



Evaluation of antimony microparticles supported on biochar for application in the voltammetric determination of paraquat



Ava Gevaerd^a, Paulo R. de Oliveira^a, Antonio S. Mangrich^{b,c}, Márcio F. Bergamini^a, Luiz H. Marcolino-Junior^{a,*}

^a Laboratório de Sensores Eletroquímicos (LabSensE), Departamento de Química, Universidade Federal do Paraná (UFPR), CP 19081, CEP, 81531-990 Curitiba, PR, Brazil

^b Laboratório de Química de Húmus e Fertilizantes, Departamento de Química, Universidade Federal do Paraná (UFPR), CP 19081, CEP, 81531-990 Curitiba, PR, Brazil

^c Instituto Nacional de Ciência e Tecnologia de Energia e Ambiente (INCT/CNPq), Brazil

ARTICLE INFO

Article history:

Received 28 August 2015

Received in revised form 14 December 2015

Accepted 7 January 2016

Available online 11 January 2016

Keywords:

Carbon paste electrode

Antimony microparticles

Biochar

Paraquat

ABSTRACT

This work describes the construction and application of carbon paste electrodes modified with biochar and antimony microparticles (SbBCPE) for voltammetric determination of paraquat using a simple and sensitive procedure based on voltammetric stripping analysis. Some parameters such as amount of biochar and antimony used in the composition of the carbon paste and instrumental parameters were examined in detail. Under optimized conditions, an analytical curve was obtained for paraquat determination employing SbBCPE, which showed a linear response ranging from 0.2 to 2.9 $\mu\text{mol L}^{-1}$, with limit of detection and quantification of 34 nmol L^{-1} and 113 nmol L^{-1} , respectively, after paraquat pre-concentration of 120 s. The repeatability study presented a RSD = 2.0% for 10 consecutive measurements using the same electrode surface and the reproducibility study showed a RSD = 2.7% for measurements with 10 different electrode surfaces. The proposed sensor was successfully applied for paraquat determination in tap water and citric fruit juice spiked samples and good recoveries were obtained without any sample pre-treatment, showing its promising analytical performance.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Mercury electrodes as a drop or a film prepared at surface of an inert substrate have been widely used in the last five decades for voltammetric (polarographic) determination of inorganic and organic species due its special characteristics like high cathodic hydrogen overpotential and its ability to dissolve many metals, aiding in the pre-concentration process [1–4]. However, in the last years, due to the growth of green chemistry concepts and knowing problems related to mercury toxicity, researchers have been searching new materials for electroanalytical application with the same properties of mercury, but with lower toxicity. These electrodes are commonly called “mercury free electrodes” [5–7].

Bismuth electrodes are the most popular mercury free electrodes on literature [8] and they have been used since 2000, with reported work by Wang et al. [9]. Another possibility of mercury free electrodes are those based on antimony, as shown by Hocevar et al. in 2007, used as stripping voltammetric sensor for lead and cadmium determination [10]. Antimony electrodes show interesting characteristics for electroanalysis as significant overpotential to hydrogen evolution, high sensitivity, well defined stripping peaks and low stripping current signal for itself. Its use has been reported in literature mainly for measuring trace heavy metals and other species of interest that are associated with environmental monitoring [9–14]. These electrodes are frequently

prepared at carbon surface electrodes such as glassy carbon or graphite paste [11,15–18]. In both cases, antimony material is not supported by carbon structures which can affect the lifetime and reproducibility of the electrode surface.

Biochar is a carbon-rich material obtained by pyrolysis of biomass achieved from different sources in the absence of oxygen. It has been applied on soil correction and removal of organic and inorganic contaminants, mainly due to its highly functionalized surface [19,20]. In our research group, we have been explored the use of biochar as modifier electrode for development of electrochemical sensors for lead and cadmium ion determination in wastewaters [21] and copper ions in spirit drinks [22] with excellent analytical performance (sensitivity and robustness). Most recently, we proposed the use of biochar as support material for preparation of mercury and bismuth nanostructures that were applied for determination of zinc ions in pharmaceutical formulations [23] and lead ions in ceramic dishes [24], respectively. However, there are no reports of biochar application for antimony incorporation and/or organic species determination.

Paraquat (1,1'-dimethyl-4,4'-bipyridinium chloride, PQ^{2+}) is a bipyridinium contact herbicide commonly used for weed combat in many crops. The use of such chemical agent is permitted when used according to specifications described in legislation, since its wastes are highly persistent and highly toxic to the environment and human health [25,26]. Several procedures exploring chromatography [26,27] and electrochemical methods [26–28] have been reported for PQ^{2+} determination.

* Corresponding author.

E-mail address: luiz1berto@ufpr.br (L.H. Marcolino-Junior).

In this work we described for the first time, the construction of a carbon paste electrode modified with biochar which was used as support for growth of antimony microparticles. The synergic effect between biochar and antimony was employed for a sensitive paraquat determination using square wave adsorptive stripping voltammetry (SWAdSV).

2. Experimental

2.1. Material and reagents

All chemicals were from analytical reagent grade, used without further purification and prepared with purified water in a Millipore Milli-Q system. A $1.0 \text{ mol L}^{-1} \text{ PQ}^{2+}$ standard stock solution was prepared by dissolving the appropriate amount of paraquat dichloride hydrate (Aldrich 98%) in 10 mL of deionized water. Working PQ^{2+} standard solutions were daily prepared by serial dilutions of appropriate volumes of the standard stock solution with deionized water. Sb^{3+} ion solution ($8.76 \times 10^{-5} \text{ mol L}^{-1}$) was prepared by dissolving 20.0 mg of SbCl_3 (Sigma Aldrich) in 0.01 mol L^{-1} HCl. Acetate buffer solutions (0.1 mol L^{-1}) were made by mixing appropriated volumes of 0.5 mol L^{-1} sodium acetate (J. T. Barker) solution with 0.5 mol L^{-1} acetic acid (Merck) solution; the required pH was adjusted with a sodium hydroxide solution. Biochar from castor oil cake was obtained according previously reported by Suguihiro et al. [21]. Tap water and citric fruit juice samples were spiked with a known-amount of paraquat and evaluated in recovery studies.

2.2. Apparatus

Voltammetric measurements were performed in a $\mu\text{AUTOLAB}$ Type III (Metrohm) connected to a microcomputer controlled by software (NOVA 1.10) for data acquisition and instrumental control. All voltammetric measurements were carried out in a 30 mL glass cell with a three-electrode configuration employing a SbBCPE as the working electrode, platinum wire as counter electrode and Ag/AgCl (3.0 mol L^{-1} KCl) as reference electrode.

A Metrohm 780 pH meter was used to determine the pH of solutions. Scanning Electron Microscopy (SEM) images were obtained from a Quanta 450 ESEM FEG and Energy Dispersive X-ray Spectroscopy (EDS) analysis were performed from an EDAX microanalysis.

2.3. Preparation of SbBCPE

Carbon paste was prepared by carefully mixing a dispersed graphite powder (35–65% (w/w) – Aldrich), with biochar sample at a varying ratio (10–40% (w/w)) and subsequently added to mineral oil (25% (w/w)). The components were manually mixed in a mortar and pestle to obtain an appropriate homogenization. Carbon pastes modified with biochar were packed into an electrode body consisting of a plastic cylindrical tube (i.d. 2.5 mm) equipped with a copper rod serving as an

external electric contact. Appropriate packing was achieved by pressing the electrode surface against a filter paper.

After this first step, biochar modified carbon paste electrode (BCPE) was immersed in an $8.76 \times 10^{-5} \text{ mol L}^{-1} \text{ Sb}^{3+}$ solution in HCl 0.01 mol L^{-1} for different times (further evaluated – step 1 Fig. 1). Subsequently, the electrode was carefully washed with distilled water and taken to the electrochemical cell for reducing Sb^{3+} ions, in a potential range of 0.0 V to -1.1 V, under SWV conditions: frequency (f) = 100 Hz; square wave amplitude (Δ_{EP}) = 50 mV; step potential (Δ_{ES}) = 4 mV, obtaining the SbBCPE (step 2 – Fig. 1).

2.4. Paraquat voltammetric determination

Firstly, SbBCPE was immersed in a PQ^{2+} solution for a period of time in order to promote the analyte pre-concentration at the electrode surface. After this, the SbBCPE was carefully washed with distilled water, transferred to voltammetric cell and submitted to SWV cathodic sweep in a potential range of 0.0 V to -1.1 V and $f = 100$ Hz, $\Delta_{\text{EP}} = 50$ mV, $\Delta_{\text{ES}} = 4$ mV. After the measurement, a stage of physical removal of the Sb/ PQ^{2+} from the electrode surface was performed by polishing the electrode (step 3, 4 and 5 – Fig. 1).

The analytical validation of proposed method was performed by using the SbBCPE for determination of paraquat in spiked tap water and commercial juices (orange and lemon). Aliquots (10.0 mL) of samples were spiked with paraquat in order to reach a final concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$. Aliquots of 25, 50, 75 and 100 μL of each sample were diluted with 10.0 mL of acetate buffer 0.1 mol L^{-1} (pH = 6.0) and submitted to electroanalysis. The PQ^{2+} content in these samples was quantified using standard addition method.

3. Results and discussion

3.1. Antimony incorporation on BCPE

The modification of the electrode surface aims to give new features to the bare electrode and these new features are coming from and dependent on the employed modifier nature. In order to verify the improvement on the voltammetric response of the carbon paste electrode modified with biochar (BCPE) in comparison to unmodified electrode (CPE), both electrodes were submitted to cyclic voltammetry measurements in presence of antimony. Fig. 2A presents a typical electrochemical behavior observed for antimony ions using CPE and BCPE, the magnitude of the signal presented by BCPE was significantly higher when compared with CPE and/or SbCPE results. This improvement on the electrochemical response can be attributed to the increased interaction of antimony with the available functional groups present on biochar surface. These groups can be identified and quantified, in order to elucidate the mechanism involved in this best response. FTIR spectrum (Supplementary material, S1) has revealed the presence of bands relating to stretches of acid groups such as phenolic, lactonics

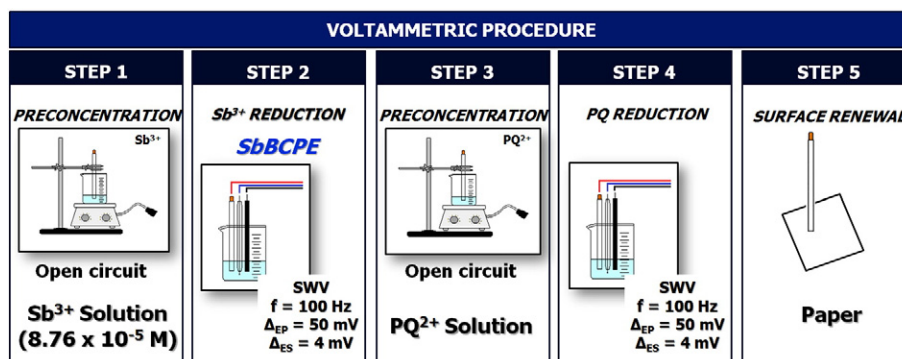


Fig. 1. Experimental steps for the proposed voltammetric procedure.

Download English Version:

<https://daneshyari.com/en/article/7867514>

Download Persian Version:

<https://daneshyari.com/article/7867514>

[Daneshyari.com](https://daneshyari.com)