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The electrochemical mineralization of oxalic and oxamic acids using modified electrodes based on carbon nanotubes

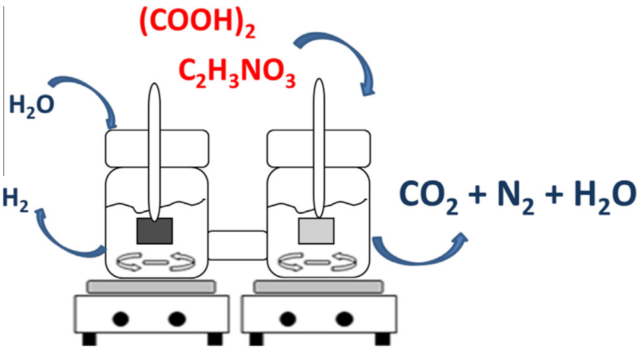
M. Ferreira [a], M.F. Pinto [a], O.S.G.P. Soares [b], M.F.R. Pereira [b], J.J.M. Órfão [b], J.L. Figueiredo [b], I.C. Neves [a], A.M. Fonseca [a], P. Parpot [a,*]

[a] *Centro de Química, Departamento de Química, Escola de Ciências, Universidade do Minho, Campus Gualtar, 4710-057 Braga, Portugal*
[b] *Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

HIGHLIGHTS

- Modified electrodes based on carbon nanotubes for the oxidation of recalcitrant compounds.
- Monometallic (Pd and Pt) and bimetallic (Ru–Cu) catalysts.
- The mineralization of oxalic and oxamic acids in wastewaters using electrochemical methods.
- Energy consumption per mass of oxalic and oxamic acids.

GRAPHICAL ABSTRACT



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ABSTRACT

Constant current and constant potential electrolyses of oxalic and oxamic acids were carried out on multiwalled carbon nanotubes (CNT) and on monometallic (Pd and Pt) and bimetallic (Ru–Cu) catalysts supported on multiwalled carbon nanotubes. Both carboxylic acids were mineralized with high conversions via hypochlorite ion produced in situ, in 0.10 M NaCl medium. Highest current efficiency, corresponding to 97%, and highest reaction rate constant for oxalic acid mineralization were obtained for the Ru–Cu/CNT modified electrode, in 0.10 M NaCl medium. The mineralization of oxamic acid was achieved with a faradic yield of 96% and an energy consumption of 14.6 kWh (kg of pollutant)$^{-1}$in the same medium. The conversion values obtained for the oxidation of oxalic acid in 0.50 M NaOH medium, on Pt/CNT, Pd/CNT and Ru–Cu/CNT modified electrodes, were respectively 42%, 60% and 85%. In this last medium, 88% of the initial oxamic acid (15.8 mM) was transformed to carbonate ion and nitrogen at Pt/CNT modified anode.

1. Introduction

Improper discharge of wastewater containing toxic organic compounds presents a major threat to the environment and must be prevented. In this context, monitoring and elimination of the organic pollutants in wastewater is of high importance [1]. New emerging technologies have been recently proposed for the degradation of these organic pollutants [2,3].

Oxalic and oxamic acids are often the main and final intermediates for the catalytic and electrochemical oxidation of many organic compounds. The electrochemical oxidation of oxalic acid on metals, metal oxide and boron doped diamond (BDD) was widely investigated [4–11], but, to our knowledge there are very few studies on the electro-oxidation of this compound on catalysts based on carbon nanotubes [12]. On the other hand the mineralization of oxamic acid which is another recalcitrant compound has been sub-

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* Corresponding author.
E-mail address: parpot@quimica.uminho.pt (P. Parpot).

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ject of very few scientific works [13,14]. There is also a problem due to the lack of efficiency concerning the direct anodic mineralization of these compounds without the use of mediators like the hypochlorite ion. Another limitation is related to the energy consumption issue. The electrocatalysts based on CNT may help to surpass these existing barriers contributing to the mineralization of these recalcitrant compounds with lower energy consumption" There has been increasing interest in multiwalled carbon nanotubes (CNTs) as heterogeneous catalyst supports [15,16] owing to their high surface area and high electrical conductivity. These peculiar characteristics qualify CNTs as adequate electrocatalysts or as catalyst support materials for the oxidative degradation of organic pollutants in wastewater [17–19]. The growing interest in the use of nanomaterials in electrochemistry is related to their small size and good electrochemical properties [20–23]. The use of CNT as electrode provides an enhancement of electrochemical properties comparing to other electrode materials [12,24,25].

The importance of the electrochemical technologies in wastewater treatment, due to their versatility, high efficiency, easy control, environment compatibility and cost effectiveness, became more relevant in the last decades considering the increasing concern related to the drinking water supply and the rigorous environmental guidelines concerning wastewater discharge [26–31]. Platinum, palladium and ruthenium are well known as active and stable electrocatalysts for small organic compounds oxidation. An enhancement of the activity for organic pollutants oxidation may be expected by the use of bimetallic catalyst considering the synergetic effect.

In the present work, the anodic mineralization of oxalic and oxamic acids was studied at different modified anodic materials such as CNT, Pt/CNT, Pd/CNT and Ru–Cu/CNT having in mind the development of a simple electrochemical route without the addition of strong oxidizing agents and without coupling methods such as photo-electrochemical techniques.

2. Experimental

2.1. Chemicals and reagents

A commercial multiwalled carbon nanotube sample Nanocyl-3100 (sample CNT) was obtained from Nanocyl S.A. The metal precursors (H_2PtCl_6, $PdCl_2$, $RuCl_3$ and $Cu(NO_3)_2$) required for the preparation of M/CNT were purchased from Alfa Aeser and from Riedl-Haden in the case of copper. The supporting electrolytes were prepared with ultrapure water (18 MΩ cm, Barnsted E-pure system) and sodium chloride (Panreac, 99.5%), sodium carbonate anhydrous (Panreac, 99.8%) and sodium bicarbonate (Panreac, 98%). Oxalic and oxamic acids were reagent grade and purchased from Sigma–Aldrich. The aqueous solutions of HPLC standards (glyoxylic, glycolic and formic acids) were prepared from Aldrich commercial reagents. The calibration mixtures of gases were purchased from Praxair. Toray Carbon paper was obtained from Quintech.

2.2. Preparation of carbon nanotubes supported metal catalysts

The active metals were supported on sample CNT. The monometallic (Pd and Pt) samples were prepared by the incipient wetness method and the bimetallic (Ru–Cu) sample by co-impregnation with aqueous solutions of the corresponding metal precursors. After impregnation, the samples were dried at 100 °C for 24 h. The samples were heat treated under nitrogen flow at 200 °C for 1 h and reduced at 200 °C under hydrogen flow for 3 h, the exceptions are the catalysts with Ru which were heat treated and reduced at 250 °C. A nitrogen flow was used during cooling till room temperature. The contents of noble metal and copper were always 1 wt%. The samples were characterized using different techniques: temperature programmed reduction (TPR), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), as determined in a previous work [32,33].

2.3. Preparation of carbon nanotubes and metals–carbon nanotubes modified electrodes

The preparation of the modified electrodes was performed on a previous established procedure described in our previous work [14,34]. For the preparation of modified electrodes, 2 mg of CNT or M-CNT were mixed in a Nafion/water solution (120 μL Nafion/120 μL ultra-pure water). The resulting suspensions were homogenized using an ultrasound bath and deposited on a Toray Carbon paper with an area of $2 \times 2\ \text{cm}^2$. Finally the Toray Carbon paper was glued to the platinum electrode using conductive carbon cement and dried at room temperature during 24 h. The cleanness of the surfaces was tested prior each experiment by recording voltammograms in the supporting electrolyte alone.

2.4. Electrochemical setup

The voltammetric study was performed in a thermostated three-electrode glass cell and a two-compartment glass cell separated by an ion exchange membrane (Nafion 117). A tap was introduced into the Luggin bridge in order to establish the contact between the reference and the electrolyte solutions without any contamination of the later by the ions of the reference electrode solution. A saturated calomel electrode and a platinum foil (99.95%) were used as reference and counter electrode, respectively. Before each experiment, the solutions were deaerated with ultra-pure nitrogen (U Quality from Air Liquide) and the nitrogen stream was maintained over the solution during the measurements. The electrochemical instrumentation consists of a potentiostat/galvanostat from Amel Instruments coupled to a microcomputer by an AD/DA converter. The Labview software (National Instruments) and a PCI-MIO-16E-4 I/O module were used for generating and applying the potential program as well as acquiring data, such as current intensities.

2.5. Product analysis

The quantitative analysis of reaction products was performed using two chromatographic set-ups: a high performance liquid chromatography (HPLC) using an isocratic pump and a double on line detection including an UV–Vis detector and refractometer, and an ionic chromatography (IC, Dionex) using a conductivity detector. The product partition was carried out in ion exchange columns: Aminex HPX-87 H from Biorad for HPLC and AS11-HC from Dionex for IC. The gaseous products of the reactions were detected by a Dual cell microvolume thermal conductivity detector (Vici, Valco Instruments Co. Inc.). The product separation, in this case, was carried out by a packed GC column: chromosorb 104 (1.8 m × 1/8 in. × 2.1 mm).

2.6. Calculation of specific energetic parameters

Important specific energetic parameters such as energy consumption per volume of treated effluent (kWh m^{-3}), and per mass of pollutant ($\text{kWh (kg pollutant)}^{-1}$), were calculated using the following equations:

$$\text{Energy consumption } (\text{kW h m}^{-3}) = \frac{IVt}{V_s}$$

$$\text{Energy consumption } (\text{kWh(kg pollutant)}^{-1}) = \frac{IVt}{\Delta m\ (\text{pollutant})}$$