Voltammetric electronic tongue based on carbon paste electrodes modified with biochar for phenolic compounds stripping detection

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Abstract

Biochar is a charcoal produced from the biomass pyrolysis process that presents a highly porous and functionalized surface. In the present work an array of carbon paste electrodes (CPE) made of different forms of carbon (graphite, carbon nanotubes and activated biochar) was evaluated in the development of electronic tongue for discrimination and stripping voltammetric determination of catechol (CAT), 4-ethylcatechol (4-EC) and 4-ethylguaiacol (4-EG) phenolic compounds. Morphological characterization of carbon materials and electrodes surfaces was performed by scanning electron microscopy (SEM) and semi-quantitative elemental composition by energy dispersive spectroscopy (EDS). Electrochemical Impedance Spectroscopy (EIS) measurements was used for electrochemical characterization of electrodes. Cyclic voltammetry measurements were performed for the phenolic compounds evaluated using different concentrations. Principal component analysis (PCA) was performed to evaluate the qualitative analysis. Quantitative data modeling was done using artificial neural networks (ANN). The proposed sensor array presented analytical potentiality allowing the distinction and determination of CAT, 4-EC and 4-EG by using chemometric processing. The method showed sensibility, reproducibility and a good linearity (R^2 > 0.9940) for three compounds evaluated. Spontaneous preconcentration of three compounds was possible using all three sensors, which allows the application of these as passive samplers for remote determinations of phenolic compounds in samples of wines.

Keywords: Activated biochar, Voltammetric tongue, Phenolic compounds; Brett character.

1. Introduction

Polyphenols are chemical compounds associate with health benefits since they act as antioxidants preventing the cell damage. These species are natural constituents of the wines and provide intrinsic characteristics [1] but, the presence of certain phenolic compounds in foods and drinks can be related with undesired aromas and flavors [2, 3]. At high concentration levels, these compounds may cause organoleptic defects, deteriorating the quality of the wines, and producing similar aromas to "leather" and "horse" odor, for example [4]. These aromas are associated with the proliferation of *Brettanomyces* and *Dekkera* yeasts families, occasioning the called Brett character [5, 6]. The presence of ethylphenols becomes problematic when the content exceeds the value of 0.5 mg L^{-1}, the lower limit at which they can be detected by the human gustatory system [3, 7].

The determination of phenolic compounds can be performed by several analytical techniques, such as chromatographic [8, 9], spectrophotometric [10, 11], colorimetric, such as Folin-Ciocalteu [12, 13], and voltammetric methods [14, 15]. Voltammetric electronic tongues (ET) can be used as an analytical tool for qualitative evaluation of wines, aiming at the differentiation of samples, or for simultaneous quantitative determination analysis of these species [16]. The approaches employed in the ET can be associated with the ability of human taste to determine flavors [17]. In general, this system is composed of a multisensor array, where each sensor can present varying sensitivity and selectivity for the analytes considered [18]. Sensors responses shall present a cross-sensitive to different species which can be used for improving the detectability and promoting a global selectivity [19]. Considering that the sensor array can generate a great amount of complex data, the application of multivariate pattern recognition techniques is mandatory as commonly used for data processing [17, 20].

For the sensing field, carbon paste electrodes (CPE) present interesting characteristics as low background currents, versatility and simplicity of construction and/or modification, and low cost [21, 22]. Several works report the use of non-modified [23, 24] and modified carbon paste electrodes for ET application [20, 25]. Modifiers such as metal complexes [26, 27], metal oxide nanoparticles [28], polypyrrole [29, 30], phthalocyanines [27, 31] and carbon nanotubes [32] have been successfully used for carbon paste construction in ET. Recently, a carbonaceous material called biochar has been used as electrode modifier for construction of voltammetric sensors [33-36]. Biochar is a charcoal produced from the biomass pyrolysis process, under low or no oxygen conditions. This material is based on research studies of highly fertile dark Amazonian soil, known as "Terra Preta de Índio" (TPI), rich in organic matter, nitrogen and phosphorus [37, 38]. Biochar can be obtained by vegetable or animal biomass residues, as industrial and agricultural wastes. This carbon-rich material present a highly porous and functionalized surface which promotes an effective interaction with organic and inorganic species [39-42]. The chemical activation of this material can promotes a significant increase of surface active sites improving its sorption capacity [43, 44]. In the present work an array of carbon paste electrodes (CPE) made of different forms of carbon was evaluated in the development of electronic tongue for discrimination and stripping voltammetric determination of catechol (CAT), 4-ethylcatechol (4-EC) and 4-ethylguaiacol (4-EG) phenolic compounds. The array used three electrodes: an unmodified carbon paste (CPE), a CPE modified with carbon nanotubes (CPME-CNT) and a CPE modified with activated biochar (CPME-AB).

2. Material and Methods

2.1 Reagents and Solutions

All reagents used were of analytical grade and used without prior purification. Solutions were prepared using deionized water by a Millipore Milli-Q system (18 MΩ cm). Sodium phosphates monobasic and dibasic, catechol, 4-ethylcatechol and 4-ethylguaiacol, mineral oil and graphite powder were acquired from Sigma Aldrich (St. Louis, USA). Nitric acid from Neon (Suzano, Brazil) was used as oxidant agent for biochar activation. Purified multi-walled carbon nanotubes were purchased from SES Research (Houston, USA) and were used as modifier electrodes. PBS used as preconcentration solution and supporting electrolyte was prepared with sodium phosphates monobasic and dibasic in concentration of 50 mmol L^{-1} and with 0.1 mol L^{-1} KCl.

2.2 Electrodes Array Construction

Voltammetric measurements were performed using an Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode and a platinum auxiliary electrode. A sensor array of three working electrodes based on carbon paste was used: unmodified electrode (CPE) and modified electrodes with multi-walled carbon nanotubes (CPME-CNT) and activated biochar (CPME-AB). Biochar was obtained from pyrolysis of castor oil cake biomass at 400 ºC and submitted to a chemical activation with HNO_3 50 % (v/v) under refluxing reaction [34].

The composition (w/w) of CPE electrode (unmodified) was of 25 % mineral oil and 75 % graphite powder. Modified electrodes were prepared using proportion (w/w) of 25 % mineral oil, 60 % graphite powder and 15 % modifier (Biochar or carbon nanotubes) [34, 45]. Carbon paste components were thoroughly homogenized and compacted in the electrodes. The working electrodes (**Figure 1**) were prepared using an electrical connector (A) and a copper disk (Ø = 5.0 mm) iron soldered to the former as the ohmic contact (B).

Subsequently, a PVC support was assembled into the connector (C) so that there was a gap of 2.0 mm between the support surface and the copper contact. Finally, the carbon paste was compacted in this gap (D), and the electrode surface was polished in paper. The electrode ready for use had dimensions of 6.0 mm in diameter and 30 mm in height (E).

Figure 1

2.3 Electrochemical Procedures

Voltammetric measurements were carried out using a Metrohm Multi-channel Autolab potentiostat/galvanostat with data management by the GPES 4.9 software. In order to evaluate the electroactive area of the carbon paste electrodes, cyclic voltammetry measurements were performed in the potential region between -0.5 and 0.5 V, varying the scan rate from 10 to 50 mV s^{-1}, in presence of 5.0 mmol L^{-1} potassium ferrocyanide (II) and potassium ferricyanide (III) ($K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$). Electrochemical Impedance Spectroscopy (EIS) measurements were also performed using potential of 0.17 V, frequency from 500 MHz to 50 mHz and amplitude of 10 mV. Electrical parameters of the sensors were obtained in function of an equivalent Randles circuit. A Methrohm Autolab potentiostat/galvanostat and FRA software for the data management were used.

The experimental procedure for phenolic compounds determination was developed in previous optimized experimental and instrumental conditions [34, 46], according to the following summarized three steps: **1)** Preconcentration of the phenolic compounds was performed in 50 mmol L^{-1} PBS solution with pH adjusted to 7.4. The electrodes were soaking in the solution under open circuit potential conditions with constant stirring for 5 minutes. **2)** After that, electrodes were gently washed and transferred to the electrochemical cell and cyclic voltammetry measurements were performed from -0.3 to 0.8 V, using 50 mmol L^{-1}

PBS pH 7.4 as supporting electrolyte, and scan rate of 50 mV s^{-1}. **3)** After each measurement, the electrodes were submitted to an electrochemical cleaning step by cyclic voltammetry in the same supporting electrolyte solution. These measurements were performed in the potential range between -0.5 and 1.2 V, with scan rate of 100 mV s^{-1} up to 10 cycles.

2.3.1 Analytical Performance of Electronic Tongue (ET)

Cyclic voltammetry measurements were performed in order to obtain analytical curves for three phenolic compounds evaluated using concentrations values in the range of 30–540 mmol L^{-1} for catechol, 0.2–350 μmol L^{-1} for 4-ethylcatechol and 1.0–120 μmol L^{-1} for 4-ethylguaiacol. To evaluate the ET performance for simultaneous quantification of the phenolic compounds, measurements in concentrations range from 5.0 x 10^{-5} to 1.0 x 10^{-4} mol L^{-1} were done. For this, two data subsets were used, training and testing sets. Training was performed with 27 samples distributed based on a 3^3 full factorial design, used to build the response model. Testing was composed for 10 samples distributed randomly in the concentration levels used, and helped to predict the results model.

2.3.2 Data Processing

Principal component analysis (PCA) was performed to evaluate the qualitative analysis of the voltammetric responses. Quantitative data modeling was done using artificial neural networks, with their input fed with voltammetric data previously compressed using the Discrete Wavelet Transform (Daubechies mother function and second level of compression).

Data chemometric processing was performed by use of MATLAB 7.1 programming environment (MathWorks, Natick, MA, USA), plus its Neural Network and Wavelet toolboxes, with use of routines written by the authors.

3. Results and Discussion

3.1 Morphological Characterization

Morphological characterization of carbon materials and electrodes surfaces was performed by scanning electron microscopy (SEM) and semi-quantitative elemental composition by energy dispersive spectroscopy (EDS). SEM images of graphite powder, carbon nanotubes and activated biochar used to electrodes construction were obtained with enlargement of 50000 times. **Figure 2A** showed the characteristic graphite structure, that can be described as parallel layers of hexagonal rings, forming called sheets [47, 48]. **Figure 2B** presented typical images of multi-wall carbon nanotubes with average size structures of 10–30 nm in diameter and lengths up to 1.0–15 μm. Activated biochar showed a distinct surface, with an irregular and porous carbonaceous structure (**Figure 2C**). This is due to the thermal and activation treatments that promote an increase of porous and functional groups in biochar, modifying the surface [34, 49]. The surface of carbon paste electrodes revealed that these three different carbon structures promote morphological and composition variations as observed by SEM images (**Figure 3D-F**) and EDS results (**Figure S1** and **Table S1**). CPE was prepared by graphite and mineral oil and showed a homogeneous surface, with a composition founded by only carbon. For CPME-CNT, the presence of carbon nanotube did not interfere in the carbon paste composition since that carbon nanotubes structure are composed by sp^2 carbon as graphite [50]. Contrarily, CPME-AB showed a distinct morphological surface, due to the presence of biochar. By the SEM image (**Figure 2F**), the presence of graphite was verified by the darker region and biochar was distinguished by the clearest region. EDS analysis of this material showed a greater amount of carbon, and in minor amount of oxygen, nitrogen, and other mineral elements (magnesium, aluminum,

silicon and sulfur). These species are also prevenient of the castor oil cake feedstock and remain after activation treatment [51, 52].

Figure 2

3.2 Electrochemical Characterization

Initial characterization of electrochemical properties of carbon paste electrodes constructed was carried out in PBS at pH 7.0 containing 5.0 mmol L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ with scan rate of 10 mV s^{-1} (**Figure 3A**). Anodic and cathodic current peaks were observed for all electrodes which are relating to $[Fe(CN)_6]^{-3} + e^- \leftrightarrows [Fe(CN)_6]^{-4}$ redox reaction. CPE (unmodified) showed higher current peak intensities with a separation of peak potentials of 100 mV. Carbon paste modified electrode employing CNTs (CPME-CNT) showed a similar voltammetric behavior. For the electrode modified with activated biochar (CPME-AB) a decrease in the peak current and an increase in the separation of anodic and cathodic potentials peaks was observed. The higher ΔEp suggests some difficulty of electron transfer for CPME-AB which can be related to low electric conductivity of modifier, as well as negative surface charge associated with functional groups (eg. carboxylic acid) present at biochar. Thus, the voltammetric profiles observed are in agreement with those expected considering that CPE and CPME-CNT are better electrically conductive materials compared with CPME-AB.

Figure 3

EIS measurements were performed in PBS pH 7.0 solution containing 5.0 mmol L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$. Nyquist plots were obtained for three proposed sensors (**Figure 3B**) and an equivalent Randles circuit was proposed to fit the experimental data to provide

solution resistance (R_s), charge transfer resistance (R_{ct}) related to the $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ redox reaction and the capacitance of interface (C_s) (**Table S2**). The Nyquist diagram shows an increase of the semicircle when comparing the CPE with the modified electrodes. An increase of the R_{ct} values from 839.1 for CPE to 855.7 and 969.6 Ω for CPME-CNT and CPME-AB was observed, respectively. This indicates that the presence of modifiers (carbon nanotubes and activated biochar) decreases the electron transfer reaction rate, making more difficult the redox process [53]. This behavior was concordant with the results obtained from CV measurements and consistent with EIS results verified by other works that used modified electrodes with carbon materials [54]. For example, Dong et al. [55] demonstrated that the presence of biochar influences the transfer resistance of the unmodified electrode. Biochar produced at moderate temperatures (300–600 ºC) showed an increase of R_{ct} of unmodified electrode from 495 Ω to 3987 Ω (biochar at 400 ºC modified electrode), in presence of $[Fe(CN)_6]^{3/4-}$. These results can be explained by properties of modifier being that biochar obtained at moderate temperatures (~400 ºC) presents more disordered carbon of nonconductive remaining cellulosic compounds [56].

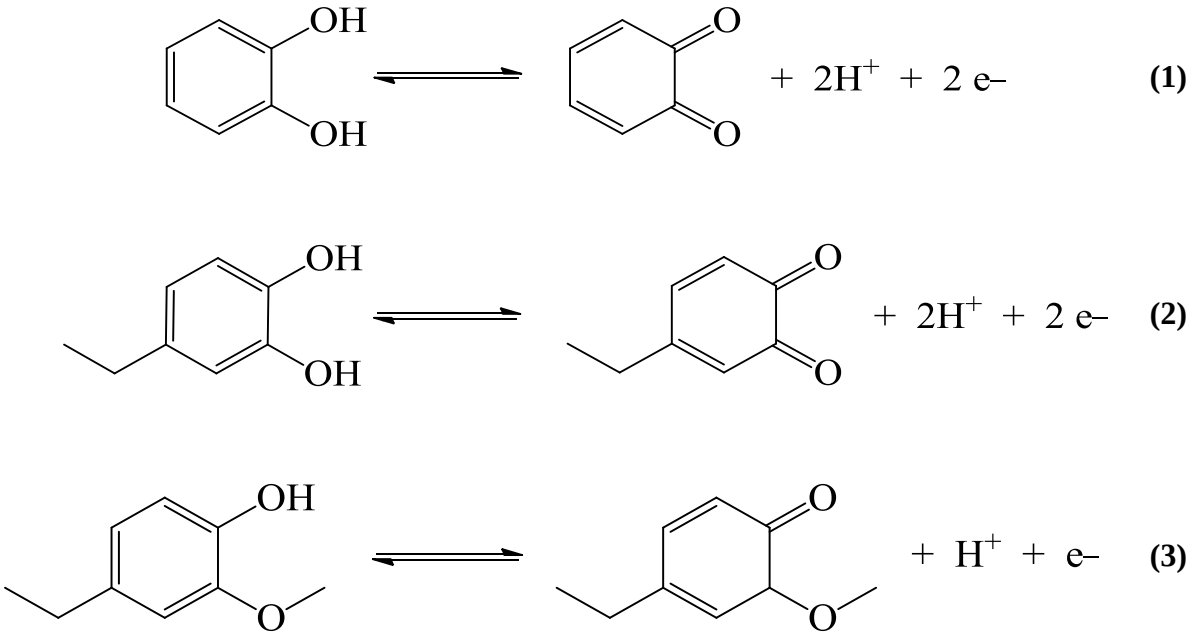
3.3 Electrochemical Behavior of Sensors Array

Cyclic voltammetric measurements were performed using CPE unmodified, CPME-CNT and CPME-AB after spontaneous preconcentration of the analytes individually. Preconcentration step was carried out in 5.0 mmol L^{-1} PBS at pH 4.5 solution containing the phenolic compound in concentration of 1.0 x 10^{-4} mol L^{-1} for 5 minutes, under constant stirring. After this, stripping cyclic voltammetry measurements were carried out in PBS at pH 7.4 solution, between -0.3 and 0.8 V, with scan rate of 50 mV s^{-1} (**Figure 4A-C**).

Figure 4

From the voltammograms obtained was possible to verify that all electrodes were efficient in the catechol (CAT), 4-ethylcatechol (4-EC) and 4-ethylguaiacol (4-EG) adsorptive preconcentration at three proposed sensors. Catechol (CAT – 1,2-dihydroxybenzene) showed a reversible response signal, related to oxidation to o-quinone (1,2-benzoquinone) and its reduction reaction in reverse scan (**Reaction (1)**) [57]. For catechol, CPME-CNT showed a higher magnitude of signal, anodic and cathodic peaks were observed at potentials of 0.16 and 0.00 V respectively, demonstrating a better reversibility of the redox reaction. CPE and CPME-AB presented a shifting of anodic peaks potential for 0.24 and 0.46 V, respectively. In addition, CPME-CNT showed an increase of anodic current peak of 1.5 and 3.0 times, compared to CPME-AB and CPE respectively. The redox reactions for volatile phenols were proposed considering the oxidation of these phenolic compounds to their respective quinones forms, as presented in **Reactions (2)** and **(3)**, for 4-EC and 4-EG, respectively. For ethylphenols, CPME-AB showed better response signals following the order: CPME-AB > CPME-CNT > CPE. For 4-EC, the biochar electrode presented approximately double of response signal in comparison to other electrodes. These results suggest that biochar has more affinity to interact and preconcentrate with volatile phenols once these are more apolar than catechol. It is known that the biochar presents a highly porous and functionalized surface, mainly with oxygenate functional groups. The biochar may present different mechanisms for sorption, such as π-π interactions between carbonaceous surface and aromatic ring presents in target molecules. This effect improves the physical adsorption of phenolic compounds at surface of modified electrode [49, 58, 59]. From the results it was demonstrated the analytical potential of the proposed sensors for the simultaneous determination of phenolic compounds, since that different voltammetric

sensibilities and distinct profiles were verified for the electrodes evaluated which contribute for model phenolic compounds quantification.



After checking the proper adsorption of the phenolic compounds at the carbon electrodes, it was also verified that their removal was not complete, promoting a "memory effect". Thus, an electrochemical cleaning step (Step 3) was performed. For this purpose, electrodes were submitted to potential scans from -0.3 to 1.2 V under cyclic voltammetry conditions in PBS pH 7.0 solution, with scan rate of 100 mV s^{-1} for 10 cycles (**Figure S2**). After the cleaning step the faradaic signals relate to phenolic compounds were not observed suggesting that the clear strategy adopted was effective for removal of the analytes from the electrodes surface. Once the above related accumulation was minimized, reproducibly of the method was evaluated by consecutive cyclic voltammetry measurements (n=25) in presence of phenolic compounds for three sensors (**Figure S3**). The studies were performed using the same analytical operating conditions as above. From the voltammetric measurements, relative standard deviations (RSD) of 6.58, 3.75 and 7.15 % for CPE, CPME-CNT and

CPME-AB, respectively, were found for the oxidation peak currents. These values demonstrated that the method presented good reproducibility for 25 successive measurements.

3.4 Analytical Performance of Sensor Array

To verify the analytical performance of the proposed sensors, analytical curves (**Figure 4D-F**) as well as figures of merits (**Table 1**) for each phenolic compound were obtained from cyclic voltammetry measurements recorded after preconcentration of target compound. Analytical curves obtained with the three evaluated sensors showed a linear dynamic range (LDR) from 30 to 540 μmol L^{-1} for catechol. Sensitivity values of 4.35, 9.28 and 6.72 μA L $mmol^{-1}$ and limits of detection of 2.47, 1.37 and 1.86 μmol L^{-1} were verified for CPE, CPME-CNT and CPME-AB, respectively. For 4-EC and 4-EG determinations, CPME-AB showed the better analytical performance with sensitivity of 18.7 and 35.9 μA L $mmol^{-1}$ and limit of detection of 0.086 and 0.094 μmol L^{-1}, respectively. Considering the difference between sensitivities obtained for electrodes and analytes is possible to suppose that the array of carbon paste electrodes can be suitable to perform the compounds discrimination and to build and predict the response model.

Table 1

Then, in order to confirm if the sensor array proposed is able to perform the identification of the phenolic compounds, i.e. the signals provided by the three sensors were not collinear, sensitivities of the voltammetric calibrations responses obtained were verified by PCA analysis. Score plots of first (PC1) and second (PC2) components were confronted in function of carbon paste electrodes and phenolic compounds (**Figure S4**). Firstly, it was

observed that the first PC takes into account most of the information obtained (96.9 %). First two PC the accumulated explained variance was almost 100 %, which means that the variance contained in the original information can be practically represented by only the PC1 and PC2 coordinates. The analyzed data showed a relative dispersion in different quadrants, between each phenolic compound, indicating that the electrodes have the ability to discriminate each species.

After the data from different subsets were collected, the voltammograms were compressed by use of DWT (discrete wavelet transform) with compression details already determined, and analyzed by ANN (artificial neural network) model, that was more adequate to the system proposed. This model was constructed by a training subset and this performance was evaluated by a testing subset, for three phenolic compounds in predicted concentrations (5.0×10^{-5}, 7.0×10^{-5} and 1.0×10^{-4} mol L^{-1}). **Figure 5** shows the predicted and expected concentrations relation for the analytes. For training subset a satisfactory trend was obtained, with a linear regression (blue solid line) very similar from the theoretical line (black dashed line). In addition, good correlation coefficients ($R^2 > 0.9940$) were obtained for three compounds, as noted by dates of **Table 2**. For testing subset, linear results also were considered satisfactory in the concentration range evaluated, with $R^2 > 0.8292$ (red dashed line). These lower correlation coefficients can be related to the random measurements carried out, but were nonetheless consistent with the expected and predicted concentrations.

Figure 5

Table 2

4. Conclusions

In this work we highlight the use of carbon paste electrodes applied in an electronic tongue to phenolic compounds stripping determination. Proposed carbon based sensors presented easy construction and manipulation, using waste materials as biochar. The sensor array

presented analytical potentiality allowing the distinction and determination of catechol, 4-ethylcatechol and 4-ethylguaiacol by using chemometric processing. The method showed a good linearity, sensibility and reproducibility for determinations. Spontaneous preconcentration of three compounds was possible using all three sensors, which allows the application of these as passive samplers for remote determinations of phenolic compounds.

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Figure 1 – Electrodes construction procedure: Copper rod coupled to a connector (A); Fixing a copper disc (Ø = 5.0 mm) (B); Assembly of PVC support on the connector (C), Compacting the carbon paste (D); Ready-to-use electrode (E).

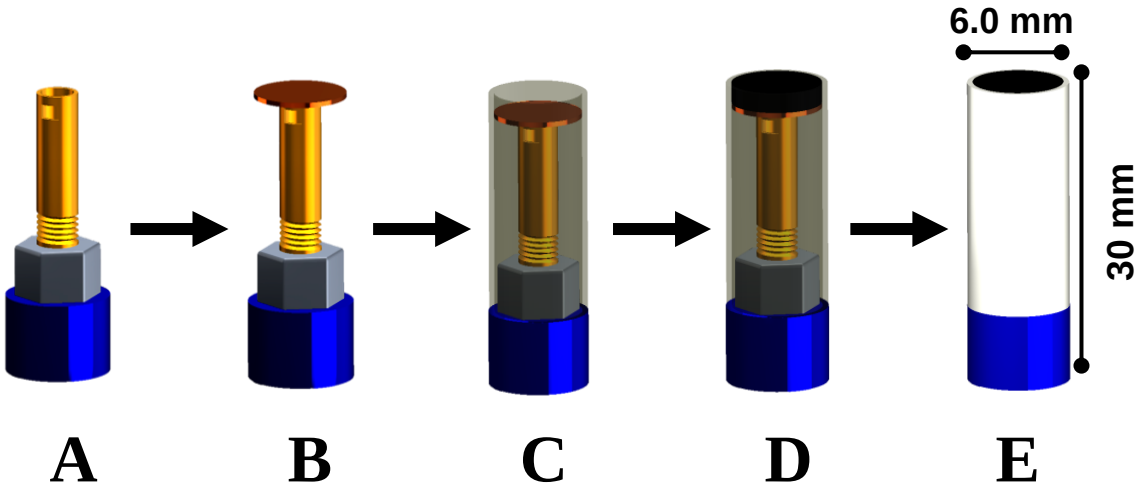

Figure 2 – Cyclic voltamograms (A) and Nyquist diagrams (B) obtained for CPE, CPME-CNT and CPME-AB in presence of 5.0 mmol L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$. Scan rate of 10 mV s^{-1}.

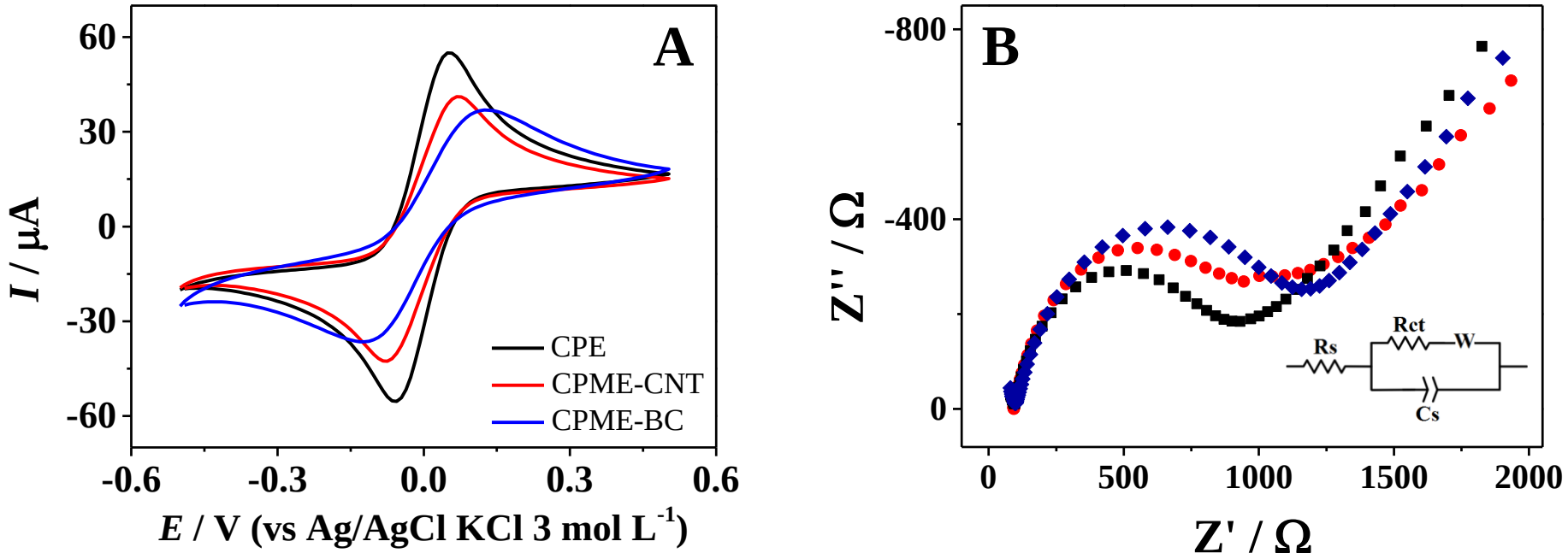

Figure 3 – SEM images obtained for graphite (A), carbon nanotubes (B) and activated biochar (C) with 50000x enlargement, and for CPE (D), CPME-CNT (E) and CPME-AB electrodes surfaces (F) with 1000x enlargement.

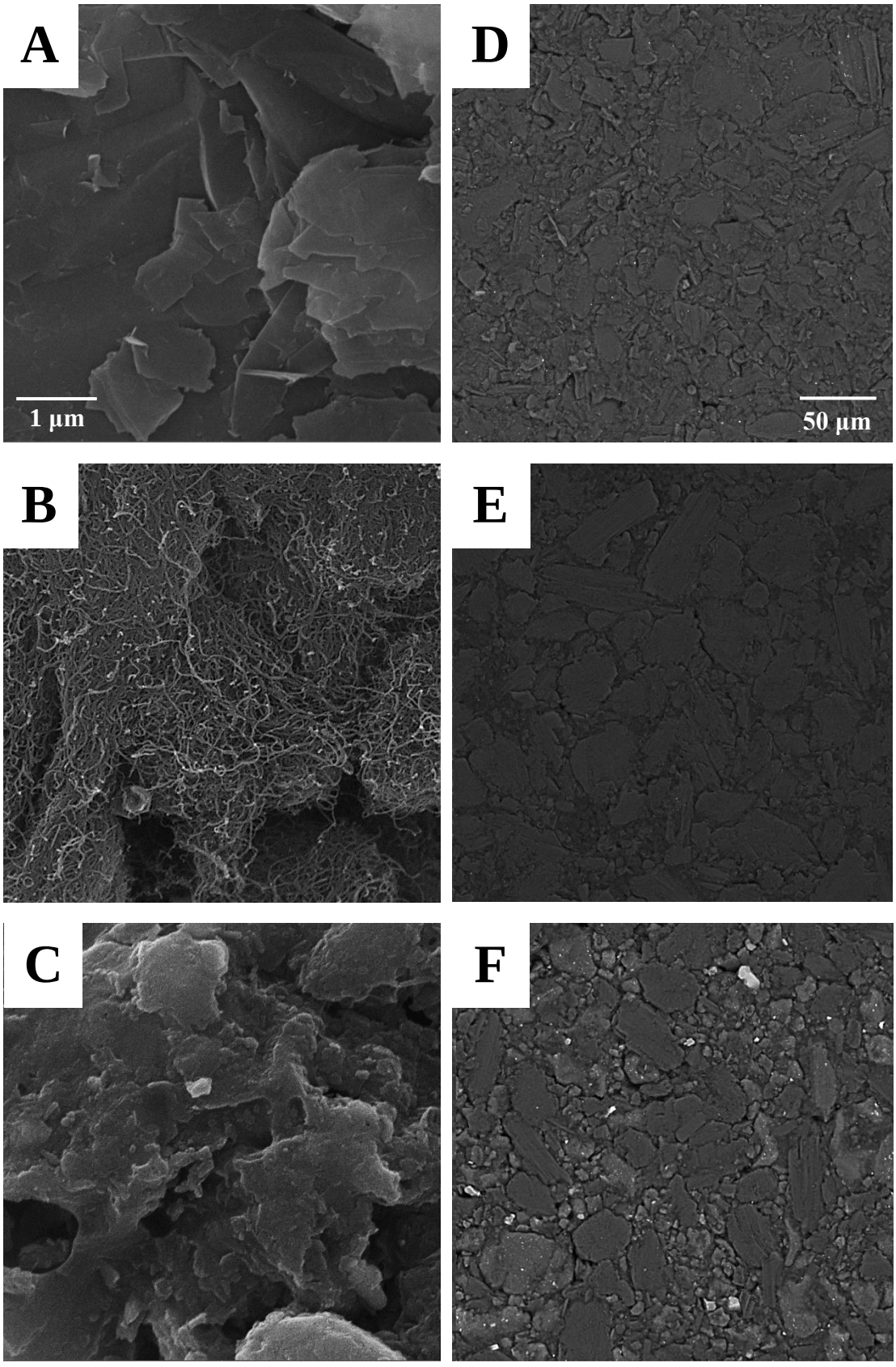

Figure 4 – Cyclic voltammograms and analytical curves obtained with CPE (A, D), CPME-CNT (B, E) and CPME-AB (C, F) electrodes for the phenolic compounds CAT (—), 4-EC (—) and 4-EG (—). Supporting electrolyte: 5.0 mmol L^{-1} PBS at pH 7.4. Scan rate: 50 mV s^{-1}.

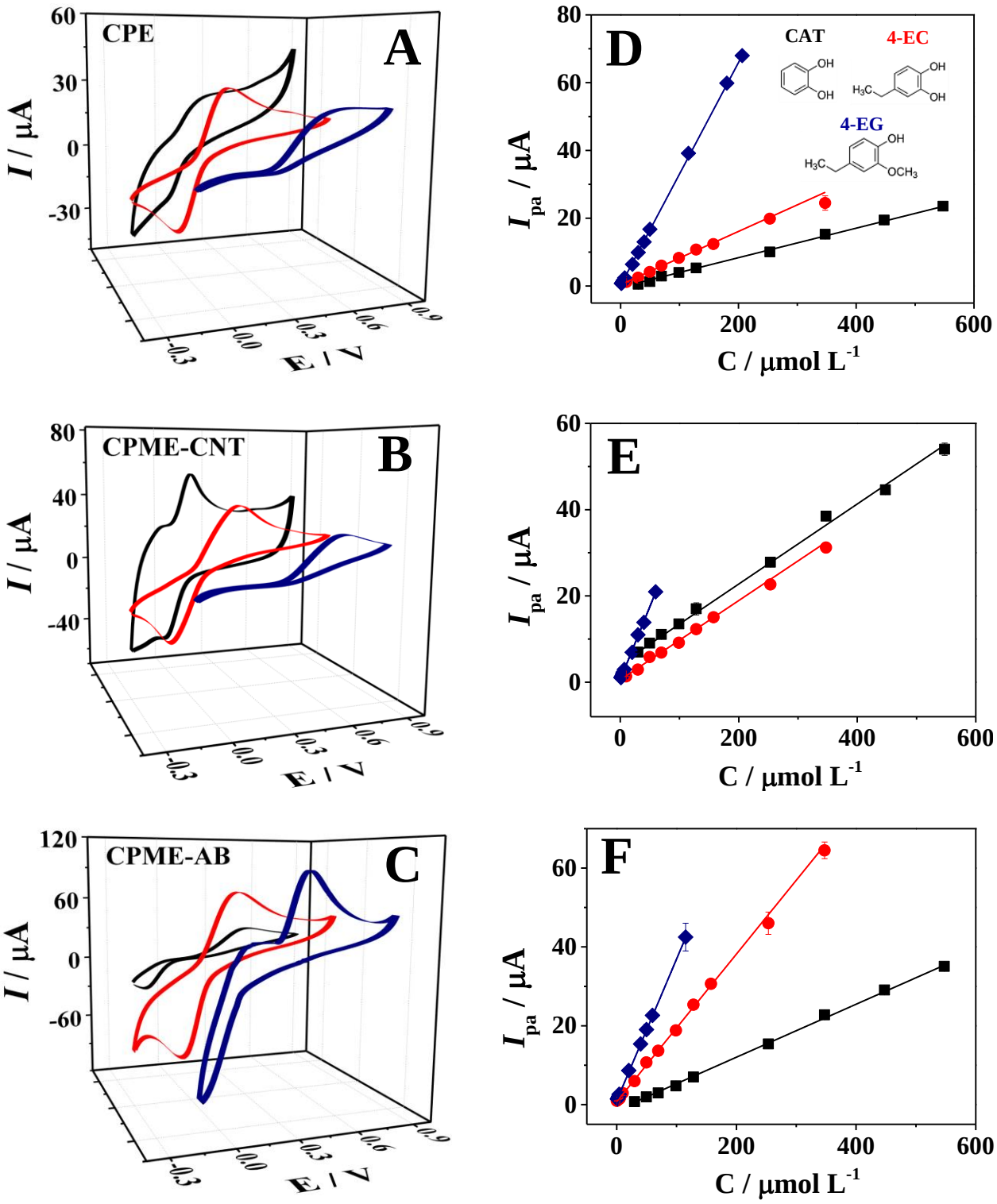

Figure 5 – Modeling ability of the optimized ANN for the expected and obtained concentrations for the training set (blue solid line) and the testing set (red dashed line) for catechol (A), 4-ethylcatechol (B) and 4-ethylguaiacol (C). Black dashed line corresponds to theoretical line.

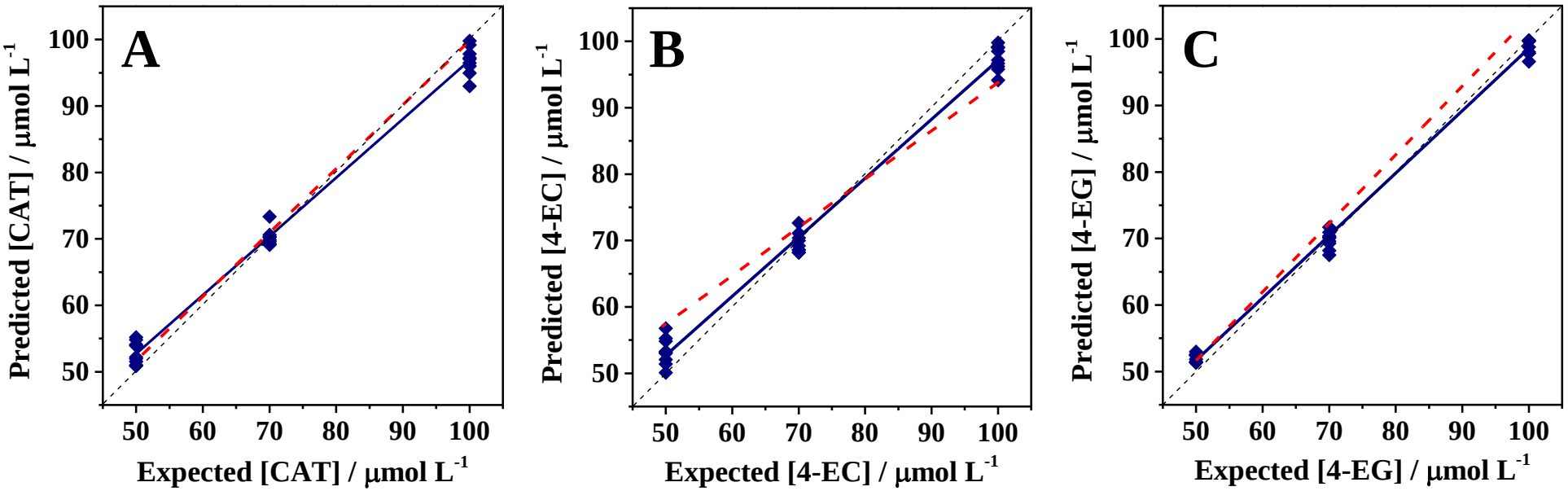

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Table 1 – Analytical parameters obtained for catechol, 4-ethylcatechol and 4-ethylguaiacol with CPE, CPME-AB and CPME-CNT sensors.

Electrode	Phenolic Compound	LDR (µmol L^{-1})	R^2	Slope (µA L $µmol^{-1}$)	LOD (mol L^{-1})	LOQ (mol L^{-1})
CPE	CAT	30–540	0.9968	0.0435	2.47×10^{-6}	8.24×10^{-6}
	4-EC	10–350	0.9965	0.0784	2.82×10^{-7}	3.39×10^{-7}
	4-EG	1.0–210	0.9992	0.328	1.11×10^{-7}	3.71×10^{-7}
CPME-CNT	CAT	30–540	0.9987	0.0928	1.37×10^{-6}	4.58×10^{-6}
	4-EC	10–350	0.9965	0.0919	1.84×10^{-7}	6.13×10^{-7}
	4-EG	1.0–120	0.9992	0.340	1.06×10^{-7}	3.53×10^{-7}
CPME-AB	CAT	30–540	0.9997	0.0672	1.85×10^{-6}	6.16×10^{-6}
	4-EC	0.2–350	0.9983	0.187	8.63×10^{-8}	2.88×10^{-7}
	4-EG	1.0–120	0.9984	0.359	9.37×10^{-8}	3.12×10^{-7}

CPE: Carbon paste electrode; CPME-AB: Carbon paste modified electrode with activated biochar; CPME-CNT: Carbon paste modified electrode with carbon nanotubes; LDR: Linear dynamic range; LOD: Limit of detection (s/N=3); LOQ: Limit of quantification (s/N=10).

Table 2 – Modeling abilities of ANN models, results of the fitted regression curves for the training and testing subsets of catechol (CAT), 4-ethylcatechol (4-EC) and 4-ethylguaiacol (4-EG).

Phenolic Compound	**R^2**	**Slope ($\mu A\ L\ mmol^{-1}$)**	**Intercept ($mmol\ L^{-1}$)**
		Training Subset	
CAT	0.9940	0.891	7.18
4-EC	0.9978	0.885	8.58
4-EG	0.9987	0.938	4.80
		Testing Subset	
CAT	0.8672	0.972	3.08
4-EC	0.8292	0.713	2.22
4-EG	0.9898	0.939	0.089