



## Mercury nanodroplets supported at biochar for electrochemical determination of zinc ions using a carbon paste electrode



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### ABSTRACT

In the present work a modified carbon paste electrode (MCPE) was prepared using mercury ions ( $\text{Hg}^{2+}$ ) supported at a biochar (bio-charcoal) surface obtained from castor oil cake and used for electrode preparation. The proposed electrode was evaluated for preconcentration and determination of zinc(II) ions present in commercial samples (collyrium and ointment) by differential pulse anodic stripping voltammetry (DPASV). The procedure is based on spontaneous interactions between the highly functionalized biochar surface and zinc(II) ions followed by reduction of ions into mercury droplets which promote a high localized zinc concentration and improvement on the stripping anodic current obtained under differential pulse voltammetric conditions. SEM images revealed dimensions of mercury droplets in the range from 16 nm to 38 nm. Parameters involved in the mercury incorporation, preconcentration of zinc ions and voltammetric stripping step were studied and optimized. Using the best set of experimental conditions a linear response for zinc(II) ions was observed for concentration range (LDR) of  $5.0 \times 10^{-7}$  to  $3.0 \times 10^{-5} \text{ mol L}^{-1}$  with limits of detection (LOD) and quantification (LOQ) of  $1.7 \times 10^{-7} \text{ mol L}^{-1}$  and  $5.8 \times 10^{-7} \text{ mol L}^{-1}$ , respectively, and sensibility of  $5.2 \mu\text{A L } \mu\text{mol}^{-1}$ . The proposed methodology was applied for quantification of zinc-containing commercial samples, whose results were compared with those given by inductively coupled plasma optical emission spectroscopy (ICP-OES) and complexometric titration. Results produced by the methods are in agreement at a 95% of confidence level.

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### 1. Introduction

The polarographic technique, together with the mercury drop electrode itself, is widespread and has been used for decades [1]. This electrode combined with stripping procedures presents numerous operational advantages over other electrochemical conventional methods including low background current, accuracy, high signal/noise ratio and extensive working range in the cathodic region [2], high sensitivity and low limits of detection and quantification [3]. However, the use of mercury drop electrodes presents some limitations, mainly reported with practicality of the system and environmental aspects, due to the known potential toxicity of mercury.

In order to use the advantages of electrochemical characteristics of the mercury and diminish its drawbacks cited above, the

development of electrodes based on films and other forms of mercury became highly desirable, since these devices employ a considerably lower quantity of mercury. A decrease in the amount of mercury on the electrode surface also results in an increased sensitivity when stripping techniques have been used, because the signal generated by the species of interest is directly proportional to the analyte concentration into mercury layer [4]. In this sense, mercury films (prepared ex-situ or in-situ from solutions containing mercuric ions) [5] and solid amalgam (mainly formed with silver) [6] have been used to improve the analytical performance of these devices. Song et al. [7] developed a printed carbon electrode modified with mercury nanodroplets supported by an array of multi-walled carbon nanotubes/chitosan for simultaneous determination of cadmium(II), lead(II) and copper (II). Using a similar approach, several different materials has been used to adsorb metal ions, such as mercury(II), and used as support for chemically modified electrodes (CME).

An interesting and alternative material is biochar (biomass + charcoal), a carbonaceous material richly functionalized

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originated from burning of biomass such as wood or leaves, in low temperature and low amount of oxygen [8,9]. This material has called attention for several applications but it is poorly explored for development of electrochemical sensors.

Due to highly functionalized surface that contains peripheral groups able to chelate metal ions [10,11], as well as a high adsorption ability for numerous ionic species such as mercuric ions. Thus, we propose in this work the use of biochar as a promising material for the development of a modified electrode with supported mercury droplets for preconcentration and determination of zinc present in pharmaceutical formulations.

Zinc is a micronutrient of fundamental importance in biological processes; they participate in protein structures and have regulatory effects [12] but high zinc concentrations can be harmful for human health [13]. The electrochemical determination of Zn is widespread and, due to the fact that its reduction occurs at very negative potentials, mercury or similar electrodes are usually employed [14–16]. Given the great importance of zinc ions in living organisms and its toxicity potential, its determination and quantification becomes of fundamental importance, especially in the view of the quality control of products containing this metal.

## 2. Experimental

### 2.1. Materials and Chemicals

Biochar was obtained as described by Suguihiro et al. [17]. Powdered graphite, mineral oil and standard  $1000 \text{ mg L}^{-1} \text{ Zn}^{2+}$  solution were acquired from Fisher Scientific, Sigma Aldrich and Merck, respectively. Analytical grade glacial acetic acid (Isifar), anhydrous sodium acetate (J.T. Baker) and mercuric chloride (LabSynth) were used as received. All solutions were prepared with deionized water obtained with a Millipore Milli-Q system.

### 2.2. Electrode fabrication

The carbon pastes employed in this work consisted of a conductive phase (powdered graphite–Fisher-Scientific CAS 7782–42–5, Fair Lawn, NJ, USA), an agglutinating phase (mineral oil–Sigma–Aldrich, St. Louis, MO, USA) and the modifier (biochar) in 75–X%, 25% and X% (w/w) ratios respectively, with X = 5, 10, 15, 25, 30 and 50%. Carbon pastes were prepared by simple mixing and homogenization of the components.

The electrode was assembled by compacting of carbon paste into a plastic cylinder with an internal diameter of 3 mm and a copper wire (electrical connection) with similar thickness to plastic support.

### 2.3. Characterization Measurements

The presence of functional groups on biochar surface was characterized by FTIR using a Bomem MB100 spectrophotometer in the range of  $4000$  to  $400 \text{ cm}^{-1}$ , with a spectral resolution of  $4 \text{ cm}^{-1}$ . The biochar particle and pore sizes were determined by the BET method in atmosphere  $\text{N}_2$  on a Quantachrome NOVA 1200 equipment, and for data acquisition an Autosorb software for Windows® Version 1.24 was employed.

Electrode surfaces morphologies were analyzed by scanning electron microscopy (SEM) for the unmodified carbon paste electrode (CPE) and the carbon paste electrode modified with biochar (CPME) in the absence and presence of mercuric and zinc ions. SEM/EDS spectra were also registered to assess the chemical composition of the electrode surfaces. The SEM analysis was performed on a JSM–6360LV Scanning Electron Microscope from

the Jeol, and the SEM/EDS analysis on a 6714 A–15US–SN Energy Dispersion Spectroscopy from the Thermo Noran.

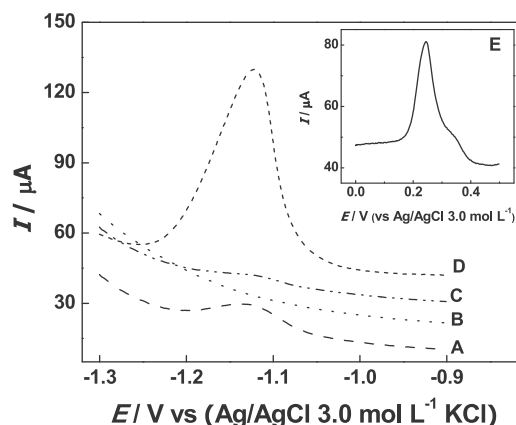
### 2.4. Voltammetric analysis

The voltammetric measurements employed a 10.0 mL voltammetric cell with the conventional three-electrode configuration, in which the working, auxiliary and reference electrodes were CPE unmodified (and MCPE), Pt wire and Ag/AgCl in  $3.0 \text{ mol L}^{-1} \text{ KCl}$ , respectively. The measurements were performed on a type III  $\mu\text{AutoLab}$  potentiostat/galvanostat, with data acquisition and experimental control by the GPES software version 4.9.

The general analytical procedure has consisted of three steps: (1) Preconcentration of  $\text{Hg}^{2+}$  ions on the working electrode surface (open circuit) by controlled stirring for two minutes in  $0.1 \text{ mol L}^{-1}$  acetate buffer solution (pH 6) containing  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  mercuric ions; (2) immersion of the electrode (containing  $\text{Hg}^{2+}$  ions previously adsorbed) in deionized water to remove not adsorbed mercuric ions; (3) Voltammetric analysis in the presence of  $\text{Zn}^{2+}$  by differential pulse anodic stripping voltammetry (DPASV). For these measurements, a step of preconcentration and reduction of  $\text{Zn}^{2+}$  was necessary, with the scanning potential being subsequently held from  $-1.3 \text{ V}$  to  $0.5 \text{ V}$  in  $0.1 \text{ mol L}^{-1}$  acetate buffer solution (pH 5).

### 2.5. Sample Analysis and Recovery

To validate the proposed method, the determination of zinc(II) ions was performed for two different samples: collyrium (Legrand, Hortolândia, SP, Brazil) and ointment (Hipoglo's, São Paulo, SP, Brazil). The sample of collyrium did not require any pretreatment. However, the ointment which is a more complex matrix, a sample pretreatment was necessary before the measurements steps. The pretreatment was carried out using the method reported by Benamor et al. [18], wherein a quantity of the sample is transferred to a separating funnel of 100 mL and treated with 10 mL of diethyl ether and 10 mL of nitric acid ( $0.5 \text{ mol L}^{-1}$ ) to dissolve the organic compounds and the zinc oxide. The mixture was stirred for 10 minutes, forming two phases and, subsequently, separated. Zinc (II) ions were contained in the aqueous phase.



**Fig. 1.** Differential pulse stripping voltammetric responses obtained in acetate buffer pH 5.0 for the following: (A) unmodified CPE in the presence of zinc(II); (B) MCPE with 20% (w/w) biochar before the preconcentration step of mercury in the absence of zinc(II); (C) MCPE with 20% (w/w) biochar before the preconcentration step of mercury in the presence of zinc(II); (D) MCPE with 20% (w/w) biochar after the preconcentration step of mercury in the presence of zinc(II); (E) Same experimental conditions of (D) but using an extended potential sweep until 0.5 V. Deposition potential:  $-1.3 \text{ V}$ ; deposition time: 60 s; scan rate:  $10 \text{ mV s}^{-1}$ ; pulse amplitude: 100 mV; pulse width: 200 ms. The zinc(II) ions concentration was  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ .

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