



Copper hexacyanoferrate nanoparticles supported on biochar for amperometric determination of isoniazid



Paulo Roberto Oliveira^a, Cristiane Kalinke^a, Antonio Salvio Mangrich^{b, c},
Luiz Humberto Marcolino-Junior^a, Márcio F. Bergamini^{a, *}

^a Laboratório de Sensores Eletroquímicos (LabSense), Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81.531-980, Curitiba, PR, Brazil

^b Laboratório de Processos e Projetos Ambientais (LabPPAm), Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81.531-980, Curitiba, PR, Brazil

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

ARTICLE INFO

Article history:

Received 15 June 2018

Received in revised form

2 August 2018

Accepted 3 August 2018

Available online 8 August 2018

Keywords:

Copper hexacyanoferrate nanostructured

Biochar decorated

Amperometric sensor

Isoniazid determination

ABSTRACT

In the current article it is described the preparation of a carbon paste electrode modified with biochar (BM-CPE) decorated with nanostructured copper hexacyanoferrate (nCuHCF) and its application as amperometric sensor for isoniazid (INZ). Decoration of biochar was carried out using copper ions previously adsorbed at activated biochar surface, followed by nCuHCF electrochemical synthesis. Morphological investigation revealed the presence of nanostructures with sizes of 305 ± 42 nm randomly distributed on the electrode surface. All parameters that influenced the formation of nCuHCF structures on the electrode's surface were evaluated in order to obtain the best conditions for INZ determination. After optimization, the nCuHCF-BM-CPE promoted a significant improvement in the current signal for INZ oxidation at a potential peak of 140 mV, which is less positive compared to the unmodified electrode. A linear response between 1.0×10^{-6} and 1.0×10^{-5} mol L⁻¹ INZ ($R^2 = 0.992$) and Limits of Detection (LOD) and Quantification (LOQ) of 6.3×10^{-8} mol L⁻¹ and 2.1×10^{-7} mol L⁻¹, respectively, were obtained. The effect of concomitant species on the amperometric response was investigated and the proposed methodology was applied for INZ determination using synthetic human urine samples spiked with INZ (three concentration levels). Recovery values varied from 98.0 to 99.4% demonstrating an excellent analytical performance for INZ quantification.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Metallic hexacyanoferrates (MHCF) have been extensively applied in the development of several technologies, such as charge storage, corrosion protection, electrocatalysis, electrochromic devices and sensors [1,2]. Iron hexacyanoferrate (FeHCF), better known as Prussian Blue (PB), is one of the most used MHCFs for the development of electrochemical sensors [3,4]. Besides of PB, its analogous such as nickel hexacyanoferrate (NiHCF) [5], cobalt (CoHCF) [6], silver (AgHCF) [7], copper (CuHCF) [8,9], and also the hexacyanoferrates obtained from metallic alloys [10,11], have been extensively evaluated in the development of electrochemical sensors for different types of species.

The success in obtaining voltammetric sensors depends not only on the characteristics, but also on the synthesis and incorporation of the modifier at the electrode surface. In this way, the use of nanostructured MHCFs anchored on metallic or carbonaceous nanomaterials allows the preparation of composites with high stability that can be used in the development of electrochemical sensors with high analytical performance [12,13]. Deng et al. [14] described the synthesis of CoHCF nanoparticles upon graphene oxide/carbon nanotubes that were used in the determination of hydrazine. The functional groups present on carbon nanotubes surface act as specific sites for adsorption of cobalt (II) ions and posterior formation of CoHCF nanoparticles. In another approach the synthesis of MHCFs is similar to that described by Oliveira et al. [7] in which is used silver nanoparticles (AgNP) chemically synthesized on the surface of a printed carbon electrode as a precursor for AgHCF preparation. The mediator was prepared under galvanostatic conditions in a solution containing $K_3[Fe(CN)_6]$, by

* Corresponding author.

E-mail address: bergamini@ufpr.br (M.F. Bergamini).

oxidation of Ag^0 to Ag^+ leading to the formation of nanostructured AgHCF at the surface of the electrode.

Functionalized materials used as supports in the preparation of MHCs are particularly interesting because they allow the formation of stable nanostructures with high electroactive area. Recently, the use of biochar, a highly functionalized carbonaceous material obtained by pyrolysis of biomass in low amounts of oxygen [15,16], has called attention by its ability for preconcentration of different species on its surface. The use of biochar as modifier in the preparation of composite electrodes have been reported for direct determination of metal ions [17–19] and organic species [20,21] with excellent stability and analytical performance. Moreover, biochar has been also used as support for preparation of micro and nanostructures of bismuth, antimony, mercury and gold [22–25]. All micro or nanostructures investigated until now (Sb, Bi, Hg and Au) for decoration of biochar provide beneficial effects on the electrochemical performance of electrode's surface such as an improvement in electrical conductivity or an enlargement of the useful potential range (cathodic region). Herein we propose for the first time the electrochemical synthesis of an active modifier (CuHCF nanostructured) anchored on biochar from copper (II) ions previously adsorbed. The stability and applicability of the synthesized metal complex were evaluated for amperometric determination of isoniazid (INZ), which is an active molecule found in medicines for tuberculosis treatment [26,27]. However, it is important to emphasize that this drug causes hepatotoxicity in about 20% of patients with severe levels in about 2% [28,29]. This substance has a voltammetric behavior well established in the literature [30,31], which allows the evaluation of a modified electrode for INZ electrochemical determination.

2. Experimental

2.1. Reagents

A solution of copper ions was prepared from copper acetate (Neopac) dissolved in ammonium acetate (Vetec) having its pH adjusted using ammonium hydroxide (Neon). The electrochemical synthesis of CuHCF was performed in potassium ferricyanide (Vetec), and potassium nitrate (Impex); for the electrochemical measurements it was used a solution of KNO_3 as supporting electrolyte. For all pH adjustments nitric acid and potassium hydroxide were used, (both Sigma Aldrich). The INZ (Sigma Aldrich) and the standard stock solutions were prepared using a solution of KNO_3 0.1 mol L^{-1} in pH 3.0.

2.2. Synthesis and characterization of CuHCF nanostructures

For construction of the INZ sensor, a carbon paste electrode modified with biochar (BM-CPE) was prepared using the following mass percentages: 25% of biochar, 50% of graphite and 25% of mineral oil. Biochar was obtained from the biomass of castor oil cake after a pyrolysis process at 400°C , heating rate of 5°C min^{-1} and residence time of 60 min. The surface activation was performed by refluxing the biochar dispersion in 50% (v/v) HNO_3 solution for 3 h at 60°C . Subsequently, the dispersion was filtered, washed with distilled water, and dried at 100°C for 24 h [32].

The preconcentration step was conducted under open circuit potential by immersion of BM-CPE in ammonium buffer solution (pH 9.0) containing copper (II) ions. The electrode construction and the preconcentration solution were performed as described by Oliveira et al. [33]. In this step, it was evaluated the best conditions of preconcentration time (1–20 min) and copper ions concentration ($1.0 \times 10^{-5} \text{ mol L}^{-1}$ to $1.0 \times 10^{-3} \text{ mol L}^{-1}$).

Electrochemical synthesis of CuHCF nanostructures were

carried out by cyclic voltammetry in KNO_3 solution containing $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of $\text{K}_3[\text{Fe}(\text{CN})_6]$ using a potential range from -0.2 – 1.2 V . The evaluated conditions were: pH of solutions (1.5–6.0), scan rate (10 – 100 mV s^{-1}) and number of cycles (10–75). The voltammetric behavior of the BM-CPE modified with CuHCF nanostructures (nCuHCF-BM-CPE) was evaluated by cyclic voltammetry in solution of KNO_3 0.1 mol L^{-1} in different pH values of 1.5, 3.0, 4.0, 5.0 and 6.0.

The morphology and chemical composition of the nCuHCF electrode's surface were obtained by High Resolution Scanning Electron Microscopy (SEM - model Quanta 450 with a FEG) and the energy-dispersive X-ray spectroscopy (EDS - EDAX TEAMTM), respectively.

2.3. Electrochemical determination of isoniazid (INZ)

Voltammetric measurements were performed using a conventional set of three electrodes: working electrode (nCuHCF-BM-CPE), platinum auxiliary electrode and reference electrode ($\text{Ag}/\text{AgCl}/\text{KCl}$ 3.0 mol L^{-1}) connected to a potentiostat/galvanostat ($\mu\text{Autolab}$ Type III – NOVA software version 1.10). All measurements to optimize sensor performance were carried out by amperometry. First, the influence of the applied potential on the INZ determination was evaluated. The sensitivity for each applied potential (0.5, 0.6, 0.7 and 0.8 V) was obtained from amperograms generated by successive additions of stock solution of INZ in order to provide a final concentration ranging from $5.0 \times 10^{-6} \text{ mol L}^{-1}$ to $5.0 \times 10^{-5} \text{ mol L}^{-1}$.

The evaluation of the interference of concomitants species (glucose (GLU), ascorbic acid (AA), rifampicin (RIF), sodium, calcium, chloride and sulfate ions) was carried out by adding these substances at three different concentration: 1.0×10^{-6} , 1.0×10^{-5} and $1.0 \times 10^{-4} \text{ mol L}^{-1}$ into a solution containing $1.0 \times 10^{-5} \text{ mol L}^{-1}$ of INZ. The recovery studies allowed to evaluate the accuracy for the proposed method. Quantification of INZ samples was performed in a solution of KNO_3 0.1 mol L^{-1} in pH 3.0 by the method of standard addition. The solution was spiked in three distinct concentrations: 1.0×10^{-6} , 5.0×10^{-6} and $1.0 \times 10^{-5} \text{ mol L}^{-1}$. The recovery percentages for each level were obtained by comparing the concentration values of INZ added and those found experimentally.

3. Results and discussion

3.1. Electrochemical synthesis and morphological characterization of nCuHCF-BM-CPE

Electrochemical synthesis of nanostructured CuHCF on the BM-CPE surface was carried out from copper (II) ions (Cu-BM-CPE) previously incorporated as a precursor. The adsorption of copper on the electrode surface occurred mainly on the biochar particles which are distributed homogeneously over the electrode surface. EDS Chemical Mapping Spectra of Cu-BM-CPE surface reveals that adsorption of copper ions occurs mainly on sites rich in oxygen atoms (Fig. 1).

Electrochemical synthesis of CuHCF nanostructures was performed by cyclic voltammetry using a solution of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ potassium hexacyanoferrate and 0.1 mol L^{-1} potassium nitrate solution in pH 1.5. Cyclic voltammograms obtained during the modifier preparation (Fig. S1) showed the formation of nCuHCF onto electrode surface suggesting a quick and effective electrochemical synthesis of nCuHCF. Afterwards, the electrode was washed to remove the excess of potassium ferricyanide and submitted to cyclic voltammetry in solution of 0.1 mol L^{-1} potassium nitrate (pH adjusted at 3.0). The measurement was performed using 15 potential scans and the voltammetric profile was compared to BM-

Download English Version:

<https://daneshyari.com/en/article/6601843>

Download Persian Version:

<https://daneshyari.com/article/6601843>

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