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Electrochemical oxidation of anesthetic tetracaine in aqueous medium. Influence of the anode and matrix composition

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HIGHLIGHTS

- Complete, quick decay of tetracaine in 0.050 M Na_2SO_4 by EO-H_2O_2 with BDD anode.
- Tetracaine decay in simulated and real wastewater: IrO_2-based < Pt ~ BDD < RuO_2-based.
- Much larger mineralization (>50%) of tetracaine using BDD, regardless of the matrix.
- Fate of nitrogen atoms: NO_3^-, soluble *N*-derivatives and volatile compounds.
- Five aromatic by-products, including a dichloroaromatic: formation of chloroderivatives.

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ABSTRACT

The degradation of 150 mL of 0.561 mM tetracaine hydrochloride at pH 3.0 by electrochemical oxidation with electrogenerated H_2O_2 (EO-H_2O_2) has been studied at a low current density of 33.3 mA cm^{-2} in three different matrices: 0.050 M Na_2SO_4, real urban wastewater and a simulated matrix mimicking its electrolyte composition. Comparative trials were performed in an undivided cell with a 3 cm^2 boron-doped diamond (BDD), Pt, IrO_2-based or RuO_2-based anode and a 3 cm^2 air-diffusion cathode that allowed continuous H_2O_2 electrogeneration. In 0.050 M Na_2SO_4, much faster and overall removal of tetracaine occurred using BDD because of the large oxidation ability of BDD(·OH) formed from anodic water oxidation. In either simulated matrix or real wastewater, the RuO_2-based anode yielded the quickest tetracaine decay due to a large production of active chlorine from anodic oxidation of Cl^-. For the mineralization of the organic matter content, the BDD/air-diffusion cell was the best choice in all aqueous matrices, always reaching more than 50% of total organic carbon abatement after 360 min of electrolysis, as expected if BDD(·OH) mineralizes more easily the chloroderivatives formed from tetracaine oxidation in the presence of active chlorine. The initial N of tetracaine was partly transformed into NO_3^-, although the total nitrogen of all solutions always decayed by the release of volatile by-products. In the Cl^--containing matrices, significant amounts of ClO_3^- and ClO_4^- were obtained using BDD, whereas active chlorine was much largely produced using the RuO_2-based anode. Five aromatic by-products, one of them being chlorinated, along with low concentrations of oxalic acid were identified. The change in toxicity during EO-H_2O_2 with BDD in the sulfate and simulated matrices was also assessed.

1. Introduction

Thousands of tons of a large number of pharmaceuticals are consumed worldwide by humans and animals. Since they are not completely metabolized, they are continuously discharged into the environment via urine and feces. This mainly affects water bodies and, eventually, the quality of drinking water supplies. Despite their low contents at μg L^{-1} level, the potential impact of pharmaceuticals on ecosystems and their long-term effects on the health of living beings have caused global alarm [1–4]. The occurrence of pharmaceuticals in water is explained by their incomplete removal by conventional physicochemical and biological treatments in wastewater treatment plants (WWTPs), thereby becoming persistent contaminants [3,4]. Tetracaine (2-dimethylaminoethyl-4-butylaminobenzoate, $C_{15}H_{24}N_2O_2$, M = 264.3 g mol^{-1}), commercially available as hydrochloride salt, is a potent local anesthetic belonging to the family of amino esters.

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It is used for topical anaesthesia in ophthalmology, spinal anaesthesia and nerve block and can be formulated as solutions, creams, gels and as the base of ointments [5,6]. Its critical toxicity has been determined [7], and it has been detected in hospital wastewater with an average concentration of 0.48 μg L^{-1} [8]. No previous work has reported the decontamination of water containing tetracaine. Research efforts are then necessary to show if this pharmaceutical can be destroyed in aqueous medium in order to prevent its toxic effects on living beings.

Advanced oxidation processes (AOPs) are powerful oxidation methods characterized by the continuous generation of reactive oxygen species (ROS) like hydroxyl radical (·OH). Since these species are formed in situ without addition of noxious chemicals, they are considered as eco-friendly technologies [9]. The very short lifetime of ·OH (~10^{-9} s) and its very high standard reduction potential ($E°$ = 2.8 V/SHE) allow its fast, non-selective reaction with most organics, showing a second-order rate constant (k_2) of 10^7–10^{10} M s^{-1}, up to total mineralization in many cases [10,11]. For this reason, AOPs have got great interest for water remediation. Among these methods, electrochemical oxidation (EO) has been widely utilized as an electrochemical AOP (EAOP) that combines a large oxidation power with simplicity of use [11–13]. EO involves the destruction of organic pollutants in a free-chlorine aqueous medium through physisorbed hydroxyl radicals (M(·OH)) originated at the surface of an anode M from water oxidation [13–15]:

$$M + H_2O \rightarrow M(^{\cdot}OH) + H^+ + e^- \quad (1)$$

The nature of the anode has major influence on the oxidation ability of EO. Materials such as Pt and dimensionally stable anodes (DSA®) based on IrO_2 and RuO_2 behave as active anodes with low production of physisorbed M(·OH) since it is transformed into an less powerful superoxide (MO) species [13,16–20]. In contrast, large amounts of physisorbed M(·OH) are formed at non-active anodes with large O_2-overvoltage. It has been found that boron-doped diamond (BDD) thin-film electrodes are the most powerful among the latter ones, having high corrosion stability in harsh media and hampering a strong adsorption of ·OH on their surface. BDD allows a large degree of mineralization of aromatics including pharmaceuticals [14,15,19–31], with much quicker removal compared to that obtained using traditional anodes such as Pt [32,33] and PbO_2 [34].

The situation is very different if EO is performed in a chlorinated medium, since active chlorine species (Cl_2, HClO and/or ClO^-) are produced from Cl^- oxidation at the anode [9,11–13]:

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \quad (2)$$

$$Cl_2(aq) + H_2O \rightarrow HClO + Cl^- + H^+ \quad (3)$$

$$HClO \leftrightarrows ClO^- + H^+ \quad pK_a = 7.56 \quad (4)$$

Under these conditions, physisorbed M(·OH) and active chlorine species compete to oxidize the organic matter. It has been found that active DSA® anodes, pre-eminently RuO_2-based ones, yield larger quantity of active chlorine that can attack rapidly the aromatic structures, even more quickly than BDD(·OH) [20,36]. However, highly persistent chloroderivatives are usually accumulated, giving rise to partial mineralization of solutions.

The EO process can be alternatively applied using continuous generation of H_2O_2 from the two-electron cathodic reduction of injected O_2 or air via reaction (5) [12,35–37], giving rise to the so-called EO with electrogenerated H_2O_2 (EO-H_2O_2) process:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (5)$$

Several carbonaceous cathodes such as activated carbon fiber [38], carbon nanotubes [39], carbon felt [40,41] and carbon-polytetrafluoroethylene (PTFE) gas-diffusion composites [20,42,43] have shown good performance for H_2O_2 generation from reaction (5).

In EO-H_2O_2, the electrogenerated H_2O_2 is partly destroyed to O_2 at the anode M yielding the hydroperoxyl radical M($HO_2^{\cdot}$) from reaction (6) [11]:

$$M + H_2O_2 \rightarrow M(HO_2^{\cdot}) + H^+ + e^- \quad (6)$$

and hence, organics can be removed by different ROS, being M(·OH) much more powerful than H_2O_2 and M($HO_2^{\cdot}$). In our laboratory, we have shown the potential applicability of EO-H_2O_2 to degrade some pharmaceuticals with a carbon-PTFE air-diffusion cathode [20,33,43]. This cathode has been chosen since it is the most effective for O_2 reduction from reaction (5), avoiding the possible cathodic reduction of organics.

This work aims to assess the oxidation ability of EO-H_2O_2 to destroy tetracaine using an undivided cell with an air-diffusion cathode. The degradation was comparatively performed in pure sulfate medium, as well as in a simulated matrix with chloride + sulfate ions as model electrolytes to better understand its further destruction in a real wastewater matrix that contained large amounts of both ions along with natural organic matter (NOM, which mainly includes humic, fulvic and tannic acids). A pH of 3.0 was chosen to compare the present results with those obtained under similar conditions using Fenton-based EAOPs in future work. Four anodes including BDD, Pt, IrO_2-based and RuO_2-based were tested to establish the best electrolytic system. The pharmaceutical decay and mineralization rate were studied for each system and matrix. Primary by-products were identified by gas chromatography-mass spectrometry (GC–MS). Final carboxylic acids were detected by ion-exclusion high-performance liquid chromatography (HPLC) and the change in toxicity was determined from the standard method based on the change in bioluminescence of *Vibrio fischeri* bacteria.

2. Materials and methods

2.1. Reagents

Tetracaine hydrochloride (>99% purity), oxalic acid dihydrate (99% purity) and fumaric acid (99% purity) were supplied by Sigma-Aldrich. Na_2SO_4, NaCl, NH_4Cl, K_2SO_4 and $NaNO_3$, used as background electrolytes, were of analytical grade from Panreac, Probus and Prolabo. Synthetic and analytical solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm at 25 °C. The initial pH was adjusted to 3.0 with analytical grade H_2SO_4 for sulfate solutions and analytical grade $HClO_4$ for the other water matrices, both of them supplied by Merck. All the other reagents and solvents needed for analysis were of analytical or HPLC grade purchased from Panreac and Merck.

2.2. Aqueous matrices

The electrolytic experiments were performed with three different aqueous matrices:

(i) A real wastewater was obtained from the secondary effluent of a WWTP located in Gavà-Viladecans (Barcelona, Spain) that treats ca. 50,000 m^3 d^{-1} of urban and selected industrial wastewater. The samples were preserved in a refrigerator at 4 °C before use. Its main characteristics were: pH 8.1, specific conductivity of 1.73 mS cm^{-1}, 12.2 mg L^{-1} of total organic carbon (TOC); cations concentration: 212 mg L^{-1} Na^+,