SONOELECTROCHEMICAL DEGRADATION OF PERCHLOROETHYLENE AT 850 kHz

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS AN OVERVIEW

- Chlorinated hydrocarbons are usually used as industrial degreasing agents: CCl_4, $CHCl_3$, C_2Cl_4, C_2Cl_3 , among others.
  Withspread chemical contaminants in the subsurface aquatic environment, which are difficult to treat by convenctional technologies.

  Perchloroethylene (C_2Cl_4) is widely used as an industrial dry cleaning solvent and metal degreaser.

- Chlorinated hydrocarbons are readly degraded to inorganic products during the aqueous phase ultrasonic irradiation.

- During the cavitational collapse of single, isolated bubbles, extreme temperatures and presures are achieved.

- The main chemical pathways for organic compound degradation include:

  (i) Hydroyxl chemical oxidation
  (ii) Direct pyrolytic degradation
  (iii) Supercritical water reactions

  Water vapor splits during bubble cavitation to yield H· and OH·

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ELECTROCHEMICAL DEGRADATION OF HALOCOMPOUNDS AN OVERVIEW

REDUCTION

Polyhalogenated compounds reduces at lower potential compared with the monohalogenated ones.

Cathodes used in electrochemical reduction of halocompounds: Ag, Zn, Cu, Pd, Pb and Sn.
There is a remarkable diferences in the final products of electrolysis for chloroform degradation.

The use of 3-dimensional electrodes such as Ag supported on carbon fiber or nickel mesh

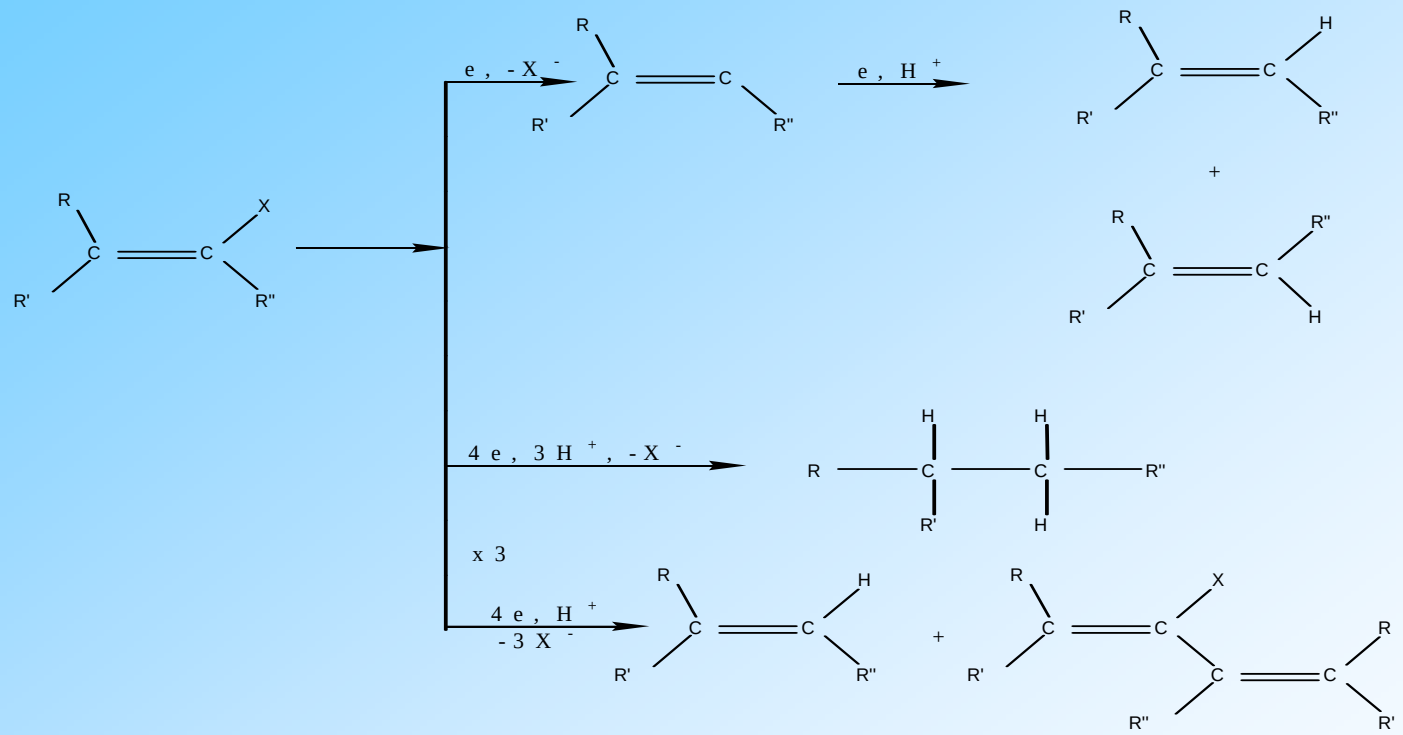
OXIDATION

Electrochemical oxidation: C/PbO_2, Ti/PbO_2, Pb/PbO_2
Potential electrode: Boron doped diamond (BDD)

Potential uses of PbO_2 and BDD materials as electrodes for the electrooxidation of halocompounds

ELECTROCHEMICAL DEGRADATION OF HALOCOMPOUNDS AN OVERVIEW

Reduction



Oxidation

$$\underline{C_2Cl_4} \xrightarrow{OH^{\cdot}} \text{Subproducts} + Cl^- + CO_2 + CO$$

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SONOELECTROCHEMICAL DEGRADATION OF HALOCOMPOUNDS AN OVERVIEW

Advantages of the combination of both methodologies:

- Decrease in the electrode diffusion layer.
- Enhancement of the active species diffusion from the bulk solution to the electrode surface.
- Switching of the reaction mechanism.
- Avoid electrode surface poisoning.
- Speed up of the degradation reaction.

Uses of sonoelectrochemistry in the degradation of:

PCBs
Phenols
Dyes
Benzene derivatives

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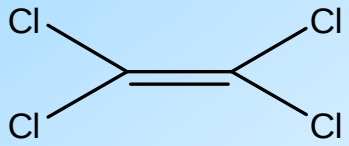
OBJECTIVES:

Study of the degradation of a chlorinated organic compound using sonochemical, electrochemical and finally the explotaition of the combination of both metodologies.

Degradation of perchloroethylene as a model molecule in aqueous solution.



Perchloroethylene

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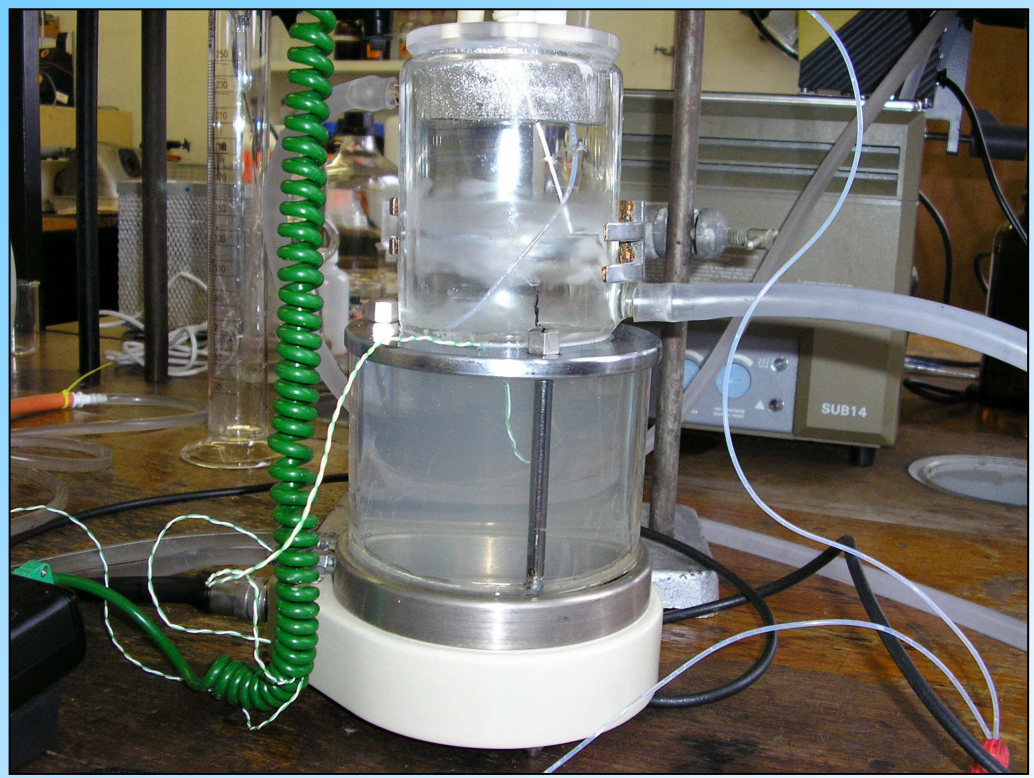
EXPERIMENTAL SET-UP
A GENERAL PICTURE FOR THE DEGRADATION OF PCE



Sonoreactor 850 kHz/140 W by Meinhardt

Ultraschalltechnik, K80-5

Transmitted power output into solution was higher!

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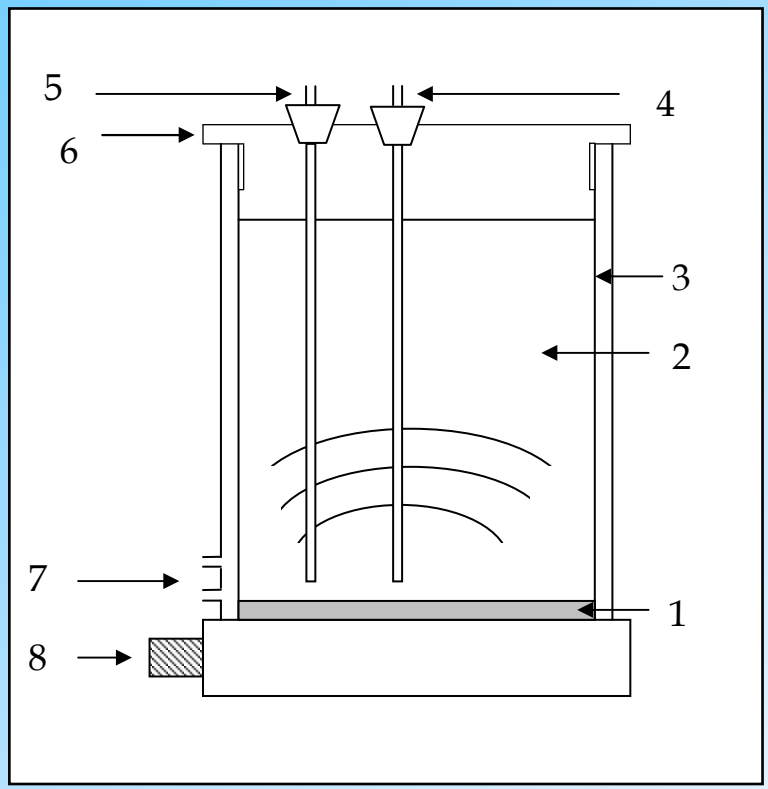
EXPERIMENTAL SET-UP FOR THE SONOCHEMICAL, ELECTROCHEMICAL AND SONOELECTROCHEMICAL DEGRADATION OF PCE



Sonoreactor 850 kHz/140 W by Meinhardt Ultraschalltechnik, K80-5

Schematic representation of the reactor cell used in this study
1) Transducer, 2) bulk solution, 3) glass cell, 4) sample withdrawing system, 5) temperature probe, 6) lid, 7) inlet and outlet of the cooling jacket and 8) interface.

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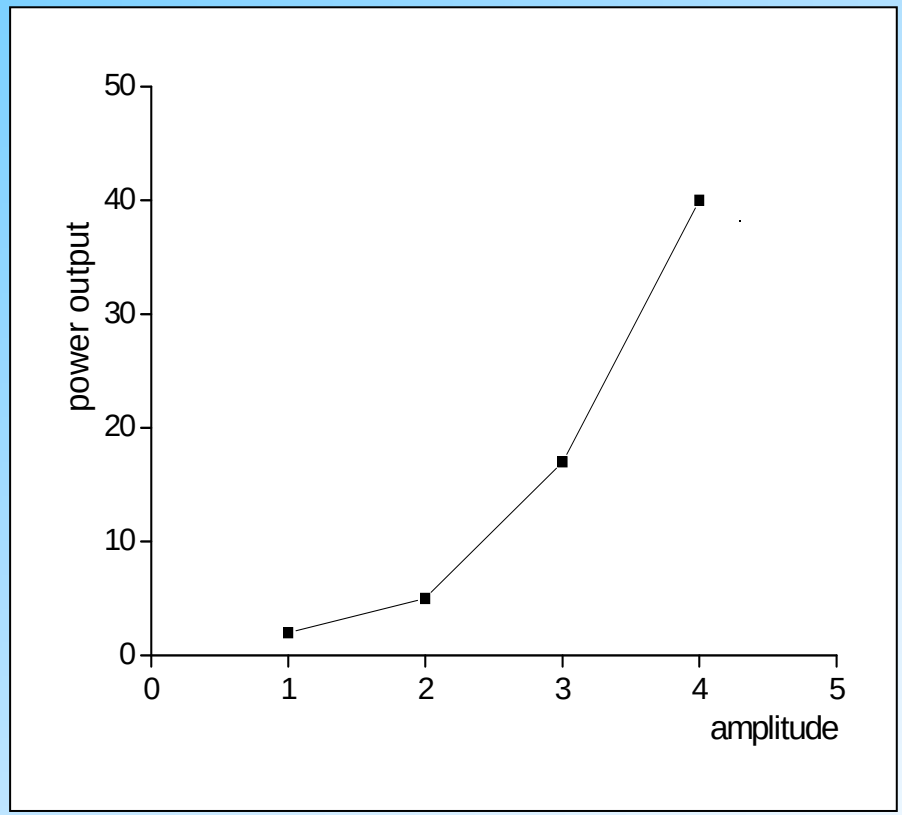
CHARACTERISATION OF AN ULTRASONIC BATH, 850 kHz, 140 W

- Ultrasonic power output was measured using standard calorimetric procedures



Power input/ watts	W cm^{-2}	W cm^{-3}
2.2±0.2	0.11	0.01
4.7±0.1	0.24	0.02
17.2±0.9	0.88	0.07
37.9±4.4	1.93	0.15

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EXPERIMENTAL PROCEDURE

SONOCHEMICAL EXPERIMENTS

Experimental conditions:

- Perchloroethylene (Aldrich 99%) used as recieved.

-Solutions were prepared with purified water obtained from a Milli-Q system, 18.2 MΩ cm .

-Temperature was mantained at 20 ±1 ^{o}C with a refrigerated bath and circulator.

- Ultrasonic irradiation was carried out at a 150 mL solution.

- Solutions were deoxygenated by bubbling argon before perchloroethylene was added.

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EXPERIMENTAL PROCEDURE
ELECTROCHEMICAL EXPERIMENTS

Electrochemical experiments were carried out at an undivided electrochemical cell utilising a lead dioxide electrode as anode and a lead electrode as cathode.

Geometric dimensions of both electrodes were 0.5x0.8x2.5 cm^3.
Lead dioxide film was performed by anodic polarisation in 0.5M H_2SO_4 using an electrode of lead.

Electrochemical oxidation of perchloroethylene was carried out at three current densities: 25, 50 and 75 mA cm^{-2} respectively.

EXPERIMENTAL PROCEDURE
ELECTROCHEMICAL EXPERIMENTS

In **sonoelectrochemical** experiments, a study of the effect of ultrasonic power was examined at 50 mA cm^{-2}

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EXPERIMENTAL PROCEDURE
ELECTROCHEMICAL EXPERIMENTS

The degradation of perchloroethylene was studied by:

A) Following the chloride concentration formation in solution either by

- Indirect spectrophotometric method

$$Hg(SCN)_2 + 2Cl^- \Leftrightarrow HgCl_{2(aq)} + 2SCN^-$$

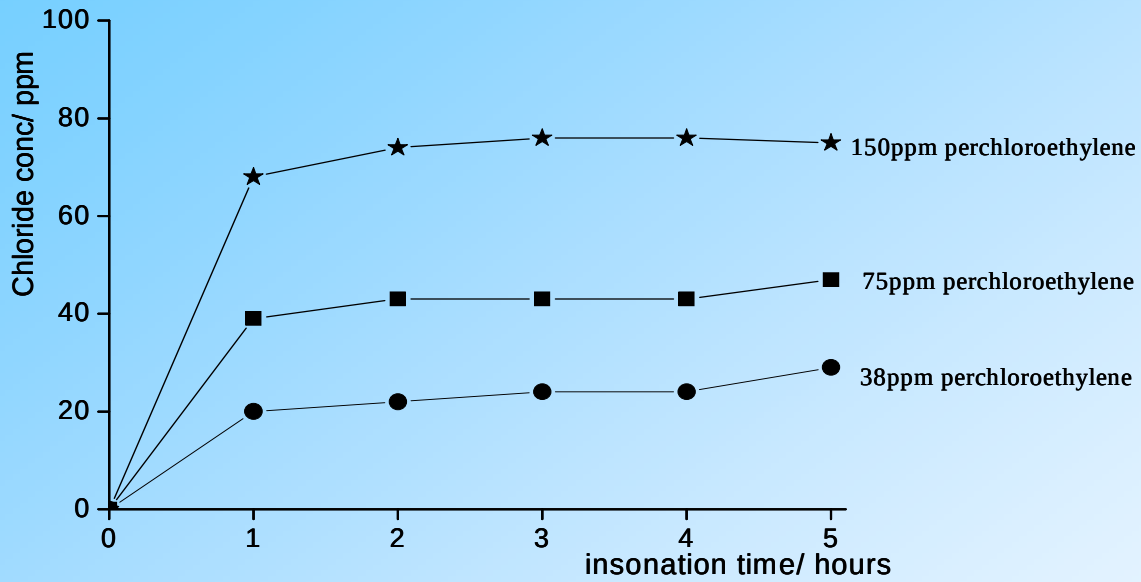
$$Fe^{3+} + 2SCN^- \Leftrightarrow Fe(SCN)^+_{2(aq)}$$

- Ion exchange chromatography
- Potentiometric titration

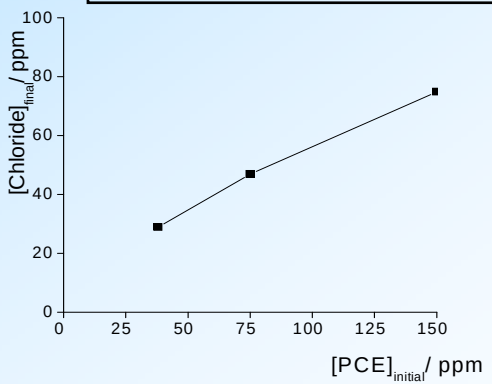
B) Monitoring of PCE by GC (GC-FID).

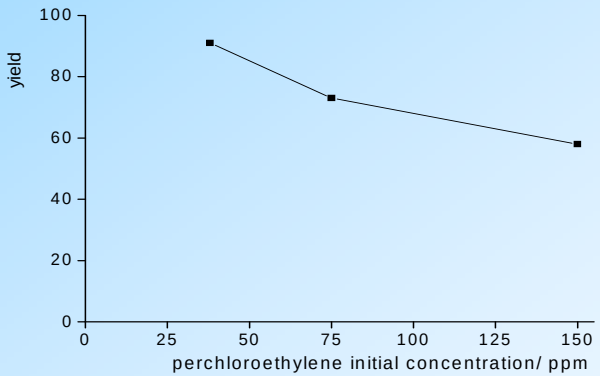
C) Detection, identification and quantification of PCE and products from the degradation obtained at the end of each experiment was done using Purge and Trap Gas Chromatography Mass Spectrometry (PT-GC-MS).

SONOCHEMICAL DEGRADATION OF PCE
RESULTS
Effect of PCE concentration



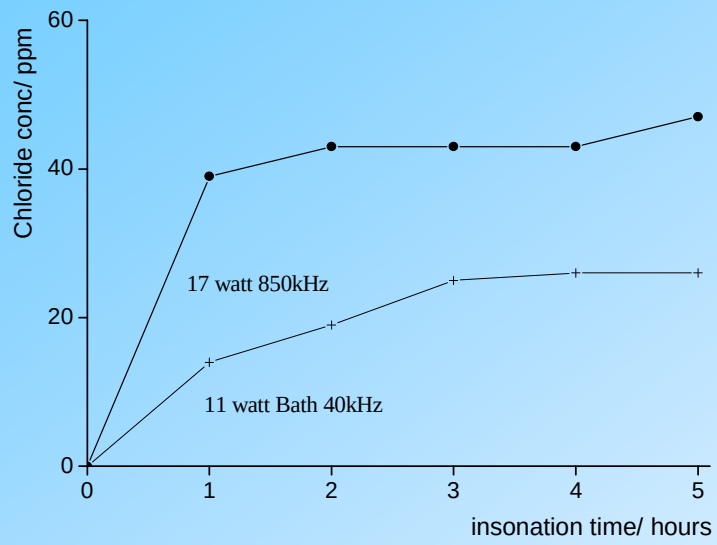
150ppm PCE
Saturation conditions!!





Initial Perchloroethylene concentration/ ppm	*Yield of Cl^- formation/ %*
150	58
75	73
38	91

SONOCHEMICAL DEGRADATION OF PCE
RESULTS
Effect of ultrasonic frequency



Sonoreactor (Ultrasonic cleaning bath 40kHz/150 W)

Frecuency: 40 kHz.

Power output: 150 W.

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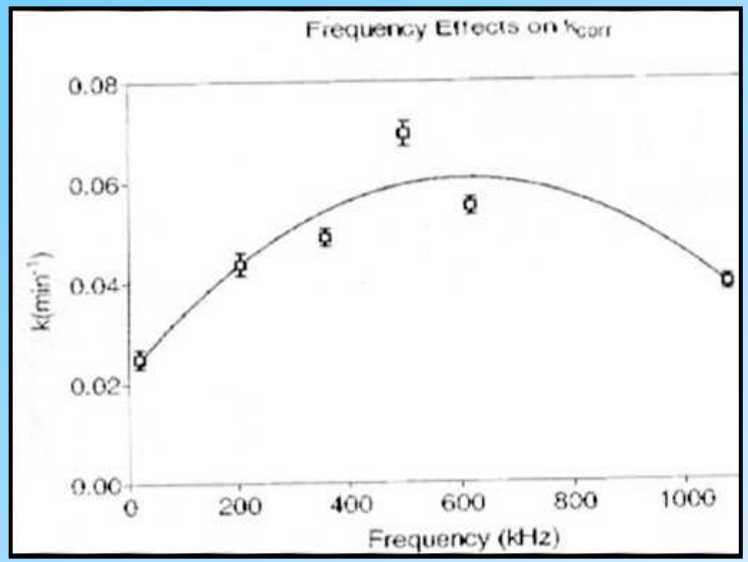
SONOCHEMICAL DEGRADATION OF PCE
RESULTS
Effect of ultrasonic frequency

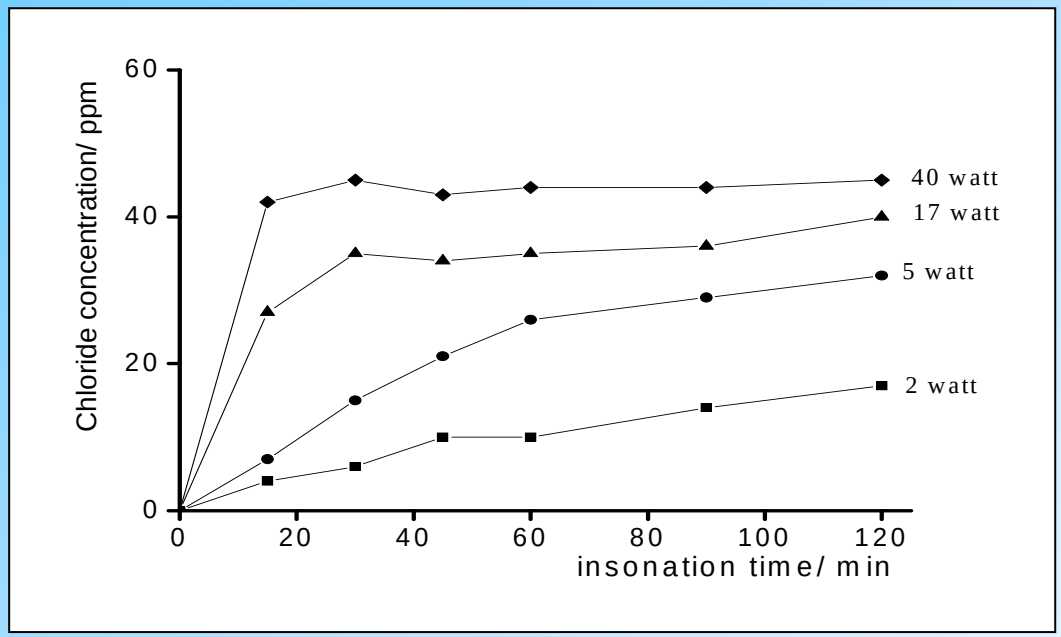


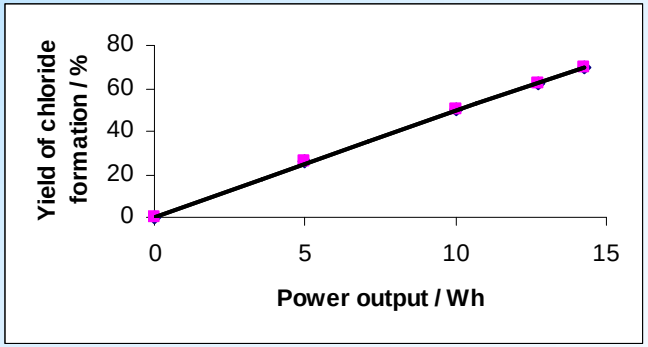
Other authors[1] have observed an increase in degradation rate with an increase in ultrasonic frequency in the sonolytic degradation of volatile/semivolatile solutes.

[1] M. R. Hoffmann and col. J. Phys. Chem. A, Vol. 103, No. 15, 1999

Variation of the CCl_4 degradation rate constant with ultrasonic frequency

SONOCHEMICAL DEGRADATION OF PCE RESULTS





Ultrasonic power / watts	*Yield of Cl^- formation/ %*
38	*70*
17	*62*
5	*50*
2	26

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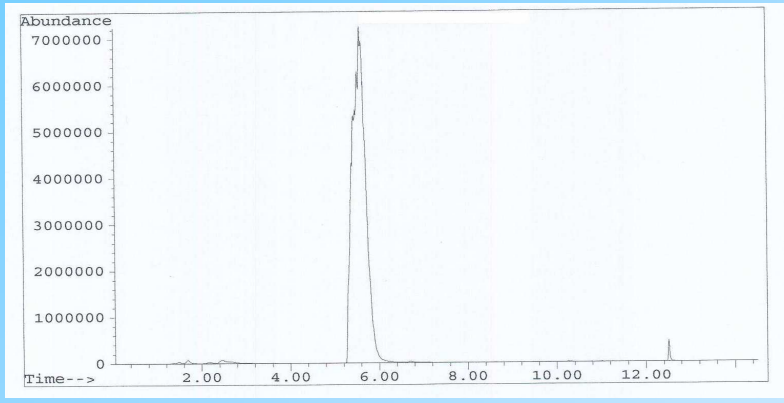
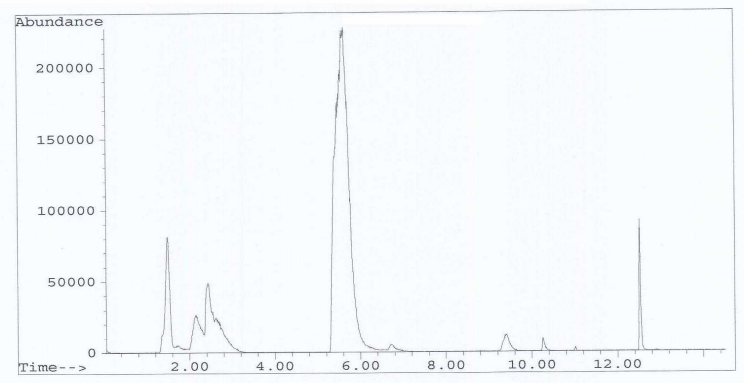
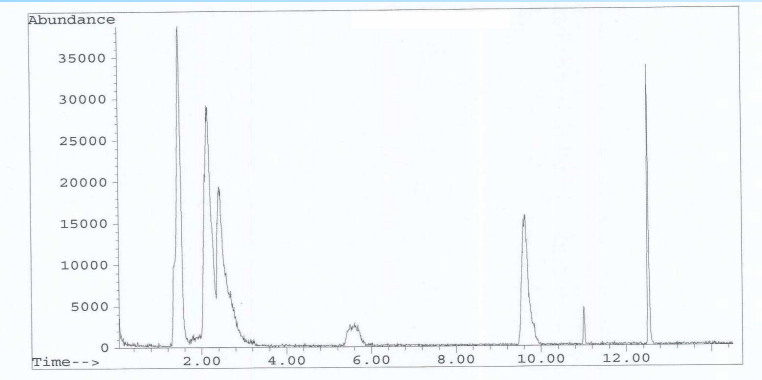
SONOCHEMICAL DEGRADATION OF PCE RESULTS



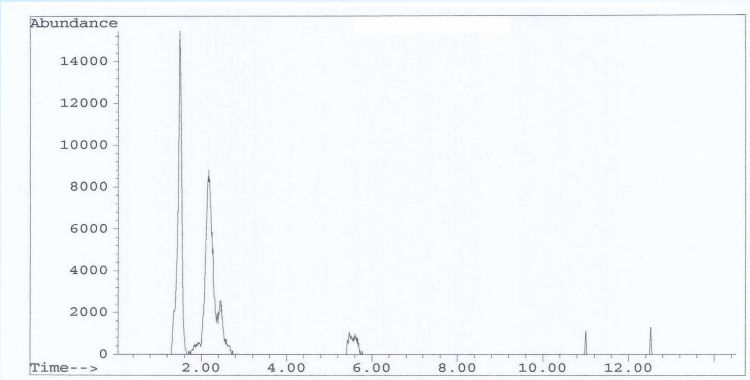
2 watts



5 watts



17 watts



38 watts

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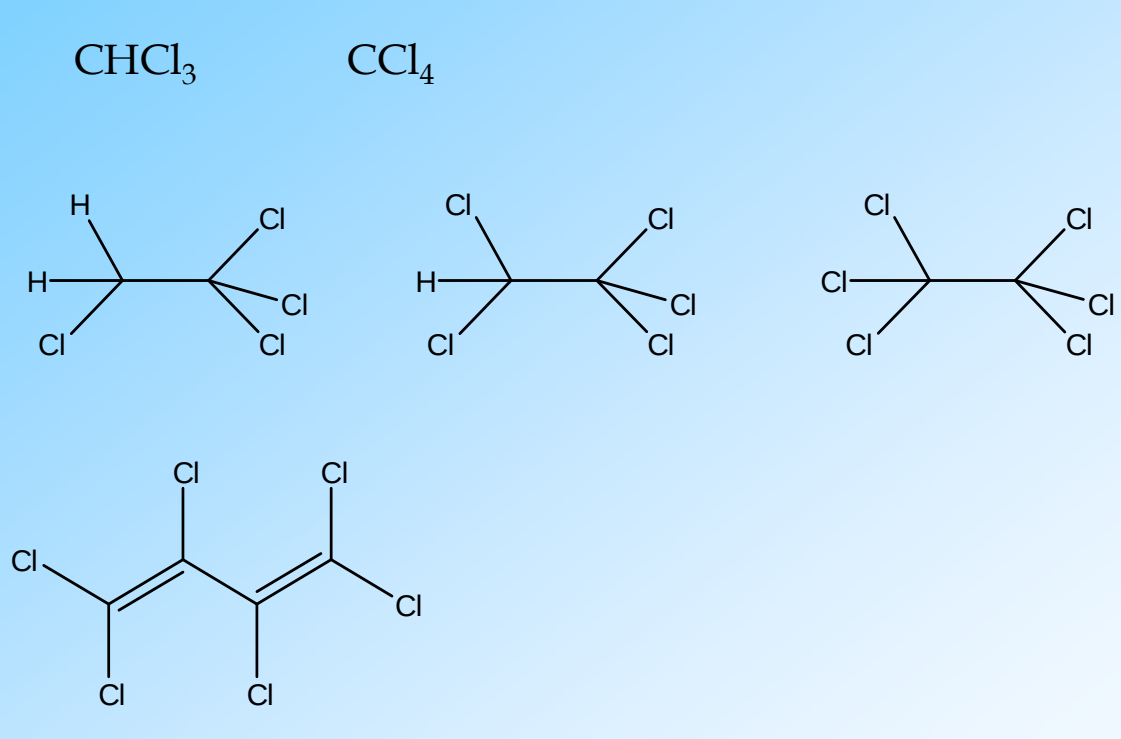
SONOCHEMICAL DEGRADATION OF PCE
RESULTS

- Main products from perchloroethylene sonochemical degradation:

$CHCl_3$ CCl_4



Mechanism?

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SONOCHEMICAL DEGRADATION OF PCE RESULTS

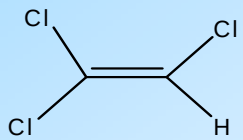
Mechanism:

$$H_2O \xrightarrow{US} \cdot H + \cdot OH$$

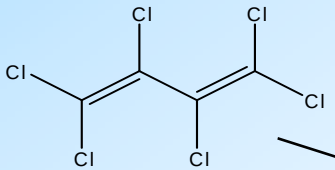
$$C_2Cl_4 \xrightarrow{US} \cdot Cl + \cdot C_2Cl_3$$

$$\cdot C_2Cl_3 + \cdot H \longrightarrow C_2HCl_3$$

$$2 \cdot C_2Cl_3 \longrightarrow C_4Cl_6$$



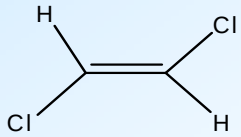
TCE

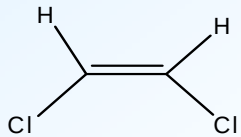


Products

$$C_2HCl_3 + \cdot H \longrightarrow HCl + \cdot C_2Cl_2$$

$$\cdot Cl_2C_2 + \cdot H \longrightarrow C_2H_2Cl_2$$





DCE

No presence of TCE and DCE during the sonolytic degradation of PCE.
Mechanism unfeasible

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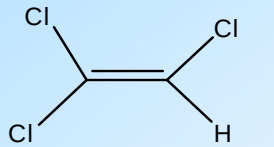
SONOCHEMICAL DEGRADATION OF PCE RESULTS

Mechanism:

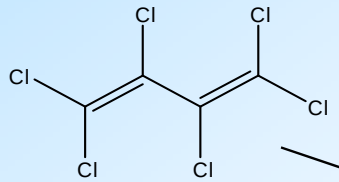
$$C_2Cl_4 \xrightarrow[(1)]{US} \cdot Cl + \cdot C_2Cl_3$$

$$\cdot C_2Cl_3 + \cdot H \longrightarrow C_2HCl_3$$



TCE

$$2 \cdot C_2Cl_3 \longrightarrow C_4Cl_6$$



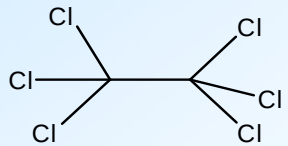
Products

US (2)

$$:CCl_3 + \cdot Cl \longrightarrow \cdot CCl_3$$

$$\cdot CCl_3 + \cdot Cl \longrightarrow CCl_4$$

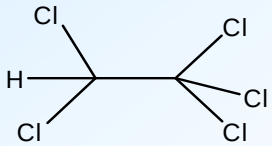
$$2 \cdot CCl_3 \longrightarrow C_2Cl_6$$



Products

$$C_2Cl_6 \longrightarrow \cdot C_2Cl_5 + \cdot Cl$$

$$\cdot C_2Cl_5 + \cdot H \longrightarrow HC_2Cl_5$$



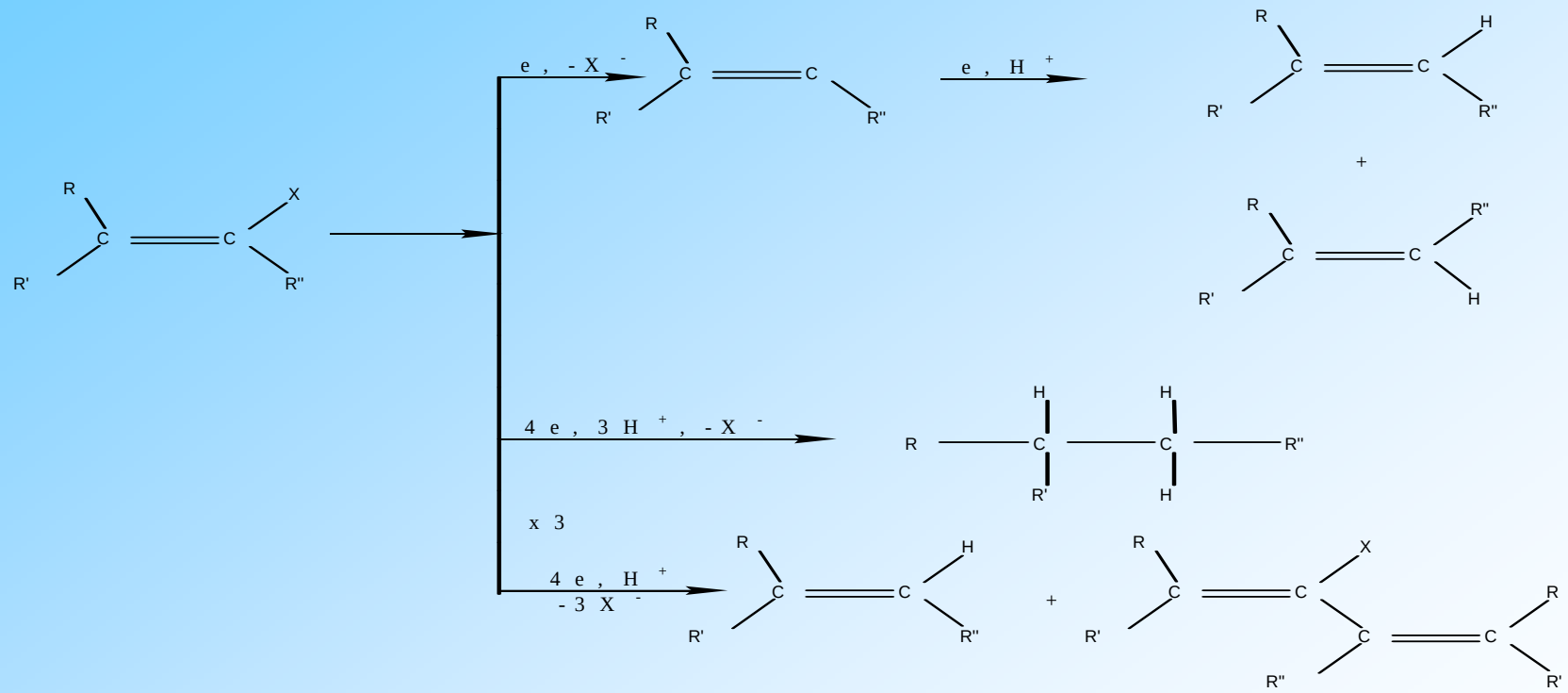
Products

$$\cdot CCl_3 \longrightarrow \cdot CCl_2 + \cdot Cl$$

$$\cdot CCl_2 \longrightarrow H_2C_2Cl_2$$

ELECTROCHEMICAL DEGRADATION OF PCE
RESULTS

Electrochemical mechanism:



Current density/ mA cm^{-2}	*Yield of Cl^{-} formation/ %*
50	20
75	20

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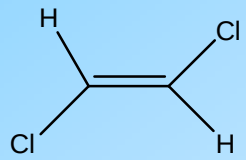
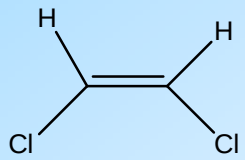
ELECTROCHEMICAL DEGRADATION OF PCE
RESULTS

- Products from perchloroethylene electrochemical degradation:

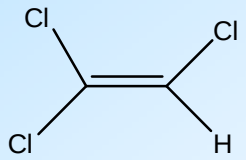
$CHCl_3$ CCl_4



trans-DCE



cis-DCE



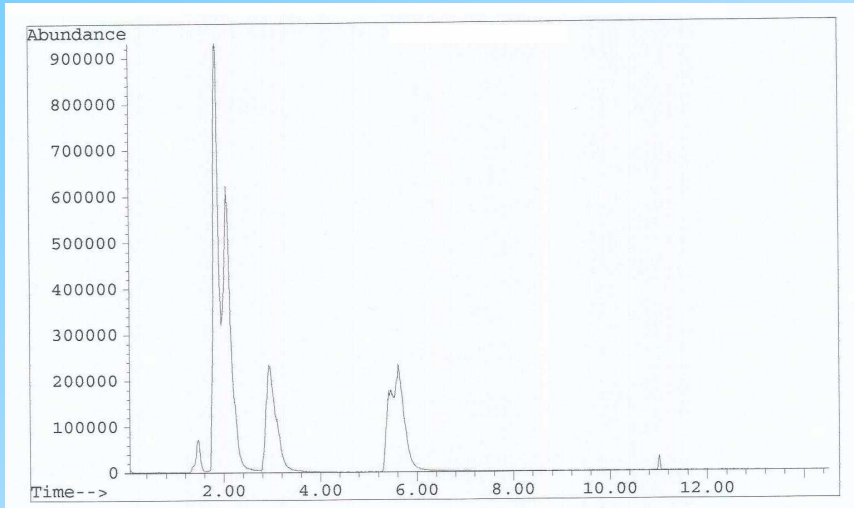
TCE

→ Formation of TCE and DCE as well as $CHCl_3$ and CCl_4

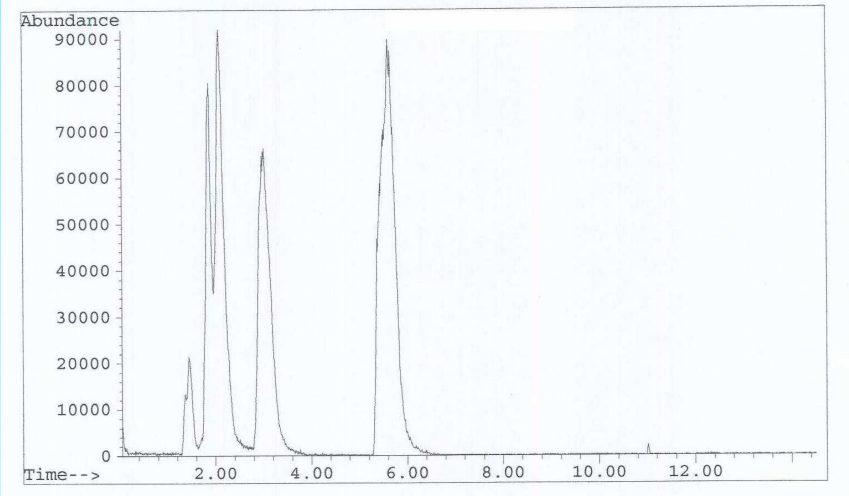
Electroreduction leads to TCE and DCE as major products

Electrooxidation gives TCE, $CHCl_3$ and $CHCl_4$ as major products

ELECTROCHEMICAL DEGRADATION OF PCE
RESULTS



50mA cm^{-2}
2 hours



75mA cm^{-2}
2 hours

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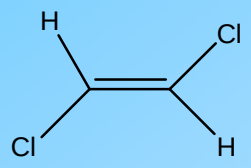
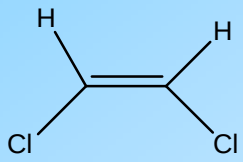
SONOELECTROCHEMICAL DEGRADATION OF PCE
RESULTS

- Main products from perchloroethylene sonoelectrochemical degradation:



trans-DCE



cis-DCE

Ultrasonic power input/ watts	*Yield of Cl^- formation/ %*
38	38
17	58
5	33

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CONCLUSIONS

- Reaction products obtained after PCE sonochenical degradation are different to those ones obtained by electrochemical degradation.

ACKNOWLEDGEMENTS

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