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Poly(Bromocresol Purple)-Based Voltammetric Sensor for The Simultaneous Quantification of Ferulic Acid and Vanillin†

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Abstract: Natural phenolic antioxidants are extensively studied compounds due to their positive health effect and widely distribution in human diet. Simultaneous occurrence in the sample requires selective methods for their determination. Electrochemical sensors based on the polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWCNT) and electropolymerized bromocresol purple has been developed for the simultaneous quantification of ferulic acid and vanillin. The electrode has been characterized by SEM and electrochemical methods and the effectivity of the modifier developed has been confirmed. Thus, novel sensitive voltammetric sensor is simple in fabrication, reliable, cost-effective and can be applied for the foodstuff screening.

Keywords: Electrochemical sensors; carbon nanomaterials; electropolymerization; dyes; natural phenolics; antioxidants

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1. Introduction

Natural phenolic antioxidants are extensively studied compounds in modern electroanalysis due to their positive health effect and widely distribution in human diet [1]. Simultaneous occurrence in the sample requires selective methods for their determination. Among a wide range of natural phenolics, vanillin and its biological precursor ferulic acid [2] are of practical interest. High-performance liquid [3, 4] and thin layer chromatography [5] are usually applied for this purposes. Both phenolics under consideration are electrochemically active that makes possible to use electrochemical methods for their quantification. Although various types of electrochemical sensors have been developed for the simultaneous quantification of natural phenolics of different classes [6-8], ferulic acid and vanillin are out of consideration as analytes.

Thus, current work is focused on the development of electrochemical sensor based on poly(bromocresol purple)-modified electrode for the simultaneous quantification of ferulic acid and vanillin.

2. Materials and Methods

Bromocresol purple (90% purity) and 99% vanillin from Sigma-Aldrich (Germany), 99% ferulic acid from Aldrich (Germany) were used. Their standard 10 mM solutions were prepared in ethanol (rectificate). The exact dilution was used for the preparation of less concentrated solutions.

Polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWCNT) ($d \times l$ is 1.1 nm×0.5-1.0 μm) were purchased from Sigma-Aldrich (Germany). Homogeneous 1.0 mg mL^{-1} suspension of f-SWCNT was got by ultrasonic dispersion for 30 min in dimethylformamide.

All reagents were chemical grade purity. Double distilled water was used for the measurements. The experiments were carried out at laboratory temperature (25±2 °C).

Electrochemical measurements were carried out on the potentiostat/galvanostat Autolab PGSTAT 302N with FRA 32M module (Eco Chemie B.V., Netherlands) and NOVA 1.10.1.9 software. The 10 mL glassy electrochemical cell with working glassy carbon electrode (GCE) with 7.07 mm^2 geometric surface area (CH Instruments, Inc., USA) or modified electrode, a silver-silver chloride saturated KCl reference electrode and a platinum wire as the counter electrode was used.

"Expert-001" pH meter (Econix-Expert Ltd., Russian Federation) equipped with the glassy electrode was applied for pH measurements.

Scanning electron microscopy (SEM) was carried out on the high-resolution field emission scanning electron microscope MerlinTM (Carl Zeiss, Germany) at the accelerating voltage of 5 kV and emission current of 300 pA.

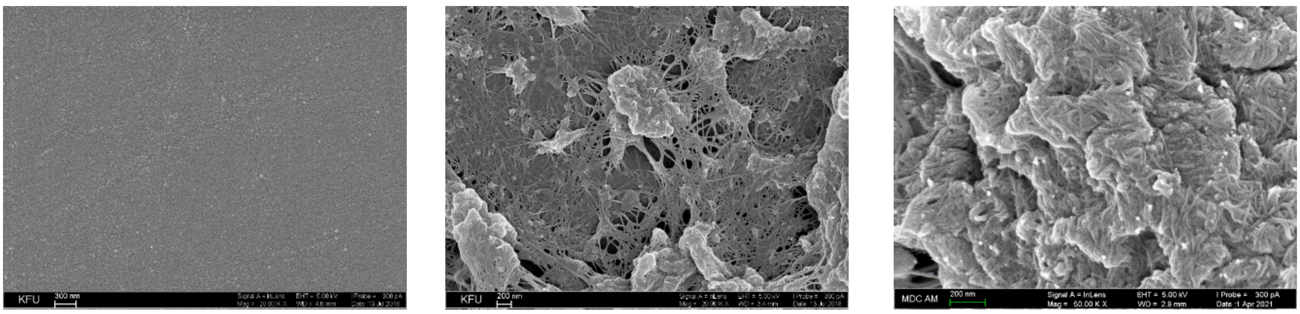
3. Results and Discussion

3.1. Characterization of the Electrodes

Bromocresol purple forms non-conducting film that is confirmed by disaaperance of the oxidation peak with increase of the cycles number and typical for the electropolymerization of phenolics [9].

Conditions of bromocresol purple potentiodynamic electropolymerization (monomer concentration, number of scans, supporting electrolyte pH, electrolysis parameters) have been optimized in order to find the best voltammetric response of the co-existed ferulic acid and vanillin. The peak potential separation of 170 mV on polymer-based electrode is not affected by electropolymerization conditions while oxidation currents change statistically significantly. The best response has been obtained for the poly(bromocresol purple) obtained by 10-fold potential cycling from 0.1 to 1.2 V with scan rate of 100 mV s^{-1} from 25 μM monomer solution in 0.1 M phosphate buffer pH 7.0.

The electrodes have been characterized by SEM (Fig. 1). The data obtained confirm successful immobilization of nanomaterial on the electrode surface.



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

Figure 1. SEM-images for (**a**) CGE; (**b**) CGE/f-SWCNT; (**c**) CGE/f-SWCNT/Poly(bromocresol purple).

Effective surface area of the electrodes have been evaluated using 1.0 mM $[Fe(CN)_6]^{4-}$ as a redox probe under conditions of cyclic voltammetry and chronoamperometry (for GCE). Cottrell equation for GCE and Randles-Sevcik equation for the cyclic voltammetry data have been applied. 5.1-Fold increase of the effective surface area for polymer-modified electrode *vs.* bare GCE has been obtained that leads to the ferulic acid and vanillin oxidation current increase. Electrochemical impedance spectroscopy (EIS) has been performed in the presence of $[Fe(CN)_6]^{4-/3-}$ as a redox probe at 0.23 V. EIS data show 7.2-fold lower charge transfer resistance for the poly(bromocresol purple)-based sensor in comparison to GCE that means increase of the electron transfer rate.

3.2. Simultaneous Quantification of Natural Phenolic Antioxidants

The well-resolved oxidation peaks of the ferulic acid and vanillin at 0.732 and 0.903 V respectively with potential separation of 170 mV has been obtained on the sensor created (Fig. 2).

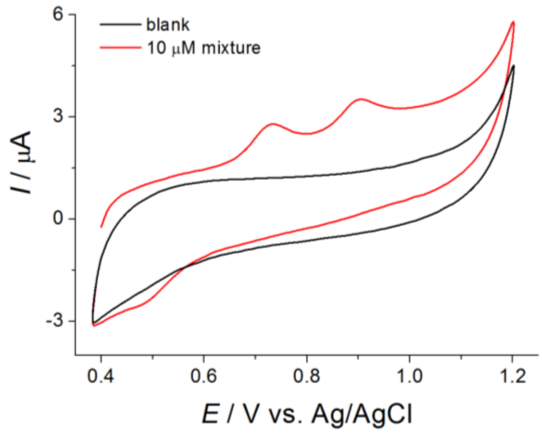


Figure 2. Cyclic voltammogram of 10 μM mixture of ferulic acid and vanillin on poly(bromocresol purple)-based electrode in Britton-Robinson buffer pH 2.0.

The analytes electrooxidation parameters have been studied. Both phenolics are oxidized under diffusion control and irreversible with participation of two electrons and protons (Fig. 3).

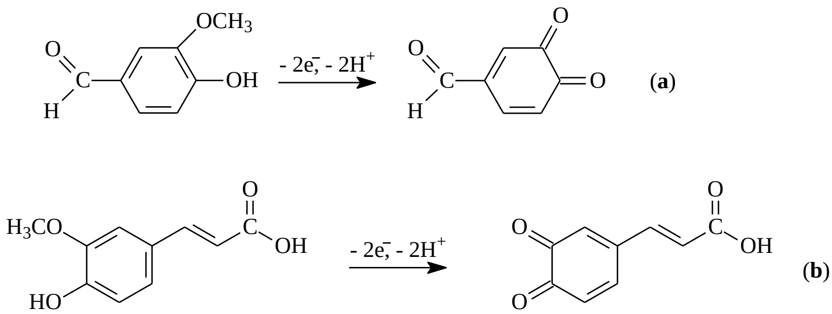


Figure 3. Electrooxidation scheme of (**a**) vanillin and (**b**) ferulic acid.

Sensor developed has been operated under conditions of differential pulse voltammetry. The pulse parameters have been optimized and found that modulation amplitude of 75 mV and modulation time of 25 ms provide the best response of target analytes. Sensor allows direct simultaneous quantification of ferulic acid and vanillin in the ranges of 0.1-5.0 and 5.0-25 μM for both analytes with the detection limits of 72 and 64 nM, respectively. The accuracy of determination has been tested on the model mixtures of ferulic acid and vanillin. The relative standard deviation and recovery values obtained confirm the absence of random error and precision of the sensor developed.

Thus, novel sensitive voltammetric sensor is simple in fabrication, reliable, cost-effective and can be applied for the foodstuff screening.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest

Reference

1. Bhuyan, D.J.; Basu, A. Phenolic Compounds potential health Benefits and toxicity; In *Utilisation of Bioactive Compounds from Agricultural and Food Waste*, 2nd ed.; Vuong, Q.V., Ed.; CRC Press: Boca Raton, USA, 2017; Chapter 2, pp. 27-59.
2. Gallage, N.J.; Hansen, E.H.; Kannangara, R.; Olsen, C.E.; Motawia, M.S.; Jørgensen, K.; Holme, I.; Hebelstrup, K.; Grisoni, M.; Møller, B.L. Vanillin formation from ferulic acid in *Vanilla planifolia* is catalysed by a single enzyme. *Nature Communications* **2014**, *5*, 4037.
3. Ranadive, A.S. Vanillin and related flavor compounds in vanilla extracts made from beans of various global origins. *J. Agric. Food Chem.* **1992**, *40*, 1922–1924.
4. Sinha, A.K.; Verma, S.C.; Sharma U.K. Development and validation of an RP-HPLC method for quantitative determination of vanillin and related phenolic compounds in *Vanilla planifolia*. *J. Sep. Sci.* **2007**, *30*, 15–20.
5. Hingse, S.S.; Digole, S.B.; Annapure, U.S. Method development for simultaneous detection of ferulic acid and vanillin using high-performancethin layer chromatography. J. Anal. Sci. Technol. **2014**, *5*, 21.
6. Ziyatdinova, G.K.; Guss, E.V.; Morozova, E.V.; Budnikov, H.C. An electrode based on electropolymerized sunset yellow for the simultaneous voltammetric determination of chlorogenic and ferulic acids. *J. Anal. Chem*. **2021**, *76*, 371–380.
7. Zhupanova, A.; Guss, E.; Ziyatdinova, G.; Budnikov, H. Simultaneous voltammetric determination of flavanones using an electrode based on functionalized single-walled carbon nanotubes and polyaluminon. *Anal. Lett*. **2020**, *53*, 2170–2189.
8. Guss, E.V.; Ziyatdinova, G.K.; Zhupanova, A.S.; Budnikov, H.C. Voltammetric determination of quercetin and rutin in their simultaneous presence on an electrode modified with polythymolphthalein. *J. Anal. Chem*. **2020**, *75*, 526–535.
9. Yang, G.-J.; Qu, X.-L.; Zhu, A.-P.; Wang, C.-Y.; Qu, Q.-S.; Hu, X.-Y. Characterization, growth mechanism and application of network poly(bromophenol blue). *J. Electroanal. Chem.* **2007**, *604*, 48–56.