



Electrocatalysis in the oxidation of acetaminophen with an electrochemically activated glassy carbon electrode



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ABSTRACT

A simple approach such as the anodic activation of a glassy carbon electrode (GCE) can be used successfully to improve the detection of acetaminophen at very low concentration levels. In this work, we observed that the exposure of a GCE to a high potential (2 V vs Ag/AgCl) for a limited time period (60 s) in the presence of 50 mM borate/phosphate buffer (pH 9) provides a strongly electro-activated surface. The activated surface was characterized by means of several techniques (electrochemistry, EIS, SEM, AFM, μ -Raman, XPS). It appeared that the anodization procedure gave rise to a strong oxygen-based functionalization that did not affect morphologically the electrode surface. The mechanism of interaction of the activated electrode with the analyte was studied by electrochemical methods, then the electrode was applied to the electroanalysis of acetaminophen by differential pulse voltammetry. In this application, the method showed promising analytical performance, detecting nanomolar traces of acetaminophen.

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1. Introduction

The occurrence of pharmaceuticals in the environment and, in particular, in surface waters is a problem of increasing concern [1]. Excretion by humans of non- or partially metabolized molecules, incorrect disposal of expired medicines and use of antibiotics for cattle breeding are the main routes of pharmaceuticals to the environment. The compounds identified in various environmental compartments belong to several classes of human drugs including analgesics, antibiotics, beta-blockers, anticonvulsants, lipid regulators, contrast agents, anti-cancer agents and hormones [2]. They may be toxic to fish and aquatic invertebrates [3], have endocrine disruption effects [4] and favor the occurrence of resistance in bacteria [5]. The purification processes of wastewaters, such as those based on activated sludge, are often unable to remove these pollutants efficiently, because wastewater treatment plants (WWTPs) were not originally designed to eliminate xenobiotics. Analgesics, anti-inflammatories and beta-blockers are among the most resistant pharmaceuticals to the WWTP treatment (30–40%

of removal efficiency), while the removal of antibiotics can reach 50% [6].

The monitoring of the environmental contamination by pharmaceuticals is worthwhile for several reasons, which include the reliable assessment of risks for the ecosystem and, through the food chain, for humans, as well as the evaluation and maintenance of the water resource quality.

Several research papers report on the application of electrochemical methods for the quantification of drugs, and in the last ten years the use of carbon electrodes in this field has considerably increased [7]. Acetaminophen (AP) is one of the most extensively employed painkiller drugs in the world and, for this reason, its occurrence in the environment is reported at concentrations of up to 10 μ g/L [8]. Several electrochemical methodologies have been used for AP determination: most of them involve hybrid or composite glassy carbon electrodes (GCE) functionalized with gold nanoparticles, multi-walled carbon nanotubes, fullerenes, boron-doped diamonds etc [9–13]. Recently, Sadikoglu and coworkers [14] presented a simple approach for an easy determination of AP with a bare GCE, claiming submicromolar detection. In this work, we studied and optimized a method for the AP determination at lower concentration using an electrochemically treated GCE, exploiting an anodization procedure. We report here in detail the study of the electrode surface activation process and the

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electrocatalytic oxidation mechanism by electrochemistry, electrochemical impedance spectroscopy (EIS), Raman spectroscopy, electron microscopy, and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Reagents

Chemicals were purchased from Sigma Aldrich. Ferrocene and $(C_4H_9)_4NPF_6$ were used, without further treatment, for the electrode area measurement, and 1,1'-ferrocenedimethanol was used as probe for electrochemical characterization. Acetonitrile was distilled over $CaCl_2$ under N_2 atmosphere prior to the measurements. Deionized water ($0.1 M\Omega cm$) from a Millipore-RIOs 3 system was used to prepare all the solutions. The stock solution of acetaminophen (AP) was prepared in deionized water every day. The borate-phosphate buffer (hereinafter, BPB solution) was prepared by dissolving K_2HPO_4 and $Na_2B_4O_7$ salts to a final concentration of 4.5 and $0.5 \cdot 10^{-2} M$, respectively, and adjusting the pH to 9.0 ± 0.1 with H_3PO_4 80%.

2.2. Instrumentation

The electrochemical measurements and treatments were performed with a Bio-Logic SP150 potentiostat. A conventional

three-electrode system in a thermostated cell (NESLAB RTE-101 thermostat) was used. Electrochemically activated GCE ($3 \cdot 10^{-3} m$ diameter, from ALS) was used as working electrode; a platinum wire was used as counter and Ag/AgCl, 3 M KCl (Metrohm, Model 6.0733.100) as reference electrodes, except where otherwise stated. A magnetic stirrer provided the convective transport during the amperometric and differential pulse voltammetric measurements. Electrochemical Impedance Spectroscopy (EIS) experiments were performed using the built-in frequency response analyzer function of the same potentiostat.

Rotation Disk Electrode linear scan voltammetry (RDE-LSV) experiments were performed on a Eco Chemie Autolab PGSTAT 10 potentiostat with a 663 VA Stand, GCE ($2 \cdot 10^{-3} m$ diameter, Metrohm) was used as working electrode; a GCE rod (Metrohm) was used as counter and Ag/AgCl, 3 M KCl (Metrohm) as reference electrodes. The potential range employed was between 0.1 and 0.8 V, the working electrode was rotated at rates ranging between 500 and 3000 rpm.

The pH was measured with a combined glass-membrane electrode controlled by a XS pH6 pH-meter (CRISON).

Scanning electron microscope (SEM) images were acquired with a Quanta™ 3D FEG DualBeam™ electron microscope, and Raman spectra were obtained with a Thermo Scientific DXR Raman microscope. The XPS spectra were taken with a PHI 5000 VERSA PROBE, Physical Electronics X-ray photoelectron spectrometer,

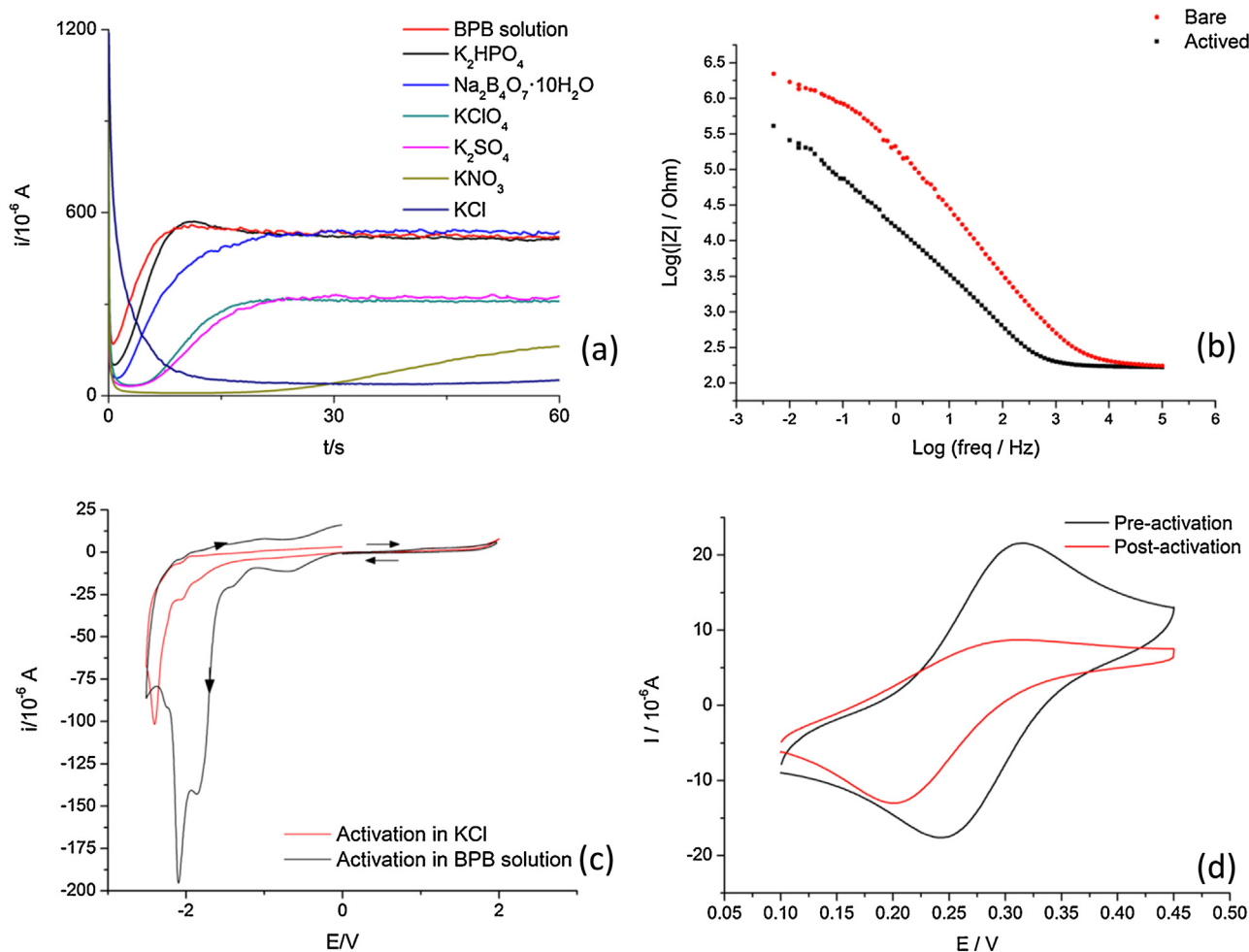


Fig. 1. (a) Chronoamperometric curves of the GCE in different electrolytes ($5 \cdot 10^{-2} M$, pH 9); (b) Bode plots obtained prior and after the activation ($1 \cdot 10^5$ to $2 \cdot 10^{-2} Hz$, sinusoidal amplitude $7 \cdot 10^{-3} V$ RMS) for $2 \cdot 10^{-5} M$ AP in BPB $5 \cdot 10^{-2} M$, pH 9; (c) CV of blank acetonitrile after the activation of GCE in KCl 50 mM, pH 9 or BPB 50 mM, pH 9 (CH_3CN , 0.1 M $(C_4H_9)_4NPF_6$, $5 \cdot 10^{-2} V/s$); (d) CV of $1 \cdot 10^{-3} M$ 1,1'-ferrocenedimethanol in 0.1 M BPB, pH 9, before and after activation of the electrode.

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