

Electrochemical determination of 5-hydroxymethylfurfural using modified electrode with nickel nanoparticles.

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Introduction

Renewable lignocellulosic materials are attractive low-cost feedstocks for bioethanol production. Acid hydrolysis of cellulose found in plants and waste materials results in production of hydroxymethylfurfural (HMF).¹ HMF is among the most potent inhibitory compounds generated from acid hydrolysis of lignocelluloses to simple sugars for fermentation,² reducing the production of second-generation ethanol. Thus, it is important measure furanic aldehydes into treated cellulosic biomass.

Resultados e Discussão

In this work was developed a chemically modified electrode with nickel nanoparticles (NiNPs/GCE) in a glassy carbon substrate for determination of HMF by electroanalytical techniques. The studies were performed using NiNPs/GCE as working electrode, reference electrode Ag/AgCl (KCl 3.0 molL⁻¹) and platinum wire auxiliary electrode.

The electrodeposited NiNPs were characterized by scanning electron microscopy (SEM - Jeol, model JSM 7500F) on glassy carbon substrate with an area covered of approximately 0.20 cm². The image shows a uniform electrodeposition of nanoparticles with a homogeneous distribution onto the glassy carbon surface. From the SEM image was observed that the NiNPs formed have spherical shape with diameter between 7 and 80 nm (250 nanoparticles were counted) and medium diameter of 41 ± 16.

HMF was characterized by cyclic voltammetry with NiNPs/GCE in basic medium (LiOH 0.1 molL⁻¹). The method was developed with the NiNPs/GCE by techniques for linear sweep voltammetry (LSV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV) in basic medium.

HMF is reduced irreversibly at potentials 1.38 V in cyclic voltammetry with NiNPs/GCE. In addition, the potential of the HMF tends to shift in the positive direction in relation to the GCE. In the scan rate study was observed that the reduction potential of the analyte is shifted to more negative region with

increasing of the scan rate and in the reverse sweep was not observed anodic peaks. The process of reduction of HMF producing 2,5-bis(hydroxymethyl)-furan involves the consumption of two electrons.

In LSV the dependence of the cathodic peak current HMF presented linear regions of concentration from 6,0x10⁻⁴ to 1.5x10⁻² molL⁻¹ with liners correlations (R) 0.9995, limit of detection (LOD) 5.1x10⁻⁵ molL⁻¹, limit of quantification (LOQ) 1.5x10⁻⁴ molL⁻¹ and amperometric sensitivity (AS) 11.5x10⁻³ Amol⁻¹L. With SWV, HMF presented an irreversible peak in -1.43 V and showed linearity from 1.0x10⁻⁵ to 1.5x10⁻⁴ molL⁻¹ with R 0.9993, LOD of 1.1x10⁻⁶ molL⁻¹, LOQ 3.3x10⁻⁴ molL⁻¹ and (AS) 53.1x10⁻³ Amol⁻¹L. In DPV, HMF presented linear regions of concentration from 5.0x10⁻⁶ to 1.5x10⁻³ molL⁻¹ with R 0.9994, LOD of 2.0x10⁻⁶ molL⁻¹, LOQ 6.0x10⁻⁶ molL⁻¹ and (AS) 14.2x10⁻³ Amol⁻¹L.

Recovery was performed in three different test concentrations studied for each voltammetric technique. The LSV presented an average recovery of 102.8 ± 2.9%, SWV obtained an average recovery of 99.3 ± 4.9% and the DPV showed an average recovery of 101.5 ± 3.6%.

Conclusões

The results show that the method developed by DPV showed a higher peak, the lower limits of detection and quantification. Thus, the results indicate that the DPV technique is more effective in quantifying the HMF using NiNPs/GCE, therefore the method can be applied to the determination of the electrochemical furanic aldehyde acid.

Agradecimentos

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¹ Ribeiro, P. R.; Carvalho, J. R. M.; Geris, R. Geris. *Quim. Nova* **2012**, 35, 1046.

² Liu, Z. L. et al. *J. Ind. Microbiol. Biotechnol.* **2004**, 31, 345.