



Electrochemical study of carboxylic acids with Nb-supported boron doped diamond anode. Part 1: Potentiodynamic measurements and bulk oxidations



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ABSTRACT

The present study was motivated by the reports that promote the use of boron doped diamond (BDD) anode for electrochemical oxidation (EO) of different organic compounds. EO approach on BDD proceeds via electrochemical generation (by water discharge) of hydroxyl radicals and their subsequent reactions. Although the discussion about the degradation of different organic compounds on Si-supported BDD anodes has been already reported; no attempts have been published about the electrochemical degradation of carboxylic acids (acetic, formic and oxalic acids) on Nb/BDD electrode. The interest to elucidate the mechanisms for removing carboxylic acids from water, as a model reaction, contributes to the understanding of more complex reactions involving organic pollutants. In this work, the results clearly demonstrate that organic molecules can be degraded in different way and level by using 0.25 M HClO₄ as supporting electrolyte due to the oxidants electrochemically generated as well as the interaction of carboxylic acid with BDD surface by adsorbed/non-adsorbed intermediates. The direct evidence for these processes was found during potentiodynamic measurements and bulk electrolysis of carboxylic acids resulting in different evolution of organic matter removals. The strong oxidants as well as the oxidation potentials were analyzed by spin trapping and voltammetry kinetic studies, respectively.

1. Introduction

Currently, there are several processes that can be carried out for treating wastewaters with organic pollutants; however, long treatment times (up to days) are required or generation of residues is attained [1–3]. Therefore, the development of other advanced technologies has been stimulated. Among the most potent methods to destroy toxic and/or biorefractory organic pollutants, the electrochemical advanced oxidation processes (EAOPs) have received recently great attention in the last years [4–7]. EAOPs are based on the in situ electrogeneration of reactive oxygen species (ROS) and other oxidant species that can mineralize most organics to CO₂, water and inorganic ions [8,9].

The most common EAOP is electrochemical oxidation (EO), also known as anodic oxidation (AO), in which organic pollutants can be directly oxidized at the surface of the anode (M) and/or much more rapidly destroyed by physisorbed hydroxyl radical M(OH) formed from water oxidation via Reaction (1) at high applied current [2,10–14]:



When active anodes such as Pt, IrO₂ and RuO₂ are used, M(OH) is

converted into a less oxidizing species such as chemisorbed MO that oxidizes organics mainly to carboxylic acids, whereas the alternative use of a high oxidation power material like boron-doped diamond (BDD) that favors the electrochemical incineration of organics at the anode vicinity by the great production of BDD(OH) [2,15], being currently considered the best anode for EO treatment [2,4,15,16].

The use of BDD electrodes for wastewater treatment has been mostly studied at Si-supported devices [2,4,16–18], however, BDD thin films deposited on Ta, Nb and W by chemical vapor deposition has been currently proposed because these are not fragile and with good electrical conductivity [1–4,11,15–18] than presented by Si/BDD.

In the case of the applicability of Nb/BDD anodes for oxidation of organic compounds, it has been successfully used for removing pharmaceuticals [19,20], dyes [21], petroleum [22], pesticides and herbicides [23]. However, no reports about the study of EO of carboxylic acids have been published yet.

Some carboxylic acids represent a class of chemical compounds that are extensively and inevitably used in industry, and these can be found in the environment as pollutants. These compounds are common intermediates or final products of oxidation in various AOPs, since

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they are more persistent than the initial contaminants. In the case of EO, oxalic, acetic and formic acids are also considered as the final intermediates of many pollutants [24–26], and consequently, these are often used as “model molecules” to investigate the electrocatalytic properties of several anode materials in the EO and, moreover, the study of the oxidation of these compounds is useful to determine the mechanisms of the reaction [27,28]. Therefore, this paper presents the results obtained for the EO of carboxylic acids (acetic acid (AA), oxalic acid (OA) and formic acid (FA)) by using Nb/BDD electrodes in HClO₄ medium. Firstly, potentiodynamic measurements were performed in order to understand the electrochemical kinetic mechanisms followed at BDD surface when carboxylic acids are present in solution. After that, the production of hydroxyl radicals and hydrogen peroxide was studied to better clarify the role of generated oxidizing agents. Subsequently, the effect of the applied current density (*j*) on the performance of each treatment was examined and the decay of the dissolved organic load for the carboxylic acids was followed by chemical oxygen demand, while the mineralization efficacy was determined by the total organic carbon. A plausible reaction sequence for acetic, oxalic and formic acids mineralization is finally proposed.

2. Experimental

2.1. Materials

The carboxylic acids (AA, OA and FA) were purchased from J.T. Baker and used without further purification. Distilled water was used in all solutions and experiments. The synthetic solutions (FA 0.18 M, AA 0.18 M and OA 0.18 M) were prepared using 0.25 M HClO₄ as supporting electrolyte.

2.2. Electrochemical measurements

Linear polarization analyses were performed at room temperature (25 °C) with a Metrohm AUTOLAB potentiostat model PGSTAT302N. The three-electrode cell was constituted by a Ag/AgCl (KCl 3 M) as reference electrode, Pt wire as the counter electrode and BDD as working electrode with an exposed geometric area of 1 cm². Quasi-steady polarization curves were carried out at a scan rate of 10 mV s⁻¹ and with a 2.44 mV step potential, by using BDD working electrode in 0.25 M HClO₄ as supporting electrolyte as well as in a solution containing with AA, OA and FA, separately.

2.3. Electrochemical system

Bulk electrochemical oxidations were carried out in a single compartment undivided cell (batch mode) containing 0.5 L of solution under constant stirring and galvanostatic conditions with a MINIPA MPL-3305 M power supply. BDD film supported in niobium substrate was supplied by Metakem (Germany) and used as anode, while titanium was employed as cathode. All electrodes had a plate format with an geometric area of about 18 cm² and these were placed in parallel with an inter-electrode gap of 1.2 cm. Experiments were performed at 25 °C for studying the role of current density (*j*) by applying 30, 60, 90 and 120 mA cm⁻² during 240 min. The temperature of the electrolyte was controlled using a water thermostat.

2.4. Analytical methods

The chemical oxygen demand (COD) was determined according to the Standard Methods (5250D) [29] through the use of HANNA Instruments equipment, where the COD kits (HI93754B-25) were mixed with the samples, and after that, these were digested in the thermal reactor HI 839800. COD values were directly given by the photometer HI 83099. Hydroxyl radicals were detected by the bleaching of N,N-dimethyl-4-nitrosoaniline (RNO). The originally yellow solution was

decolorized through reaction between RNO and [•]OH, forming an adduct [30]. The bleaching of the 2 × 10⁻⁵ M RNO solution in 0.25 M HClO₄ was followed by spectrophotometry using an Analytik Jena Specord 210 Plus UV-Vis spectrophotometer in 350 nm. The spectrophotometric methodology using ammonium metavanadate proposed by Nogueira et al. [31] was used for detection and quantification of hydrogen peroxide formed in solution. Some parameters described by Oliveira et al. [32] were also used.

2.5. Efficiency parameters

The energy consumption of the each experiment was estimated and expressed in kWh m⁻³. It was used the average cell voltage during the electrolysis and this value used to estimate energy consumption by the expression reported in [1,3,4]:

$$\text{Energy consumption} = \frac{\Delta E_c \times I \times t}{1000} \times V_s \quad (2)$$

where *t* is the time of electrolysis (h); *E_c* (V) and *I* (A) are the average cell voltage and the electrolysis current, respectively; and *V_s* is the sample volume (m³). Total current efficiency (%TCE) for EO experiments of the carboxylic acids was estimated by using the initial and final COD values, following relationship reported in [1,3,4]:

$$\text{TCE}(\%) = FV \left(\frac{\text{COD}_0 - \text{COD}_f}{8I\Delta t} \right) \times 100 \quad (3)$$

where (COD)₀ and (COD)_{*t*} are the chemical oxygen demands (g dm⁻³) at times *t* = 0 (initial) and *f* (final), respectively; *I* is the current (A), *F* the Faraday constant (96,487 C mol⁻¹), *V* is the electrolyte volume (dm³), 8 is the oxygen equivalent mass (g eq.⁻¹) and *t* is the electrolysis time, allowing for a global determination of the overall efficiency of the process.

3. Results and discussion

3.1. Electro-generation of hydroxyl radicals and hydrogen peroxide

Hydroxyl radicals formed by water discharge at the Nb/BDD electrode (Eq. (4)) can be detected using UV-visible measurements.



The indirect technique for the detection of low concentrations of hydroxyl radicals is carried out by trapping with p-nitroso-dimethylaniline (RNO) to produce a more stable radical (spin adduct) [28,30]. The use of this particular spin trap is particularly advantageous because under these conditions of concentration the addition reaction occurs at a very high rate constant (1.3 × 10¹⁰ M⁻¹ s⁻¹) being very selective, however, the oxidation of RNO must be also considered under specific electrolytic conditions. Fig. 1 shows the adsorption spectrum of aqueous RNO solution (2 × 10⁻⁵ M) during galvanostatic electrolysis by applying 60 mA cm⁻² with Nb/BDD anode. A rapid decrease in optical density at 350 nm during electrolysis is attained. This result shows that there is accumulation of [•]OH radicals at the Nb/BDD anode surface. Similar behavior was achieved at all *j* values (30, 60, 90 and 120 mA cm⁻²), indicating that significant concentrations of [•]OH radicals are electrochemically generated in all experimental conditions, but their concentration depends on the *j* used (Fig. 2). In fact, higher *j* favors a more rapid disappear of adsorption spectrum of aqueous RNO solution, confirming the higher production of [•]OH radicals.

The evolution of the concentration of free hydroxyl radicals (deduced from the concentration of RNO adduct quantified by spectrophotometry) as a function of time for Nb/BDD electrolysis was also obtained (data not showed). This behavior shows that the amount of free hydroxyl radicals electro-generated at the Nb/BDD electrode surface depends on the *j*. These results are in agreement with data reported in Fig. 2 as well as the proposed model by Cominellis in

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