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Electrochemical determination of total reducing sugars from bioethanol production using glassy carbon electrode modified with graphene oxide containing copper nanoparticles

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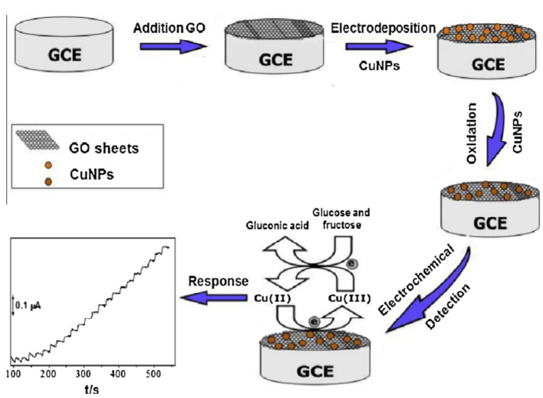
HIGHLIGHTS

- A electrochemical sensor modified was proposed with GO containing CuNPs using PAD technique.
- The detection limit reached 6.4×10^{-6} mol L^{-1} in a wide linear range from 2.0×10^{-5} to 4.4×10^{-4}.
- The developed method is fast and simple compared to classical methods currently used.
- The sensor showed quick response, sensitivity, accuracy and selectivity.
- The sensor was successfully applied to detect total reducing sugars in residual waters samples.

GRAPHICAL ABSTRACT



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ABSTRACT

This work presents the analytical method development for total reducing sugars determination in residual water samples obtained from sugarcane processing for ethanol production. This method was developed using pulsed amperometry with a glassy carbon electrode modified with graphene oxide containing copper nanoparticles. With pulsed amperometry detection was achieved a limit of detection of 6.4×10^{-6} mol L^{-1}. The amperometric sensitivity was 1.6×10^{-2} A mol^{-1} L. The recovery study showed that the method has good accuracy and repeatability, with recovery of $92.8 \pm 0.5\%$. Experiment results obtained showed that the sensor has good long-term stability, sensitivity and is interference free, and the method developed is simple and fast.

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1. Introduction

Nowadays, the bioenergy sector is facing a major challenge: to ensure and prove its sustainability. Environmental issues such as the availability of fossil fuels and environmental problems generated from their use [1], as well as economic and geopolitical

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reasons put emphasis in the search for clean and renewable energy sources. In this search, biofuels derived from different biomass stands out as a potential source, as well as the ethanol derived from sugarcane [2].

The chemical composition of sugarcane is very variable depending on the physical and chemical properties of the soil, climate and maturation stage [3]. The two main fractions of sugarcane as regards to its processing are the fiber and the broth, the latter being the raw material for the production of ethanol. The sugarcane broth is an impure solution of sucrose, glucose and fructose. Sucrose is in larger amount, having an average composition of 14%, while for others sugars, depending upon the state of maturation is 0.4% [4].

Monosaccharides like glucose and fructose are the two types of reducing sugars found in sugarcane broth, they receive this name due to the presence of free ketonic carbonyl group, able to oxidize in the presence of oxidizing agents in alkaline solutions. However, sucrose is a disaccharide that does not have this characteristic, so it is referred to as a non-reducing sugar. The total reducing sugars represent the sum of reducing sugars and inverted sucrose. The inverted sucrose is the sucrose present in sugarcane broth that converts to reducing sugars (glucose and fructose) by acid hydrolysis, and thus can be quantified.

The determination of reducing sugars in various stages of the processing of sugarcane has great importance because it allows evaluating the quality of the raw material used to produce ethanol as well as possible losses enabling the optimization of production ensuring a better use of the raw material. Studies in the literature for determination of reducing sugars in different matrices showed that the classical chemical methods known for the analysis of reducing sugars are mostly based on reduction of copper ions in alkaline solutions – Fehling Solutions – [5]. There are also those based on the dehydration of sugars by using concentrated acid, with subsequent staining with organic compounds [6], or the simple reduction of organic compounds, forming other measurable coloring compounds in the visible region [7,8].

Among these methods, the Somogyi–Nelson is widely applied in the sugarcane production to quantify the reducing sugars content in different samples providing reliable and accurate results for the industrial losses in general. However, this method, has major disadvantages such as relatively large analysis time, use of controlled temperature as well as low selectivity because it is prone to interference from other molecules that can act as reducing agents [9].

Most recently, some studies have shown the determination of glucose and fructose using non-enzymatic amperometric sensors [10,11]. A study was performed for applying a non-enzymatic glucose sensor in biological samples using a lead–tin oxide electrode modified with copper oxide microfibres (CuO-NPs) showing satisfactory results for biological samples [10]. Cobalt oxide-doped copper oxide composite nanofibers (CCNFs) were successfully achieved via electrospinning followed by thermal treatment processes and then exploited as active electrode material for direct enzyme-free fructose detection by cyclic voltammetry and amperometry [11].

Copper as an electrode material is of interest for analysis of carbohydrates and amino acids [12–15] because of the possibility of performing amperometric detection at a constant potential in solutions with a high value of pH. In comparison to Pt, Au, Ni, Ag and Co, Cu was reported to be better in terms of range of response, detection limit, and especially stability [12].

Recent trends in the use of chemically modified electrodes (CMEs) in electrochemical detection systems are searching for new materials that can be operated without loss of the electrode activity, at constant applied potential [16]. Among these materials used for modification, the metallic nanoparticles (NPs) have been widely studied due to their physical and chemical properties, which differ of their bulk material [15]. NPs can display unique advantages over macroelectrodes, such as, enhancement of mass transport, higher signal-to-noise ratio, electrocatalysis, high surface area and effective control over the microenvironment of the electrode [17,18].

In this context, graphene also stands out because of its two-dimensional plane, which provides itself with a large specific surface area for the immobilization of large amount of substances including a wide range of metals, nanoparticles, biomolecules, etc. Since every atom in a graphene is a surface atom, molecular interaction and thus electron transport through graphene can be highly sensitive to absorbed molecules [19]. Due to these properties, graphene has the ability to promote electron transfer reactions when used as an electrode, which provides an inexpensive alternative to carbon nanotubes [20].

CMEs with copper nanoparticles and graphene were used for electrochemical determination of glucose by flow injection analysis (FIA) and amperometry. Many advantages were found for the proposed system including high sensitivity and stability. Wide range of linearity and good reproducibility [21,22]. Chen and co-authors [23] prepared microdisc electrodes of graphene–copper nanoparticle composite by the in situ chemical reduction. The results indicated that copper nanoparticles with an average diameter of 20.8 nm were successfully deposited on graphene nanosheets. The CMEs were applied for sensing carbohydrates in combination with cyclic voltammetry and capillary electrophoresis. The sensitivity and detection limits were determined to be 85.96 nA/mM and 0.87 μM for mannitol, 52.63 nA/mM and 1.42 μM for sucrose, 50.88 nA/mM and 1.47 μM for lactose, 63.16 nA/mM and 1.19 μM for glucose, and 45.61 nA/mM and 1.64 μM for fructose, respectively [23].

The determination of reducing sugar content is extremely important in studies that provide a greater appreciation of waste materials, in particular, development of processes for production of ethanol from sugarcane. Thus, the scope of the present work was the development of a glassy carbon electrode (GCE) modified with graphene oxide (GO) containing copper nanoparticles for the simultaneous determination of glucose and fructose, which are the reducing sugars, in residual waters from ethanol production plant. The technique employed in this study was the pulsed amperometry, which solves the problem of losing activity alternating anode and cathode polarization to clean and reactivate the electrode surface [24–26]. After an extensive literature review, we could not find any work involving the simultaneous determination of glucose and fructose by electroanalytical techniques in wastes from ethanol production plant. Therefore, this study can overcome one scientific lack with the development of a new electroanalytical tool, which should contribute to the better use of sugarcane as well as to improve the production process by reducing possible losses.

2. Experimental

2.1. Reagents and solutions

Solutions were prepared from analytical-reagent grade chemicals without further purification and by using ultrapure water (MILLI-Q). Sodium hydroxide (⩾98%), copper sulfate pentahydrate (⩾98%), glucose (⩾97%), fructose (⩾97%), sucrose (⩾97%), graphene oxide (2 mg mL^{-1}), Nafion® 117 solution, sulphuric acid (98% w/w) were obtained from Sigma–Aldrich, hydrochloridric acid (37% w/w) from J.T. Baker and ethanol absolute P.A from Merck. The carbohydrates solutions were prepared with ultrapure water (MILLI-Q). Residual waters sample was supplied by a sugarcane plant in Araraquara, São Palo, Brazil.

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