Electrochemical oxidation and electroanalytical determination of xylitol at a boron-doped diamond electrode

Anabel S. Lourenço [a], Fátima A.C. Sanches [a], Renata R. Magalhães [a], Daniel J.E. Costa [a], Williame F. Ribeiro [a,b], Kátia M. Bichinho [a], Giancarlo R. Salazar-Banda [c], Mário C.U. Araújo [a,*]

[a] Universidade Federal da Paraíba, Centro de Ciências Exatas e da Natureza, Departamento de Química, P.O. Box 5093, 58051-970 João Pessoa, PB, Brazil
[b] Universidade Federal da Paraíba, Centro de Ciências Agrárias, Departamento de Ciências Fundamentais e Sociais, 58397-000 Areia, PB, Brazil
[c] Instituto de Tecnologia e Pesquisa/Programa de Pós-graduação em Engenharia de Processos, Universidade Tiradentes, Avenida Murilo Dantas, 300, Farolândia, 49032-490 Aracaju, SE, Brazil

ARTICLE INFO

ABSTRACT

Xylitol is a reduced sugar with anticariogenic properties used by insulin-dependent diabetics, and which has attracted great attention of the pharmaceutical, cosmetics, food and dental industries. The detection of xylitol in different matrices is generally based on separation techniques. Alternatively, in this paper, the application of a boron-doped diamond (BDD) electrode allied to differing voltammetric techniques is presented to study the electrochemical behavior of xylitol, and to develop an analytical methodology for its determination in mouthwash. Xylitol undergoes two oxidation steps in an irreversible diffusion-controlled process ($D = 5.05 \times 10^{-5}$ cm^2 s^{-1}). Differential pulse voltammetry studies revealed that the oxidation mechanism for peaks P_1 ($3.4 \leq pH \leq 8.0$), and P_2 ($6.0 \leq pH \leq 9.0$) involves transfer of 1 $H^+/1e^-$, and $1e^-$ alone, respectively. The oxidation process P_1 is mediated by the $^{\bullet}OH$ generated at the BDD hydrogen-terminated surface. The maximum peak current was obtained at a pH of 7.0, and the electroanalytical method developed, (employing square wave voltammetry) yielded low detection (1.3×10^{-6} mol L^{-1}), and quantification (4.5×10^{-6} mol L^{-1}) limits, associated with good levels of repeatability (4.7%), and reproducibility (5.3%); thus demonstrating the viability of the methodology for detection of xylitol in biological samples containing low concentrations.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The biggest challenge in preventive dentistry is tooth-surface biofilm control (this for both natural and synthetic dental surfaces). Bacterial populations in the oral cavity are the primary causes of many problems, such as cavity formation, bad breath, hypersensitivity, gum bleeding, periodontitis, and tooth loss [1–3]. These problems are associated with excessive consumption of sucrose in human diets, and the absence of proper oral hygiene [4]. To prevent these problems, and to maintain good oral health, the use of antibacterial agents [1,3–5], such as mouthwash, and toothpaste, and both natural and artificial sweeteners, are frequently employed. Due to its high sweetening ability, its anticariogenic properties, and its potential for use by insulin-dependent diabetics [4–7], xylitol has attracted much attention in the pharmaceutical, cosmetics, food, and dental industries.

Xylitol has also become a product of great economic interest, it is approved by the US Food and Drug Administration (FDA), and current world production exceeds 10,000 t per year. This is directed mainly towards food, pharmaceutical, cosmetic, and oral hygiene uses [7,8].

Xylitol (1,2,3,4,5-pentahydroxypentanol—molecular weight: 152.2 g mol^{-1}), with the structural formula shown in Fig. 1, is a reduced sugar, derived from xylose hydrogenation [4–8].

This polyalcohol (also known as a sugar alcohol, or polyhydric alcohol) is a hydrogenated form of a carbohydrate, whose carbonyl group (aldehyde, or ketone reducing sugar) has been reduced to a primary or secondary hydroxyl group (hence the alcohol) [9]. It is naturally found in fruits, legumes, vegetables and wild mushrooms in small amounts [4–6], but can be artificially produced thru chemical or biotechnological processes [4,7,8]. In the late 1960s, dental studies showed the beneficial effects of xylitol, when replacing sucrose, for disease prevention [5,6,10]. The sugar inhibits the growth of various bacteria, including Streptococcus mutans, thus reducing the biofilm thickness [4,5]. Hence, it is used in the prevention of tooth decay [4,10,11]. However, the consumption of large amounts of this sugar can produce side effects, including osmotic diarrhea, flatulence, and gastrointestinal pain. The usual recommended daily maximums of xylitol are 60–70 g for adults (10–30 g per intake), and 50 g for children (10 g per intake) [12].

* Corresponding author. Tel.: +55 83 3216 7438; fax: +55 83 3216 7437.
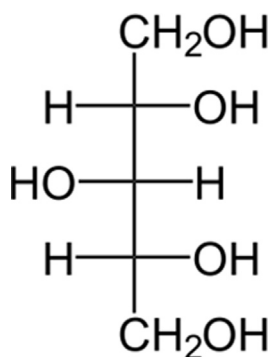E-mail address: laqa@quimica.ufpb.br (M.C.U. Araújo).

Fig. 1. Xylitol structural formula.

Xylitol has been determined by both enzymatic, and chemical methods [4,13,14]. Chemical detection of xylitol in different matrices is generally based on separation techniques, coupled with characterization [4]. Various methods, such as colorimetric [15,16], chromatographic [13,17–22], flow injection analysis [23,24], capillary electrophoresis [25] and isotachophoresis [26] have been applied to the determination of xylitol. However, electroanalytical techniques are a promising alternative for the determination of organic molecules in complex matrices, because they deliver lower cost and analysis time, high selectivity, and high sensitivity. Electroanalytical techniques have not been largely used for the determination of xylitol. However, electrochemical studies devoted to the use of xylitol as a fuel in fuel cell systems [27], and applications such as amperometric detectors [13,24,25] can be found in the literature.

The electrochemical oxidation of xylitol on Pt (111) [28], and on differing platinum single crystal electrodes [29], in acid medium (0.1 mol L^{-1} $HClO_4$) was studied using cyclic voltammetry (CV), which implies that xylitol oxidation would occur in the range of $+0.4$ V to 1.1 V (*versus* the reversible hydrogen electrode—E_{RHE}). In all cases, the current density decreased between the first and second cycle. This deactivation might have been due to modification of the electrode surface structure, and/or to poisoning, through accumulation of adsorbed species.

Boron-doped diamond (BDD) electrodes are very attractive (for their many potential applications), and due to their interesting properties, and they are significantly different from conventional electrodes, *e.g.*, glassy carbon (GC), gold (Au), and platinum (Pt) electrodes [30,31]. The main properties of BDD electrodes are their very low and stable background current, corrosion stability in very aggressive media, extreme electrochemical stability (low adsorption of contaminants), high response sensitivity, and a very wide working potential window, which can be larger than 3.5 V [30–36]. These properties make it useful in electroanalysis, especially for the determination of organic substances; (adenosine, ascorbic acid, caffeine, carbamate pesticides, chlorophenols, cysteine, histamine, indoles, nucleic acids, tetracycline antibiotics, and xanthine among others), and inorganic substances; (azide anion, hydrogen peroxide, nitrates, nitrites, dissolved oxygen, and the metal ions Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+}) [35,36].

This study describes the application of a BDD electrode allied to CV, linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV) to the study of xylitol's electrochemical behavior, and the development of a methodology for its analytical determination in mouthwash samples using SWV.

2. Experimental

2.1. Apparatus and reagents

All voltammetric experiments were carried out using an Eco Chemie, μAutolab® Type II, potentiostat coupled to a Metrohm,

663 VA Stand®, three-electrode module, and a 3 mL single-compartment electrochemical cell. A platinum wire with Ag/AgCl (3 mol L^{-1}, KCl) were employed as counter and reference electrodes. GC ($\varnothing=3$ mm), carbon paste (CP, $\varnothing=3$ mm), Au ($\varnothing=2$ mm), Pt ($\varnothing=2$ mm), and BDD (surface area of 0.36 cm^2) were used as working electrodes. BDD film electrodes (pieces of 1.2 cm $\times$ 1.2 cm) were prepared in the Centre Suisse d'Electronique et de Microtechnique SA (CSEM), Neuchâtel, Switzerland, using a hot filament chemical vapor deposition technique with a filament temperature between 2440 and 2560 °C and a gaseous mixture containing methane, H_2 and trimethylboron, having a final boron content of the order of 8000 ppm [33].

Xylitol (99.5%) and all the other chemicals were analytical grade and purchased from Sigma-Aldrich. The solutions and subsequent dilutions were prepared daily with deionized water in a Millipore Milli-Q System (conductivity ≤ 0.1 μS cm^{-1}). Stock solutions of xylitol (10 mmol L^{-1}) were prepared in water. Buffer solutions 0.1 mol L^{-1} were prepared and employed as supporting electrolyte following the procedure described by Oliveira et al. [37]: HCl/KCl (pH 2.2); HAc/NaAc (pH: 3.4, 4.2 and 5.4); NaH_2PO_4/Na_2HPO_4 (pH 6.0, 7.0 and 8.0); borax/NaOH (pH 9.0 and 10.2) and NaOH/KCl (pH 11.8). In addition, a 0.1 mol L^{-1} sulfuric acid solution (pH 1.0) was also used.

2.2. Electrode preparation and measurement procedure

Prior to each experiment the BDD electrode was submitted to an anodic treatment ($+3.0$ V) for 120 s followed by a cathode treatment (-3.0 V) for 240 s using a 0.5 mol L^{-1} aqueous H_2SO_4 solution as the supporting electrolyte [34]. For each pretreatment a different electrochemical cell was used without stirring the solution. Afterward, the BDD electrode surface was rinsed with ultrapure water. This procedure was repeated daily before voltammetric measurements and between measurements at different values of pH in order to obtain reliable and reproducible results, in view of possible structural changes on the BDD surface resulting from the superficial loss hydrogen caused by BDD surface oxidation by oxygen from the air [34].

All the voltammetric experiments were performed at room temperature. LSV and CV used scans rates (v) of 25–100 mV s^{-1}; DPV used a pulse (a) of 50 mV amplitude, a modulation time of 70 ms, and v of 10 mV s^{-1}; SWV used a frequency (f) of 25 s^{-1}, scan increment (ΔE_s) of 2 mV, scan rate of 50 mV s^{-1}, with the a at 50 mV.

2.3. Recovery

Recovery [38] experiments were carried out in order to evaluate the performance of the method by measuring xylitol concentrations in two commercial mouthwash samples from differing fabrication lots acquired in the city of João Pessoa (PB, Brazil).

The mouthwash samples were first diluted by addition of water at 1:200 (v/v) and then analyzed. Sample (25 μL) was added to an electrochemical cell containing 3 mL of the support electrolyte, and recovery curves were obtained for the sample spiked with three aliquots of 25 μL of 1.0×10^{-3} mol L^{-1} xylitol solution using the standard addition method. Each sample was evaluated in triplicate.

3. Results and discussion

3.1. Electrochemical oxidation of xylitol

3.1.1. Choice of the working electrode

The electroactivity of fresh 164 μmol L^{-1} xylitol solutions, in 0.1 mol L^{-1} phosphate buffer (pH 7.0) was studied using SW voltammograms, recorded on different working electrodes, Fig. 2.