degradation of PCE at high frequencies follows a multipath mechanism providing as major products Cl^- and CO_2/CO . However, it has been detected not only non-hydroxylated compounds, reported routinely in literature, but also hydroxylated compounds, being them (chloroacetic acids) the second group of major products.

In some experimental conditions, the mass balance is closed, being the best conditions high power density and frequencies around 580 to 850 kHz. Inside of these experimental conditions, the deviation of this situation is related to the presence of DCCA and MCAA and the concentration on the initial product.

With experiments at other experimental conditions, specially higher and lower frequencies, the mass balance is not closed. Further work is ongoing in the moment to detect possible additional remaining chlorinated compounds.

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