



# Towards the complete dechlorination of chloroacetic acids in water by sonoelectrochemical methods: Effect of the cathode material on the degradation of trichloroacetic acid and its degradation by-products



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## ABSTRACT

The effect that the cathode material has on the electrochemical and high-frequency sonoelectrochemical degradation of TCAA in water samples with no background electrolyte has been studied in the work here presented. For all the cathode materials employed (Ti, AISI 304 stainless steel, carbon and Pb), the high-frequency sonoelectrochemical treatment yielded significantly higher fractional conversions for trichloroacetic acid and a significantly higher degradation efficiency when considering the removal of chlorinated species from the treated solutions. Moreover, differences in fractional conversion, degradation efficiency, current efficiency, C mass balance error and the concentration of the different trichloroacetic acid degradation by-products show how the cathode material has a strong effect on the efficiency of the electrochemical and high-frequency sonoelectrochemical treatments and the degradation mechanisms that may take place. Regarding this, complete dechlorination was virtually achieved in the high-frequency sonoelectrochemical degradation using a Pb cathode, where C mass balance results suggested the mineralization of TCAA.

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## 1. Introduction

Chloroacetic acids (CAAs) are receiving an increasing attention from researchers and legislators around the world as they are becoming one of the largest fractions of disinfection by-products (DBPs) found in drinking waters [1–3], trichloroacetic acid (TCAA) being one of the most targeted CAAs in academic studies due to its widespread presence in the environment [4]. TCAA, a former herbicide, is not only one of the most common DBPs, but it is also formed by different natural processes [5–7] and is a common by-product of the degradation of other chlorinated organocompounds such as perchloroethylene [8,9]. The concentration of TCAA may lie within a wide range in surface and ground waters due to its high solubility and different natural and anthropological sources [4], and the increasing presence of TCAA and other CAAs (dichloroacetic acid

or DCAA and monochloroacetic acid or MCAA) in waters and soils constitutes a serious risk to human health [10,11]. In some cases, the exposure to TCAA and other CAAs is extremely high, as recently reported by Cardador and Gallego [12] who studied the exposure of workers and swimmers to TCAA, DCAA and MCAA in indoor and outdoor pools, finding that, in such places, TCAA and DCAA may reach concentration levels above the maximum concentration level set by the U.S. EPA [13] for haloacetic acids (HAAs). Traditional bioremediation methods have unsuccessfully been employed in the degradation of HAAs, including CAAs, in water, TCAA being the most recalcitrant among them [14,15]. Phase-transfer techniques such as adsorption have shown promising results [16] in recent years, although a more environmentally friendly approach where the degradation of the C–Cl bond, which is toxic in nature, is preferred.

In recent years, different chemical methods have been developed in order to degrade the C–Cl bond in CAAs, in general, and TCAA, in particular. Zero-valent iron and bimetallic particles [17–19] have been successfully used to remove TCAA and its degradation by-products. Nevertheless, the potential release of metals in these processes may affect water quality in long term [20] and

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therefore have a harmful effect on the environment [21]. Fe (II) minerals from corroded iron/steel pipes have also been employed with different results: while TCAA was not affected at all in the presence of goethite/magnetite and aqueous Fe (II) [22], TCAA and DCAA were removed in aqueous solutions containing a carbonate green rust [23]; however, no degradation of MCAA was noticed in the latter. Photocatalytic degradation over bare and silver-deposited TiO<sub>2</sub> was not very effective in removing TCAA from aqueous solutions [24], although it showed promising results in the degradation of DCAA and MCAA. And the catalytic hydrodechlorination over Pd/ZrO<sub>2</sub> catalysts has also been very effective in the degradation of TCAA, DCAA and MCAA in water [25]. Nevertheless, the small size of the Pd catalysts (from 1 to 3.5 nm) and the concentration used (150 mg/L) could potentially become an important issue in the scaling-up of the process.

The electrochemical degradation of CAAs in aqueous solutions has received a wide attention in the last years since Korshin and Jensen [26] studied the electroreduction of diverse HAAs on gold or copper electrodes, showing that both TCAA and DCAA were electrochemically active and could be reduced by electrochemical methods, although no signs of the degradation of MCAA were clearly observed in their study. Li et al. [27,28] showed that the dechlorination of HAAs on haemoglobin-loaded carbon nanotube (Hb/CNT) cathodes was stepwise, following in the case of TCAA the pathway of TCAA → DCAA → MCAA. However, very slow degradation rates were noticed for MCAA. This issue was resolved by Li et al. [29] with newly developed electrodes consisting of Pd/Fe nanoparticles electrodeposited onto carbon paper (Pd/Fe-C), achieving very high degradation rates for TCAA, DCAA and MCAA. All these results demonstrate that the electrochemical treatment of waters polluted with CAAs is technically feasible, although some important drawbacks arise from these studies that should be dealt with: (i) the use of expensive and/or rare cathodic materials that may not be commercially available (gold [26], Hb/CNT [27,28], Pd/Fe-C [29]), and (ii) the necessary addition of a background electrolyte (0.01 M Na<sub>2</sub>SO<sub>4</sub> or 0.01 M K<sub>2</sub>HPO<sub>4</sub> [26], 0.1 M phosphate buffer containing 10 mM KCl [27,28], 10 mM Na<sub>2</sub>SO<sub>4</sub> [29]) in order to achieve a certain conductivity to prevent resistance-controlled kinetics and enable a good control of the electrochemical system.

The use of ultrasound in electrochemistry, also known as sono-electrochemistry, has been deeply studied and evaluated in recent years due to its potential application in environmental remediation [30]. In this sense, many research groups have demonstrated how ultrasound may catalyse the overall electrochemical degradation process of different chlorinated organocompounds such as diuron [31] or perchloroethylene [32], achieving for the latter the complete degradation of C-Cl bonds in water samples where no background electrolyte was added [33]. In previous studies by the authors, the removal of TCAA and its main degradation by-products, DCAA and MCAA, was also achieved by sonoelectrochemical methods [34,35], showing that high-frequency ultrasound and the absence of a background electrolyte were key parameters in order to achieve the complete dechlorination of TCAA. The use of high-frequency ultrasound did not only catalyse the progressive C-Cl bond cleavage mechanism, but also seem to enhance the dissociative adsorption/incineration paths that may occur on both cathode and anode. In addition, it was shown how the anode material may also affect the overall process, as complete dechlorination of TCAA was achieved when using a steel cathode and a PbO<sub>2</sub> anode.

The present work completes the study of the feasibility of high-frequency sonoelectrochemical methods as a way to completely remove CAAs in water by evaluating the effect that the cathode material may have on the process. The cathode material is expected to have a strong influence on the degradation of TCAA by electrochemical and sonoelectrochemical methods, as the main dechlorination mechanism is the sequential C-Cl bond cleavage,

which is enhanced by the physical and chemical effects produced by the presence of cavitation phenomena. For this purpose, commercially available materials such as stainless steel, carbon and Ti were evaluated as potential cathode materials for the sonoelectrochemical degradation of TCAA and its by-products, along with a less usual material such as Pb, which has already been successfully employed in the electroreduction of other chlorinated organocompounds [36].

## 2. Experimental

The same chemicals, analytical methods and experimental set-up previously used for the evaluation of the anode material on the sonoelectrochemical degradation of TCAA [35] were again used in the experiments included in the present study.

### 2.1. Chemicals and analytical methods

For all the experiments, 0.5 mM TCAA (99.9%, Aldrich) aqueous solutions were prepared with purified water (18.2 MΩ cm resistivity) from a Milli-Q UV Plus system. The concentration of TCAA and its main degradation by-products was monitored by analyzing 1 mL of sample filtered through a 0.45 μm PTFE filter with two different methods:

- High-performance liquid chromatography (HPLC) to monitor TCAA, DCAA, MCAA and acetic acid (AA). An Agilent 1100 HPLC device fitted with a Hypersil ODS (C18) column (250 mm × 4 mm and particle diameter 5 μm) and a UV-VIS detector set to a wavelength of 210 nm was used injecting 40 μL aliquots. The mobile phase was a phosphate buffer (pH 2.7) at 1 mL min<sup>-1</sup>.
- Ionic chromatography (IC) to monitor TCAA, DCAA, MCAA and Cl<sup>-</sup>. A basic IC 792 System (Metrohm, Switzerland) equipped with a Metrosep A Supp 4/5 guard column, and an anion column Metrosep S Supp 9 μm (4.6 × 250 mm) was used injecting 20 μL aliquots. The mobile phase was 1 mM Na<sub>2</sub>CO<sub>3</sub>, 4 mM NaHCO<sub>3</sub> solution at 1 mL min<sup>-1</sup>.
- Atomic absorbance spectroscopy (AAS) to monitor any traces of the metal cathodes in the treated water samples. A Perkin-Elmer 2100 equipped with an air-acetylene flame and an automatic simple injector AS-70 was used.

### 2.2. Experimental setup

All the reactions were carried out in a sonoreactor (0.5 L of volume) consisting of a cylindrical flask equipped with a cooling jacket where the electrodes (18 cm<sup>2</sup> on each side) were placed as shown in Fig. 1. The sonoreactor was assembled with an MFLG multifrequency system from Meinhardt Ultraschalltechnik, which operated at 863 kHz and 0.054 W cm<sup>-3</sup> during the experiments with ultrasound. Electrochemical treatment (ECT) and sonoelectrochemical treatment (SECT) of prepared aqueous solutions were carried out for 10 h for each of the different cathode materials used. In all cases, the experiments were conducted at either a maximum current density of 4 mA/cm<sup>2</sup> or a maximum applied potential between cathode and anode of 14.3 V, depending of the different anode materials employed. In all the experiments, a homemade galvanostat (120 mA–13.4 V maxima power) was used. Four commercially available cathode materials were evaluated: Ti, AISI 304 stainless steel, carbon and Pb, all of them supplied by Goodfellow. Pt/Ti (50 g of platinum per m<sup>2</sup>) supplied by I.D. Electroquímica was used as the anode material in all the experiments as it was the anode where less anodic contributions to the overall degradation of TCAA and its main by-products were noticed in a previous work by the authors

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