

Hydroxyl radicals at the anode and in the bulk for the remediation of water containing organochlorinated pollutants. Elucidation of the reaction pathways.

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The chlorinated aliphatic hydrocarbons conjugate toxicity with high chemical stability, bioaccumulation and long-range diffusivity. Chloroethanes are particularly ubiquitous in the industry and in household products, and their entry to the environment may entail potential risks for the living beings. At present, the US Environmental Protection Agency is carrying out the Endocrine Disruptor Screening Program (EDSP), where 1,2-dichloroethane (DCA) and 1,1,2,2-tetrachloroethane (TCA) are considered as priorities for their potential effects on the endocrine system. DCA is also found in the list of priority substances drawn up by the European Commission. To avoid the release of chloroethanes into the aqueous environment, powerful water treatment technologies such as the advanced oxidation processes (AOPs) must be applied in the wastewater treatment facilities. Among them, electrochemical AOPs (EAOPs) such as anodic oxidation (AO) and electro-Fenton (EF) processes have gained much interest for the removal of organic compounds due to their outstanding technical characteristics and the reduced use of expensive chemicals. Here, acidic aqueous solutions of DCA and TCA have been treated by the EF and AO processes. Bulk electrolyses were performed at constant current using a BDD anode and an air diffusion cathode (ADE) able to generate H₂O₂ in situ, which reacts with added Fe²⁺ to yield [•]OH from Fenton's reaction. At 300 mA, almost total mineralization was achieved at 420 min for solutions containing 4 mM of either DCA or TCA. Comparative treatments without Fe²⁺ (AO) or with a Pt anode led to a poorer mineralization. The better performance of the EF process with BDD is explained by the synergistic action of the oxidizing radicals, BDD([•]OH) at the anode surface and [•]OH in the bulk, and the minimization of diffusional limitations. The decay of the initial pollutant accomplished with pseudo first-order kinetics. Chloroacetic and dichloroacetic acids were the major by-products during the degradation of DCA and TCA, respectively. Acetic, oxalic and formic acids were also identified. The proposed reaction pathways include oxidative and reductive (cathodic) dechlorination steps. Chlorine was released as Cl⁻, being further oxidized to ClO₃⁻ and, mostly, to ClO₄⁻, due to the action of the largely generated BDD([•]OH) and [•]OH. In conclusion, it has been proven that EF with a BDD/ADE cell is a very effective technology for the decontamination of single and multicomponent DCA and TCA aqueous solutions, which is encouraging to proceed with the treatment of real waters.