



Determination of trace heavy metal ions by anodic stripping voltammetry using nanofibrillated cellulose modified electrode



K. Zinoubi^a, H. Majdoub^a, H. Barhoumi^{a,*}, S. Boufi^b, N. Jaffrezic-Renault^c

^a Laboratory of Interfaces and Advanced Materials, Faculty of Sciences, University of Monastir, Monastir, Tunisia

^b Laboratory of Material Sciences and Environment, Faculty of Sciences of Sfax, Tunisia

^c Laboratory of Analytical Sciences, Doua 69100 Villeurbanne, Lyon, France

ARTICLE INFO

Keywords:

Nanofibrillated cellulose
Chemically modified CGE
DPASV
Heavy metal sensor
Seawater analysis

ABSTRACT

In this work, nanofibrillated cellulose (NFC) has been used as a sensitive matrix to develop electrochemical sensor trace heavy metal ions quantification via differential pulse anodic stripping voltammetry (DPASV). Cellulose fibers from Eucalyptus were fibrillated into nano-sized fibrils throughout the homogenization process. To facilitate the fibrillation process, fibers were previously oxidized under neutral conditions to bring the carboxyl content up to 500 $\mu\text{mol/g}$. NFC layer was deposited on a carbon glassy electrode (CGE) by simple adsorption. The adopted DPASV method was achieved by optimizing some parameters such as the accumulation time, the deposition time and the deposition potential. As a result, the modified electrode with nanofibrillated cellulose exhibited reproducible response, high sensitivity and good stability for Cd(II), Cu(II), Pb(II) and Hg(II) ions. The developed ion sensor was used for heavy metal determination in seawater.

1. Introduction

The rapid development of industries and the competitive use of fresh water in many parts of the world cause the severe contamination of water by heavy metals. The presence of heavy metals in industrial effluents above the permitted level leads to serious environmental pollution, threatening human health and the ecosystem [1]. Heavy metal ions such as Cd(II), Cu(II), Pb(II) and Hg(II) ions, as well as others, in small quantities play an important role in living organisms existence which is essential for maintaining metabolism. However, even very small doses or excessively high levels of toxic metals can cause serious problems for human health and the environment. The accumulation of these metals in the human body can cause diseases in the central nervous system, liver, kidneys, skin, bones and teeth [2–4]. Hence, monitoring the concentration of these species in water bodies is imperative in developing new strategies for the detection of heavy metals [5–9]. Currently, various detection techniques have been reported to quantify the trace of heavy metal ions, including electrochemical determination [10–14], atomic absorption spectrometry [15], plasma-optical emission spectrometry [16], and fluorescence spectrometry [17]. However, spectrometric methods are expensive, cumbersome, time consuming and unsuitable in situ measurements owing to the required complex instrumentation. In contrast, electrochemical techniques are attractive according to their remarkable sensitivity,

probability and low cost. Among the electrochemical methods, differential pulse anodic stripping voltammetry (DPASV) has been widely deemed to a forceful technique for the quantification of heavy metal ions due to an effective preconcentration process followed by electrochemical dissolution of the accumulated heavy metal ions [18–21]. Many electrochemical strategies are based on the modification of the working electrode surface by chemicals reagents such as: monomolecular ligands [22–27], thiolamine [28,29], polymers [30–33]. In this context, it is possible to use chemically modified electrodes with renewable materials of miniaturized elements of plant origin [34]. Cellulose is the most abundant natural renewable and biodegradable polymer. The main sources of cellulose fibers are annual plants and wood with its two species namely hardwoods and softwoods. It exists in a quasi-pure state in the form of cotton seed hair, but most often it is found as being combined with other polysaccharides. By intelligent processing techniques, they could be used as classical nanoreinforcing elements in the fields of modified electrodes. They are organized in a cellular hierarchical structure build up by bundles of thin microfibrils aggregated into larger structures embedded into hemicellulose and enclosed by lignin. The NFCs were produced by mechanically treating cellulose suspensions through high pressure homogenizers. The typical cross section of the nanofibrils ranges from 4 to 20 nm depending on their origin, and each of them is formed by the association of many cellulose molecules, which are linked together in repeating lengths

* Corresponding author.

E-mail address: Houcine.Barhoumi@fsm.rnu.tn (H. Barhoumi).

along their chains. The NFCs present a jelly aspect with pseudo-plastic properties [35].

In this study, we report the development of a modified glassy carbon electrode (GCE) with nanocellulosic fibers for trace heavy metal ions determination using differential pulse anodic stripping voltammetry (DPASV).

2. Experimental

2.1. Chemicals and reagents

$K_4[Fe(CN)_6] \cdot 3H_2O$, $K_3[Fe(CN)_6]$, (KCl), $CuCl_2$, $Pb(NO_3)_2$, $CdSO_4$ and $HgCl_2$ were purchased from Fluka Chemika. An acetate buffer solution was prepared by adjusting 0.2 M of sodium acetate solution to pH 4.5 with the addition of 0.2 M of acetic acid CH_3COOH . This solution was then further diluted with distilled water to give final buffer strength of 0.1 M. The NFC material was fabricated by using Eucalyptus pulp (eucalyptus globules) in the form of dry sheets.

2.2. Apparatus

The electrochemical measurements were performed using an Autolab (PGSTAT 302 N, Eco Chemie). All measurements were performed in a dark Faraday cage. The electrochemical cell comprises three electrodes: a platinum counter-electrode, an Ag/AgCl/KCl as reference electrode and a glassy carbon (GC) as working electrode.

AFM image was recorded in Tapping Mode using atomic force microscopy IIIa digital instruments. Measurements were carried out at ambient atmospheric and temperature. The AFM probe was characterized by a spring constant of 12–103 N/m and a resonance frequency range of 200–400 kHz.

2.3. Production of NFC

Firstly, fibers were treated by TEMPO-mediated oxidation to generate carboxyl groups at a content of 500 $\mu\text{mol/g}$, in order to facilitate the disintegration process. The oxidation was investigated at pH 10 following the method reported previously [36]. Briefly, 2 g of cellulose fibers were suspended in 200 mL of water. Additional product such as TEMPO (30 mg) and NaBr (250 mg) were mixed with the prepared solution. Then, a solution of NaClO (50 mL) was added dropwise to the cellulose suspension at a temperature around 5 °C, kept constant throughout the oxidation reaction. The pH of the mixture was adjusted to 10 by addition of a 0.1 M of NaOH solution. After the washing step with water to remove salt, a suspension of 1.5 wt% of prepared fibers was homogenized in a high pressure homogenizer (NS1001L PANDA 2 K-GEA, Italy) applying six shear cycles (3×300 bar; 3×600 bar). A thick transparent NFC gel was obtained after six passes.

2.4. Functionalization of the working electrode

The GCE was polished with alumina solution (0.5 μm), rinsed and ultrasonicated in water for 3 min. Then, the GCE was scanned between -0.2 and 1.3 V in 0.5 M H_2SO_4 at 50 mV s^{-1} for 10 cycles to remove possible contaminations. Subsequently, 5 μL of NFC solution was deposited on the electrode. The modified surface was dried at ambient temperature overnight. A good adhesion of the NFC film on the carbon surface electrode was obtained. The high stability of the NFC/Electrolyte interface can be attributed to the high adhesion of the deposit NFC membrane on the carbon electrode surface. The long β -glucans found in NF cellulose interact with the carbon surface through hydrogen bonding.

2.5. Apparatus and electrochemical test procedure

The electrochemical measurements were carried out in an electro-

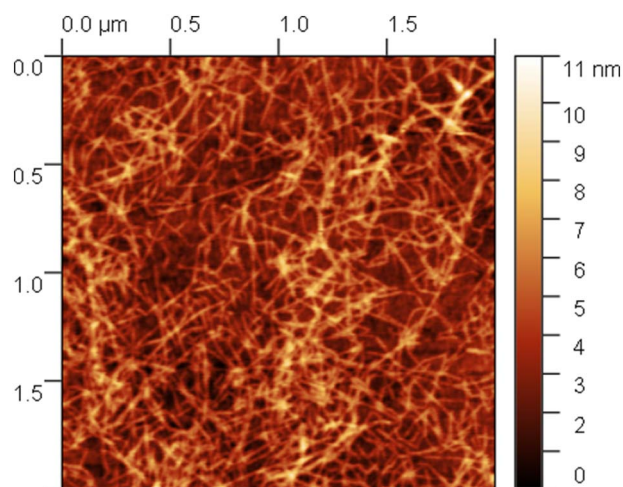


Fig. 1. AFM observation of the CNF film.

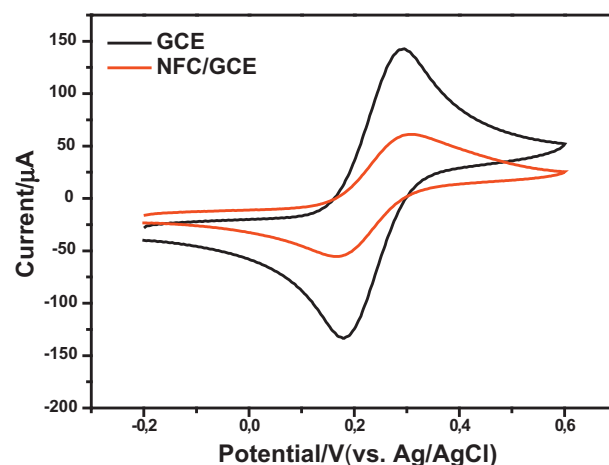


Fig. 2. Cyclic voltammograms of modified and unmodified GCE in 0.1 M KCl solution containing 5 mM $[Fe(CN)_6]^{3-/4-}$ at scan rate of 100 mV s^{-1} .

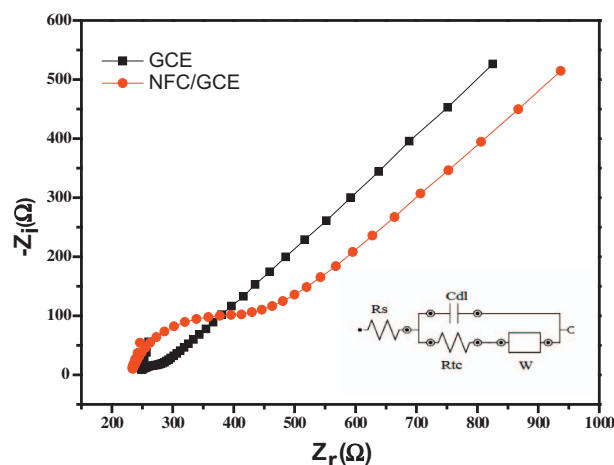


Fig. 3. Nyquist plots of modified and unmodified GCE in 0.1 M KCl solution containing 5 mM $[Fe(CN)_6]^{3-/4-}$. Equivalent electrical circuit of the Nyquist plots.

chemical cell containing a three-electrode such as the modified GCE ($\Phi = 3$ mm) as working electrode, the Ag/AgCl/KCl as the reference electrode and a platinum wire ($\Phi = 1$ mm) as the counter electrode. Acetate buffer solution as electrolyte support (0.1 M, pH = 4.5). The accumulation of metal ions onto the NFCs film was performed at open circuit by dipping the GCE/NFCs modified electrode during an accu-

Download English Version:

<https://daneshyari.com/en/article/4907724>

Download Persian Version:

<https://daneshyari.com/article/4907724>

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