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Morphological and Chemical Analysis of the Molecularly-Imprinted Polymer-Based D-Arabinose Sensor on a Modified Electrode with Functionalized Carbon Nanotubes †

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Abstract: The sensors modified carbon nanotubes and molecularly imprinted polymers are an excellent choice for the determination of D-arabinose, because they have high selectivity and sensitivity for analysis. This allows the control and optimization of the second generation ethanol production process, given the clear understanding of the chemical changes that occur through the hydrolysis of lignocellulosic biomass. For this reason, the present work presents a chemical study of the functional groups of the chemical species present on the sensor surface by the Fourier transform infrared spectroscopy (FT-IR) technique and a morphological analysis by the scanning electron microscopy (SEM) technique.

Keywords: D-arabinose; electrochemical sensor; ethanol

1. Introduction

In order to promote the sustainability and independence of fossil fuels, first generation ethanol is an attractive option as it results in a net free emission of CO_2 due to the fixation of atmospheric CO_2 by plants during their growth [1]. The United States through corn and Brazil through sugarcane are the main producers of first generation ethanol. However, although the technology used for converting these raw materials is well established, they compete with the food chain, leading to the need to find other alternative sources of energy [2,3].

The second and third generation of ethanol are obtained from lignocellulosic biomass and algae, respectively [4]. Brazil has enormous potential to obtain second generation ethanol, given the high availability of this raw material, and even if the development of second generation (2G) production is not very advanced compared to the first one, it must be compensated. by scientific research that validates its use in energy vectors [4,5].

The production of 2G ethanol is mainly characterized by the preprocessing, hydrolysis and fermentation stages [6]. The hydrolysis process, which consists of the degradation of polysaccharides in fermentable sugars, plays an extremely important role for the final yield in 2G ethanol. Thus, the optimization of this process can lead to increased ethanol production [7].

In this sense, a clear understanding of the chemical changes that occur during lignocellulosic biomass hydrolysis is essential for process control and optimization. Through the use of analytical

techniques, process efficiency can be verified by compositional analysis of hydrolysates. The electrochemical technique is characterized by the acquisition of information in real time and in situ, through sensors (electrodes) that promote a fast and sensitive detection of the analyte, with low cost [8]. This makes them a great alternative to other analytical techniques, characterized by slow response and high cost. Electrochemical sensors can be chemically modified to improve their performance. These modifications can be made by introducing thin electroactive films and thick coatings, which would essentially improve greater selectivity and sensitivity of the analyte due to increased surface area [9].

Among the materials used for surface modification, carbon nanotubes stand out for their highly sensitive electrical properties, mechanical strength, chemical stability and volume-surface ratio, where their functionalization helps to improve specificity and interaction with the solution [10,11]. The surface modification can be performed by electrodeposition, whose process is controllable, simple, economical and fast, producing complex nanoscale structures that can be used as active sensor elements for the detection of various materials [12].

The use of nanomaterials in the development of molecularly imprinted polymer (MIP) based sensors is a current trend [13]. A synthesized polymer with predetermined selectivity for some analytes or a group of structurally related species has: high selectivity for the template molecule, chemical stability, low detection limit, easy preparation, low cost and possibility of reuse [14,15].

Electropolymerization of MIPs directly on the sensor surface provides good control of polymer film thickness. A well-established monomer is o-phenylenediamine (o-PD), where interactions with the template molecule are preserved in their spatial arrangement and subsequently stabilized by polymer crosslinking [13,16].

In this research work, the structural and morphological surface characterization of the electrochemical sensors was performed with the FT-IR and SEM techniques. The electrochemical sensors developed are graphite and paraffin compounds, modified with functionalized carbon nanotubes (FMWCNTs) and based on molecularly printed polymers (MIPs), for the determination of D-arabinose. These sensors are an excellent low cost alternative, featuring fast analyzes with high selectivity and good sensitivity, which is extremely important for the control and optimization of second generation ethanol production.

2. Materials and Methods

Potassium chloride (KCl, purity: ≥99.0%), potassium ferrocyanide ($K_3[Fe(CN)_6]$, purity: ≥99.5 %) and histological paraffin (56–58 °C), were purchased from Synth. Acetic acid (CH_3COOH, purity: 97.3%), D-arabinose ($C_5H_{10}O_5$, purity: ≥98.0%), o-Phenylenediamine ($C_6H_8N_2$, flaked, 99.5%), nitric acid (HNO_3, purity: ≥98.0%), dimethylformamide (C_3H_7NO, purity: ≥98.9%) and graphite (<20 μm, synthetic), were purchased from Sigma-Aldrich. Sodium acetate ($C_2H_3NaO_2$, purity: ≥99.0%) was purchased from Dinamica Quimica Contemporanea Ltda (Diadema, Brazil). The oxidation probe solution was 10.0×10^{-3} mol L^{-1} $K_3[Fe(CN)_6]$ in 1.0 mol L^{-1} KCl. Stock solution of FMWCNTs was prepared in 0.55 mol L^{-1} of HNO_3. Stock solution of 3.0×10^{-4} mol L^{-1} $C_5H_{10}O_5$ and 7.0×10^{-3} mol L^{-1} $C_6H_8N_2$, were prepared in acetate buffer solution under pH 5.1 for electropolymerization.

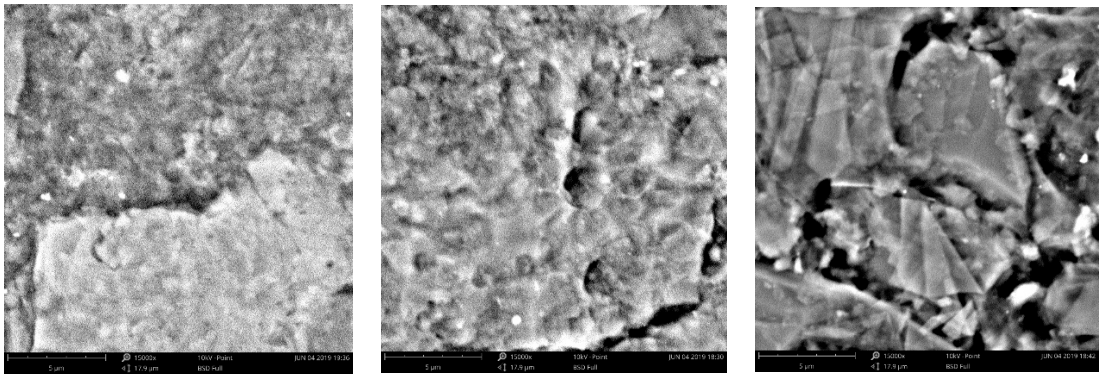
The electrochemical measurements were performed using a Potentiostat/Galvanostat 600E (CH Instruments, Inc.). A conventional three electrodes system was employed with a modified working electrode, a platinum electrode as counter electrode and Ag/AgCl as the referenced electrode. All experiments were carried out at room temperature. Fourier transform infrared spectroscopy (FT-IR) was performed using the IRPrestige-21 (Shimadzu, Japan) with the KBr sample pellet method, using approximately 1% of the sample relative to the mass of KBr per pellet. The analyzes were performed in the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and with 40 replicates per analysis. A scanning electron microscope (PHENOM WORLD Pro X, Thermo Fisher Scientific, Waltham, MA, USA) was used to obtain high resolution images on chemically modified sensor surfaces.

3. Results and Discussion

Electrochemical sensors composed of graphite/paraffin in proportion 7:3 (v/v) are initially modified by electrodeposition of the FMWCNTs in the range of −0.5 V to 1.0 V for 15 consecutive cycles, with a sweep speed of 50 mVs^{-1} [17–20]. And then they are modified by electropolymerization of the MIPs in the range of −0.4 V a 1.0 V for 20 consecutive cycles at a sweep rate of 50 mVs^{-1} in acetate buffer at pH 5.1 containing 7.0×10^{-3} mol L^{-1} o-PD and 3.0×10^{-4} mol L^{-1} D-arabinose (template molecule) [21].

In order to study the morphological specifications of the sensors, the scanning electron microscopy (SEM) technique is used. Figure 1a shows the surface of the graphite and paraffin composite electrode without any modification, while Figure 1b shows a change in its surface due to the electrodeposition of the FMWCNTs. Nanotubes have a highly tangled structure caused by π-pi stacking interactions, which increases the surface area of the electrode and allows the electroactive probes to diffuse easily [22,23].

In addition, functionalized carbon nanotubes cause an increase in effective binding sites, facilitating electron transfer and assigning better catalytic and conductive properties so that the sensor has a higher voltage [24]. Figure 1c shows the sensor morphology after electropolymerization of the MIPs. In this process, a complex is formed between the template molecule and the o-PD functional monomer. Thus, matrix-adapted binding sites are established, ensuring that the polymer has an affinity condition for the analytical object of interest [24].



(**a**) (**b**) (**c**)

Figure 1. Scanning electron microscopy images of the graphite and paraffin composite electrode (**a**), after modification of its surface by electrodeposition of functionalized carbon nanotubes (FMWCNTs) (**b**), after further modification of its surface by electropolymerization of molecularly imprinted polymers (MIPs) (**c**).

The determination of the functional groups present on the electrode surface was performed by the Fourier Transform Infrared Spectroscopy (FT-IR) technique. In Figure 2, spectrum (a) represents graphite/paraffin substrate bands, where at the peak of 3430 cm^{-1} an elongation of -OH associated with the absorbed water is identified. In the region corresponding to the frequencies of 2965–2850 cm^{-1} are the characteristic vibrations of the methyl and methylene group, which correspond to paraffin. In the region of 1600–1100 cm^{-1}, the flexion of OH and the elongations C=O, C-OH and C-O are identified [25]. At peak 2360 cm^{-1}, the CO_2 absorbed by this material is observed [25,26].

In spectrum (b) a broad peak around 3440 cm^{-1} is identified, attributed to the elongation of the vibrations of methyl and methylene groups produced in carbon nanotubes when functionalized with acid; in the region of the peaks 1630 cm^{-1}, 1400 cm^{-1} and 1260 cm^{-1} is identified C=O, O-H and C-O of the stretching vibrations -COOH [27,28]. The peaks of 1550 cm^{-1}, 1100 cm^{-1}, 800 cm^{-1} were attributed to the vibrations C=C, C-O and C-H, respectively [28].

In spectrum (c) MIPs bands are shown, peaks in the region of 1630–1614 cm^{-1} were attributed to elongation C=N, the peaks of 1483 cm^{-1} and 1466 cm^{-1} are attributed to the double C=C bonds of atoms present in the aromatic ring of the phenylenediamine molecule, the 1261 cm^{-1} peak at C-N-C

elongation in benzene units and the 714 cm^{-1} and 524 cm^{-1} peaks at the C-H plane vibrations in the phenylenediamine ring [29].

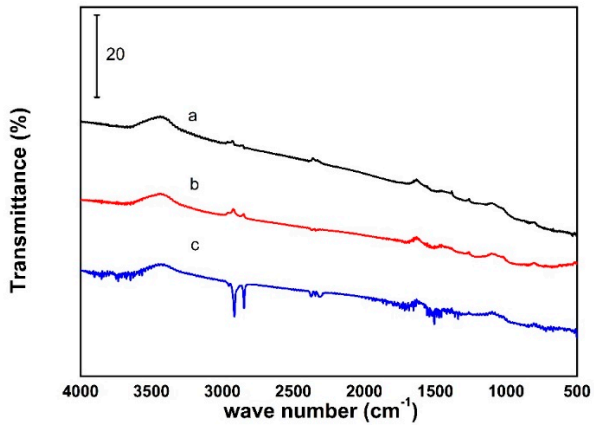


Figure 2. FT-IR spectra of graphite/paraffin (a), functionalized carbon nanotubes (FMWCNTs) (b), molecularly imprinted polymers (MIPs) (c).

4. Conclusions

The morphological and chemical characterization of the molecularly imprinted polymer-based D-arabinose sensor on a modified electrode with functionalized carbon nanotubes was performed using the FT-IR and SEM techniques. Where, morphological change and the presence of new functional groups prove the success of the sensor surface modification, which allows high selectivity and good sensitivity when performing analyzes.

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Conflicts of Interest: The authors declare no conflict of interest.

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