

STSM Scientific Report

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Purpose of the visit

The ultrasonic irradiation is widely used in wastewater treatment due to that during the cavitation bubbles process, where high temperatures and pressures are generated, distinct different highly reactive oxidizing species can be produced from the sonolysis of water. These species at those extreme conditions can degrade organic pollutants such as for example chlorinated hydrocarbons and toxic aromatic compounds present in dilute aqueous solutions. Among the chlorinated organic compounds we put emphasis on dichloromethane, trichloroethylene and perchloroethylene as mostly used solvents in large industry. These organic compounds are extremely toxic and harmful to human health and the environment. Moreover they are persistent in the environment and can be broken down to other compounds which are hazard to the ozone layer. Conventional degradation or removal procedures of these compounds from water are not easy. In the literature we find numerous methods of removal and degradation but all of them have their own limitations and drawbacks. The aim of this work is to study the degradation of a chlorinated organic compound using sonochemical, electrochemical and finally the exploitation of the combination of both methodologies. To accomplish that, the study of the following parameters on the degradation of perchloroethylene in aqueous medium, as a complex model molecule, must be addressed:

- Ultrasonic frequency
- Ultrasonic power output
- Current density
- Initial perchloroethylene concentration

Before this short visit at the School of Science and the Environment at Coventry University, the perchloroethylene degradation is being studied currently at the Physical Chemistry Department at Alicante University by applying an ultrasound field generated by a 20 kHz sonoreactor; therefore, other objective of this work is the comparison of our experimental results with those which will be obtained at the Coventry University laboratory.

Description of the work carried out during the visit

The degradation of perchloroethylene was mainly carried out using sonochemical, and electrochemical methods, whilst sonoelectrochemical procedure was used after optimisation of the above methods in a separate way.

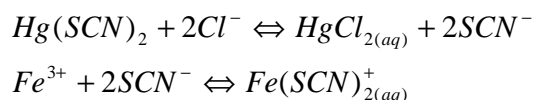
In **sonochemical** experiments, two different set up configurations were performed. On the one hand, the sonoreactor cell was filled with water, and the reaction cell containing perchloroethylene solution was placed on water whereby ultrasonic irradiation at the reaction cell was indirect and, therefore the sound passed through the aqueous solution contained in the sonoreactor cell before penetrating the reaction cell. On the other hand, the sonoreactor cell acts as a reaction one. Using the first configuration, a small amount of cavitation bubbles could be observed in solution during the insonation process and the transmitted power input into the reaction cell was lower as demonstrated by calorimetric measurements. This fact decided us to work with the second configuration since the

transmitted power into solution was higher. The operational variables studied were ultrasonic intensity and initial concentration.

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 cm³. Lead dioxide film was performed by anodic polarisation in 0.5M H₂SO₄ using an electrode of lead. Electrochemical oxidation of perchloroethylene was carried out at three current densities: 25, 50 and 75 mA cm⁻² respectively.

Finally, in **sonoelectrochemical** experiments, a study of the effect of ultrasonic power was examined at an optimum current density.

In all cases during this work, the degradation of perchloroethylene was studied following the chloride concentration formation in solution. Chloride concentration was determined using a spectrophotometric method. Chloride reacts with mercuric(II) thiocyanate to form a strong aqueous complex mercuric (II) chloride. Released thiocyanate ions react in the acid solution with iron (III) nitrate to give a red coloured iron (III) thiocyanate complex. The concentration of this complex is determined spectrophotometrically at 460 nm. Main reactions are depicted below:



Perchloroethylene and products from the degradation of perchloroethylene obtained at the end of each experiment were analysed using Gas Chromatography Mass Spectrometry (GC-MS). These analyses were carried out at the Physical Chemistry Department at Alicante University.

Description of the main results obtained

The ultrasonic power transmitted into an aqueous solution is a crucial characteristic of the ultrasound field as the radical production associated with the cavitation process is modified. When ultrasonic amplitude increases, the radical production also increases, so it is expected that the oxidation process related to these radicals must also enhance.

In sonochemical experiments, using a 850 kHz sonoreactor, the effect of the ultrasonic power was investigated upon the degradation of 75 ppm of a perchloroethylene solution for 2 hours. Results demonstrated that the chloride concentration coming from the perchloroethylene decomposition increased quickly with short insonation times before a steady state was achieved. All the ultrasonic powers studied showed the same behaviour. Besides, an increase in the ultrasonic power caused an increase in the chloride concentration formation in solution.

The following table presents the yield of the chloride ion obtained at different ultrasonic powers, where yields have been calculated assuming that the degradation process of perchloroethylene leads to the lost of four chloride ions.

Table 1.- Degradation of the perchloroethylene at different ultrasound powers

Ultrasonic power / watts	Yield of Cl ⁻ / %
38	70
17	62
5	50
2	26

Perchloroethylene and other reaction products in the final solutions were analysed by GC/MS. Perchloroethylene was only detected at the two lowest ultrasonic powers. Chloroform and carbon tetrachloride, as most important reaction intermediates, were detected in a concentration below 1 ppm.

On the other hand, the effect of the initial concentration of perchloroethylene was investigated on the degradation process efficiency. Experiments were carried out at three different concentrations of perchloroethylene: 38, 75 and 150 ppm, respectively. The solubility of perchloroethylene in aqueous solutions is limited by its concentration whereby 150 ppm of perchloroethylene lies closed to saturation. In all the above experiments perchloroethylene solutions were ultrasonically irradiated at 17 watts for 5 hours. Yields of chloride ion formation showed that the degradation process was more efficient at the lower concentration.

Table 2.- Degradation of the perchloroethylene at different initial concentrations

Initial Perchloroethylene concentration/ ppm	Yield of Cl ⁻ / %
150	58
75	73
38	91

After insonation for 5 hours, GC/MS analysis revealed no peaks regarding perchloroethylene, chloroform and carbon tetrachloride.

Electrochemical and sonoelectrochemical experiments were carried out using a lead dioxide electrode as anode and a lead electrode as cathode. Solution tested in these experiments comprises of 75 ppm of perchloroethylene in 0.5M Na₂SO₄ as supporting electrolyte. Two current densities were chosen, 50 and 75mA cm⁻², for the electrochemical degradation for 5 hours. Chloride ion determination showed the same value for both applied current densities. GC/MS analysis showed the presence of perchloroethylene, trichloroethene and (Z,E)1,2 dichloroethene. Next table shows the chloride ion yields obtained at both current densities.

Table 3.- Degradation of the perchloroethylene at different current densities

Current density/ mA cm ⁻²	Yield of Cl ⁻ / %
50	20
75	20

Finally, sonoelectrochemical experiments were carried out at a current density of 50 mA cm⁻² for 2 hours, and the effect of the ultrasonic power on the degradation of perchloroethylene was examined. The table below shows the chloride ion yields obtained at the above conditions.

Table 4.- Degradation of the perchloroethylene at different ultrasonic power in sonoelectrochemical experiments, $j = 50 \text{ mA cm}^{-2}$

Ultrasonic power input/ watts	Yield of Cl ⁻ / %
38	38
17	58
5	33

At the lowest ultrasonic power, perchloroethylene and trace amounts of (Z,E)1,2 dichloroethene were detected by GC/MS, whereas at other ultrasonic powers the unique compound detected was perchloroethylene.

Interestingly at higher ultrasonic power and current density GC/MS analysis demonstrates that chlorinated compounds are undetectable. This fact indicates that at those experimental conditions perchloroethylene solution was completely dehalogenated and decomposed into inorganic compounds. However, it would be necessary further experimental work such as analysis of the gaseous phase in order to identify and quantify the formation of inorganic compounds such as CO₂ and/or CO.

It is important to emphasize that the reaction products detected by the GC/MS analysis obtained after the sonochemical degradation are different to those ones obtained by the sonochemical and electrochemical degradation. This fact could indicate different mechanism of degradation. In order to elucidate possible mechanisms, it would be useful to analyse fractions of solutions by GC-MS at early stages of the reaction.

By using electrochemical and sonoelectrochemical treatments, it would be interesting to investigate the effect of other electrodes on the perchloroethylene degradation. On this work has been used lead dioxide as anode because of its good properties as anode as well as its low cost compared with precious metal electrodes at an industrial scale. Other suitable anodic material to be used for the degradation of perchloroethylene might be boron doped diamond.

Future collaboration with the host institution (if applicable)

The work developed during this Short Term Scientific Visit constitutes one part of the Ph.D. Thesis from Ms. Verónica Sáez Bernal, which will be presented before February 2005. The chlorinated hydrocarbons degradation is a very important issue for the Physical Chemistry Department at University of Alicante, which will be object of further work inside the Working Group entitled "Electrochemistry with ultrasound" (D32/004). The collaboration with the Coventry University laboratory, one of the pioneer centres in ultrasound technology, will be a strong force helping the success of the project. Several

items remains to be analysed as four weeks is a period of time insufficient, so a future visits is being planned.

Projected publications/articles resulting or to result from the STSM

A paper in an international journal comparing the influence of the ultrasound frequency on the sonoelectrochemical degradation of perchloroethylene is in preparation, However, the project would benefit from further work to be performed in future visits. It is also expected that results from this study will be presented at an international conference, possibly 'Electrochemistry 2005' to be held at Newcastle, UK in September 2005.

Confirmation by the host institution of the successful execution of the mission

This was a successful visit. Ms Saez performed useful experimentation in the Coventry laboratory, using both the electrochemical apparatus and the ultrasonic equipment available here, the latter offers a range of frequencies for examination. The analysis method exploited our spectroscopic facilities. The candidate was also able to improve her English language skills during the visit. She was assisted in the laboratory by Dr J Iniesta, a Postdoctoral Researcher currently supported by the UK EPSRC. Ms Saez worked hard, achieving the aims of the Mission, and obtained the sets of results given in the tables. This is a good effort in the time available.

Other comments

STSM actions are an excellent way to reinforce the Working Group consolidation but its duration would be longer, at least 3 months (6 months will be beneficial) in order to optimise the visit from an operative point of view. Perhaps a lone STSM of 6 months by researcher and laboratory from the Working Group during the 5 years of the COST action will be better than these too short visits.

In this way, it must be stressed that the use of a 512 kHz ultrasonic source had been planned during the visit at the Coventry University Laboratory, but due to the extremely compressed planning work, the degradation of perchloroethylene was focussed on the utilisation of a 850 kHz sonoreactor. Nevertheless, further experiments will be performed at the laboratory of Coventry in future visits.