Carbon-Based Electrodes for Parabens Detection

Aniela Pop, Ianina Birsan, Corina Orha, Rodica Pode, Florica Manea

Abstract—Carbon nanofiber-epoxy composite electrode has been investigated through voltammetric and amperometric techniques in order to detect parabens from aqueous solutions. The occurrence into environment as emerging pollutants of these preservative compounds has been extensively studied in the last decades, and consequently, a rapid and reliable method for their quantitative quantification is required. In this study, methylparaben (MP) and propylparaben (PP) were chosen as representatives for paraben class. The individual electrochemical detection of each paraben has been successfully performed. Their electrochemical oxidation occurred at the same potential value. Their simultaneous quantification should be assessed electrochemically only as general index of paraben class as a cumulative signal corresponding to both MP and PP from solution. The influence of pH on the electrochemical signal was studied. pH ranged between 1.3 and 9.0 allowed shifting the detection potential value to smaller value, which is very desired for the electroanalysis. Also, the signal is better-defined and higher sensitivity is achieved. Differential-pulsed voltammetry and square-wave voltammetry were exploited under the optimum pH conditions to improve the electroanalytical performance for the paraben detection. Also, the operation conditions were selected, i.e., the step potential, modulation amplitude and the frequency. Chronomaprometry application as the easiest electrochemical detection method led to worse sensitivity, probably due to a possible fouling effect of the electrode surface. The best electroanalytical performance was achieved by pulsed voltammetric technique but the selection of the electrochemical technique is related to the concrete practical application. A good reproducibility of the voltammetric-based method using carbon nanofiber-epoxy composite electrode was determined and no interference effect was found for the cation and anion species that are common in the water matrix. Besides these characteristics, the long life-time of the electrode give to carbon nanofiber-epoxy composite electrode a great potential for practical applications.

Keywords—Carbon nanofiber-epoxy composite electrode, electroanalysis, methylparaben, propylparaben.

I. INTRODUCTION

APPLICATION of carbon nanofibers (CNF) as electrode materials for environmental electroanalysis of different emerging pollutants has been extensively studied in the last decades [1]-[5]. One of the advantages of using CNF in electrochemical detection as sensing material is their dual role, as immobilization matrix for certain molecules and also, as electrocatalytic based transducers for the electrochemical signal [1].

CNF based composite materials give the possibility to obtain sensitive, stable, long-life electrodes with reproducible signal that can be applied for the detection of a broad spectrum of pollutant into environment, e.g. pharmaceuticals [2], [3]; persistent organic pollutants [4]; preservatives [5].

Parabens, due to their large utilization as antimicrobial preservatives in food-stuffs, pharmaceuticals and personal care products [6] arrive into environment as emerging pollutants. Their determination is a challenge for the researchers in order to find appropriate methods for their accurate quantification. Electroanalysis using carbon fibers electrode seems to be suitable for this purpose [5]. Also, promising results for direct electrochemical detection of parabens using other carbon types based sensors was achieved using imprinted polymer-carbon paste [7], carbon nanotubes modified electrode with Langmuir-Blodgett film [8], boron-doped diamond [9], [10] and glassy carbon modified with CNF and Co-Ni-Pd [11].

Due to the peculiar solubility of parabens in aqueous solution [12], selection of an adequate supporting electrolyte represents a key step for their electroanalytical determination in aqueous matrix. Several supporting electrolytes as hydro-alcoholic solutions [9], methanol and aqueous phosphoric acid [13], phosphate saline buffer solution [14], mixture of glacial acetic acid-acetonitrile-sodium acetate [5] have been successfully applied for paraben detection. A decisive aspect is represented by the ability of the supporting electrolyte to dissolve hydrophobic parabens and their matrix [15] for an accurate determination.

Elaboration of a detection protocol for parabens imply optimization of the operation parameters for each voltammetric and amperometric technique, in order to achieve fast signals, characterized by high sensitivity, low detection limit, selectivity and/or specificity for target analyte detection [14].

In our paper, we exploit the features of CNF "in-lab" obtained composite electrode for the detection of methyl and PPs at optimum condition. Optimization of the detection parameters required the study of the pH influence of the supporting electrolyte on the electroanalytical oxidation of parabens. Also, the operational parameters for the employed electrochemical techniques, i.e., cyclic voltammetry (CV), differential pulse voltammetry (DPV), square wave voltammetry (SWV) and chronoamperometry (CA) were optimized. In addition, the simultaneous determination of PP and MP was tested.

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World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

II. Experimental

The carbon-nanofiber-epoxy (CNF-Ep) composite electrode was obtained by two roll mill method, which assured a good distribution of CNF within epoxy insulating matrix. The content of CNF (Pyrograf III, PR-19-PS) conductive filler was 20%, wt. within epoxy resin. Also, a previous step of dispersion of CNF in tetrahydrofuran (THF) solvent by ultrasonication was achieved before the main preparation step (homogenization by two roll mill). A PVC tube was filled with the composite material and then cured at 60 ᵒC for 12 hours, in order to obtain a disc surface electrode with a geometrical area of 0.196 cm².

The electrical characterization of the electrode was performed by four-point probe method. The devices used to determine the electrical resistance were an ampere-meter (FLUKE8010A), a DC source (HP6181C) and a voltmeter (KEITHLY195). The potential difference of the composite material electrode was measured at different current intensities between -10 mA and 10 mA. After plotting the recorded potential difference vs. current, the electrical resistance of the electrode materials was determined from the slop.

Morphological characterization of the composite material was achieved through scanning electron microscopy (SEM XL20, Philips).

All the electroanalytical experiments were conducted using a potentiostat/galvanostat PGSTAT 302 (EcoChemie, The Netherlands), with a standard three electrodes cell, using CNF-Ep electrode as working electrode, a platinum as counter electrode and a saturated calomel electrode (SCE) as reference.

Electroanalytical parameters, i.e., lowest limit of detection (LOD) and lowest limit of quantification (LOQ) for each electrochemical tested technique were calculated by [4]:

$$LOD = \frac{3S_D}{b} \qquad (1)$$

$$LOQ = \frac{10S_D}{b} \qquad (2)$$

where: S_D represents the standard deviation and b represent the slope of the calibration plots.

PP and MP used in the experiments were pharmaceutical secondary standards purchased from Sigma-Aldrich. The dissolution of parabens was achieved in a mixture of glacial acetic acid, 0.2 mol/L sodium acetate and 20% acetonitrile [5].

An acetate buffer was prepared and applied as supporting electrolyte, using glacial acetic acid and sodium acetate, purchased from Sigma-Aldrich, with addition of a 20% of acetonitrile provided by Merck. The pH of the acetate buffer was 5.6.

III. Results and Discussion

A. Working Electrode Characterization

Electrical characterization of the composite electrode was performed on CNF-Ep plates of 1 mm thickness by four-point probe method. The electrical conductivity of the electrode material depends on many factors, namely; structure of the physicochemical carbon filler within the matrix, composition and distribution of the filler into the epoxy matrix, shape and particle size of the conductive filler and the method and conditions for composite preparation. A value of 0.247 S·cm⁻¹ was determined for the electrical conductivity of the composite material, revealing the electrode material suitability for electrochemical application.

The images obtained by SEM showed a well-embedded CNF into epoxy resin and a good distribution within the matrix (see Fig. 1).
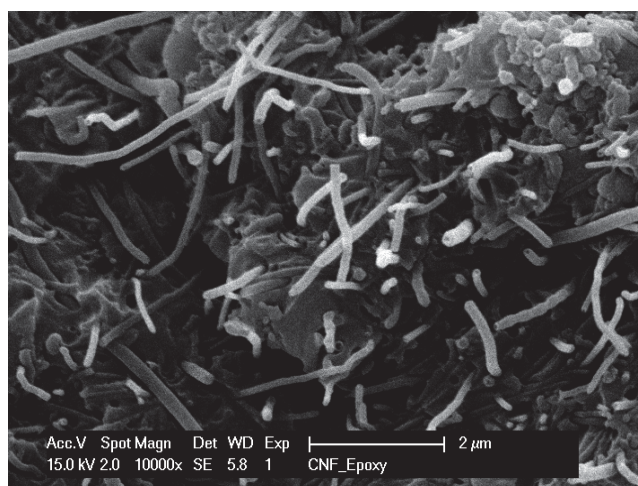

Fig. 1 SEM image of CNF-Ep composite material

B. Electrochemical Characterization

The CV was applied in order to study the behavior of CNF-Ep electrode in acetate supporting electrolyte and in the presence of PP, at different pH of the acetate solution. A well-defined oxidation peak for PP was recorded at a potential value ranging between 0.89 and 1.34 V/SCE, depending on the solution pH (see Fig. 2). The absence of the PP reduction peak on the recorded cyclic voltammograms gives information about a possible irreversible reaction. pH increase led to shifting to less positive values of the oxidation potential, which is a desired aspect in the elaboration of the electrochemical detection protocol.

The well-defined peak for PP oxidation and the useful signal corresponding to the detection of 0.5 mM PP led to choose acetate buffer solution with pH of 5.6 as optimal for further detection experiments.

C. Electrochemical Detection

Voltammetric and amperometric techniques were tested in order to find the best operational condition for PP detection on CNF-Ep electrode.

Cycling voltammograms were recorded between 0 and +1.5 V vs SCE, at a scan rate of 50 mV·s⁻¹ in acetate buffer supporting electrolyte (pH=5.6), by successive addition of PP in the concentration range between 0.02 and 0.14 mM (see Fig. 3). No electrode fouling was recorded during the PP determination by CV. The advantages of the obtained

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

electrode are its renewable surface, by simple polishing with abrasive paper and washing with distilled water. By this technique, the CNF-Ep electrode sensitivity for PP detection was 0.455 mA/mM, with a detection limit of $4.7 \cdot 10^{-3}$ mM.
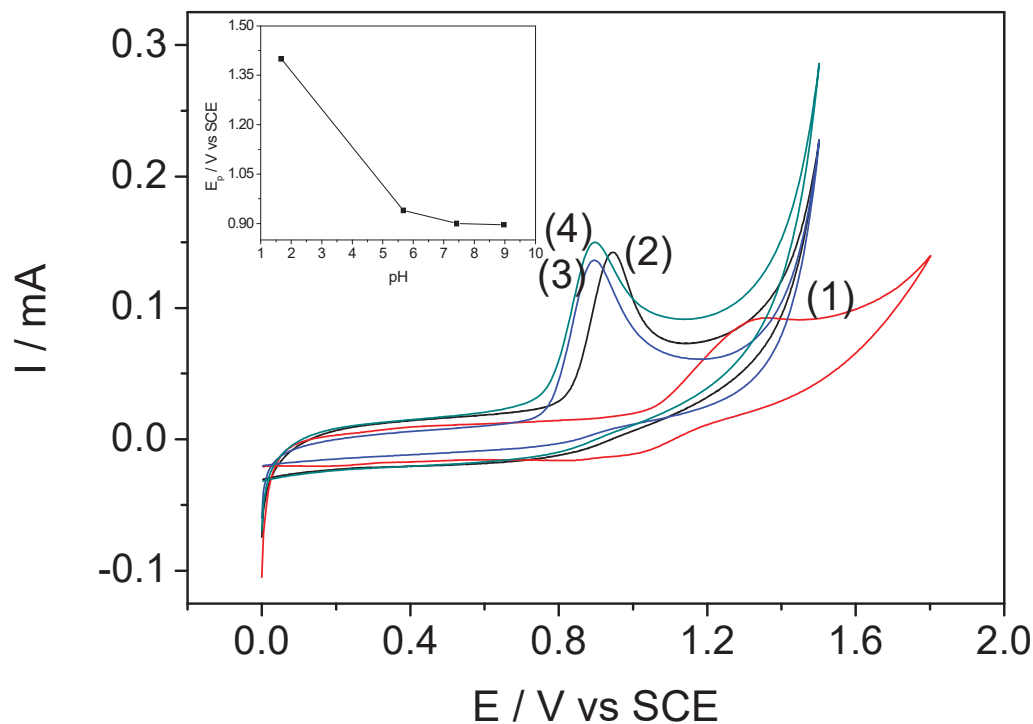

Fig. 2 Cyclic voltammograms (CVs) recorded on the CNF-Ep electrode at different pH: (1) 1.3; (2) 5.6; (3) 7.4 and (3) 9.0 in the presence of 0.5 mM PP. Scan rate 50 mV·s^{-1}. Inset: dependence of PP oxidation peak potential (E_p) on pH of the supporting electrolyte
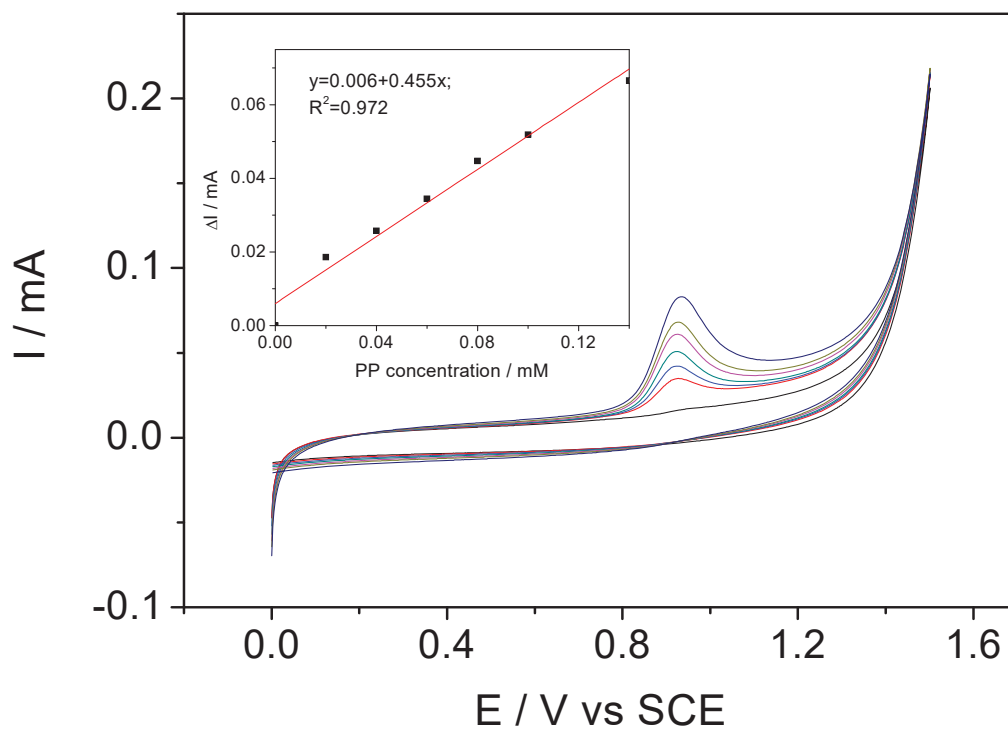

Fig. 3 CVs recorded on CNF electrode in acetate buffer (1) and in the presence of different PP concentrations: 1-0 mM; 2-0.02 mM; 3-0.04 mM; 4-0.06 mM; 5-0.08 mM; 6-0.10 mM; 7-0.14 mM; potential range: 0 V → +1.5 V vs. SCE; scan rate: 50 mV·s^{-1}. Inset: dependence between anodic peak current recorded at potential of +0.93 V vs SCE on CNF electrode and PP concentration

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

Due to their synergetic effect, PP and MP usually are used in mixture as preservatives, in the electrode response for a supplementary addition of 0.040 mM MP to a concentration of 0.14 mM PP in acetate buffer was tested. The current increased linearly with the added MP concentration at the same potential. This behavior informed that the selective detection of PP and MP should not be expected. However, the total concentration of parabens can be quantified on this composite electrode as a paraben index, without each to other interference.

Pulsed voltammetric techniques were tested to establish the optimum operation parameters for SWV and DPV in order to achieve superior electroanalytical performance for PP detection on CNF-Ep electrode. The advantages of applying these two techniques are the fast analysis, good reproducibility and sensitivity, lower detection and quantification limits. For all voltammetric techniques the potential range was kept constant between 0 and +1.5 V/SCE and the experiments were performed in buffer acetate supporting electrolyte with a pH of 5.6.

The optimized operational electroanalytical parameters for SWV technique were the frequency (F), step potential (SP) and amplitude (A). In Fig. 5 are presented the voltammograms and the linear dependence between current and PP concentration recorded by SWV, at less positive potentials compared to CV technique.

The electrode sensitivity, detection potential, LOD and LOQ were compared in order to establish the optimal condition for PP detection through SWV technique. The best electrode sensitivity for PP detection by SWV was achieved at a frequency of 20 Hz, a SP of 2.5 mV and an amplitude of 100 mV. The least positive potential for the PP oxidation peak was recorded at 0.76 V/SCE in the operating conditions of: F=10 Hz; SP=5 mV and A=50 mV. The sensitivity in these conditions was 0.803 mA/mM. These operating conditions should be optimal regarding the detection potential, sensitivity and the LOD.
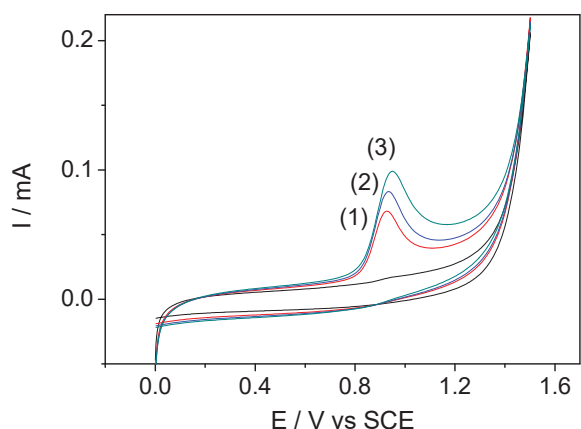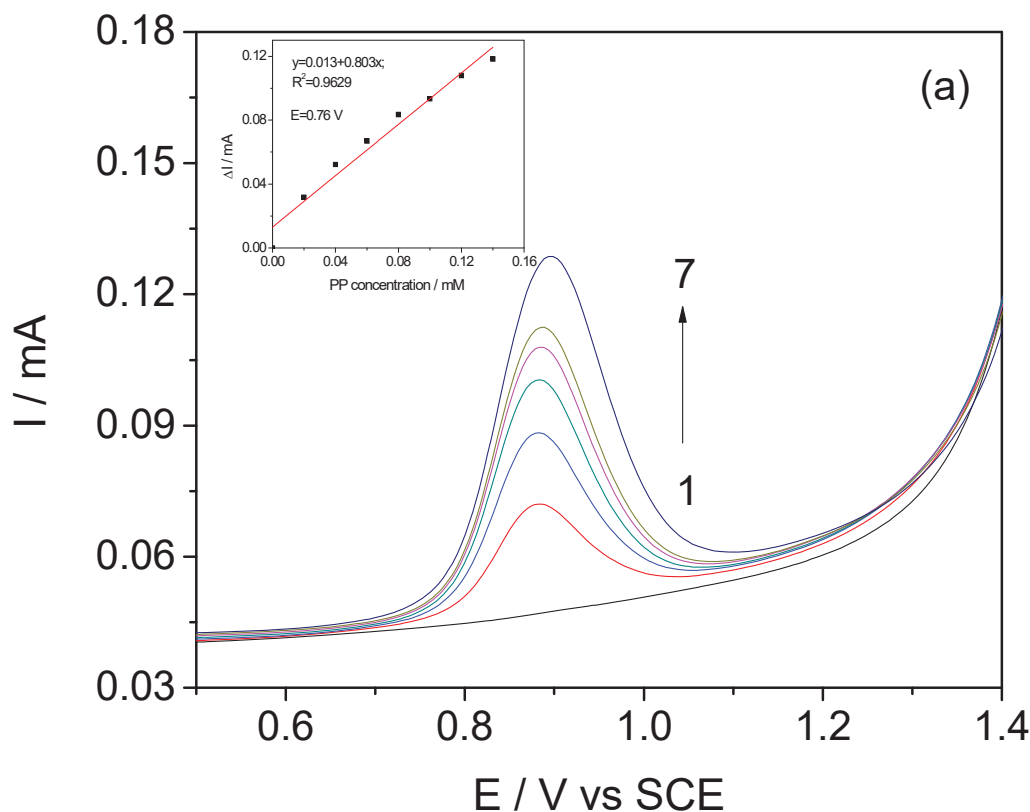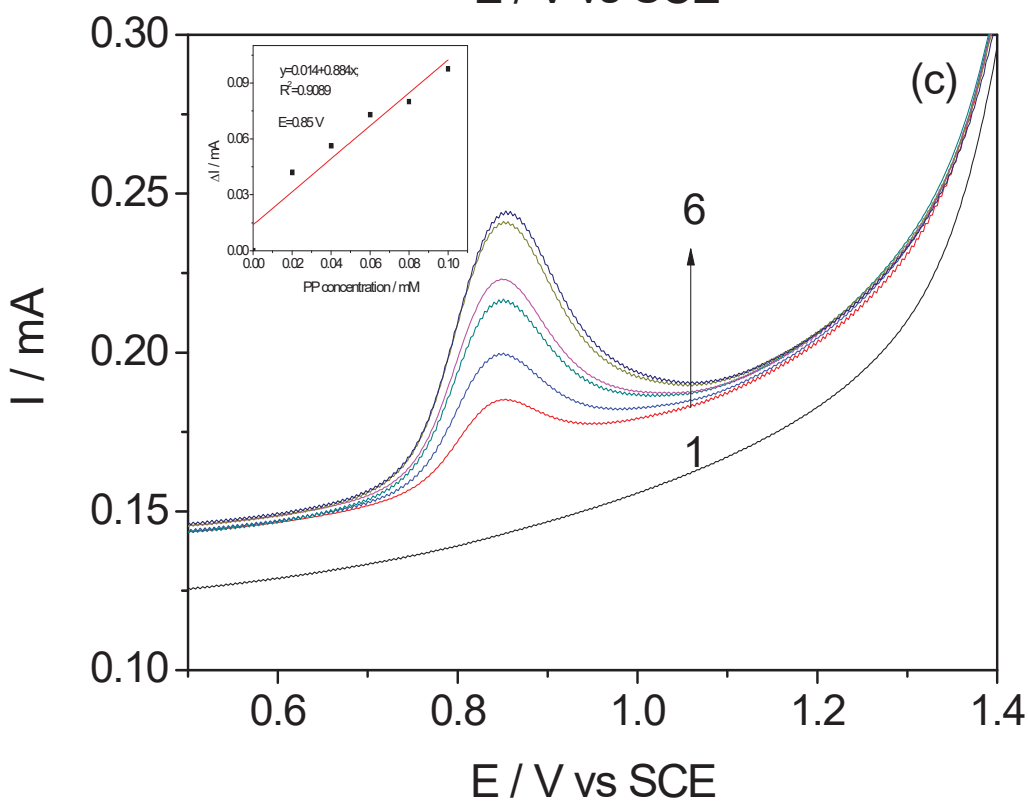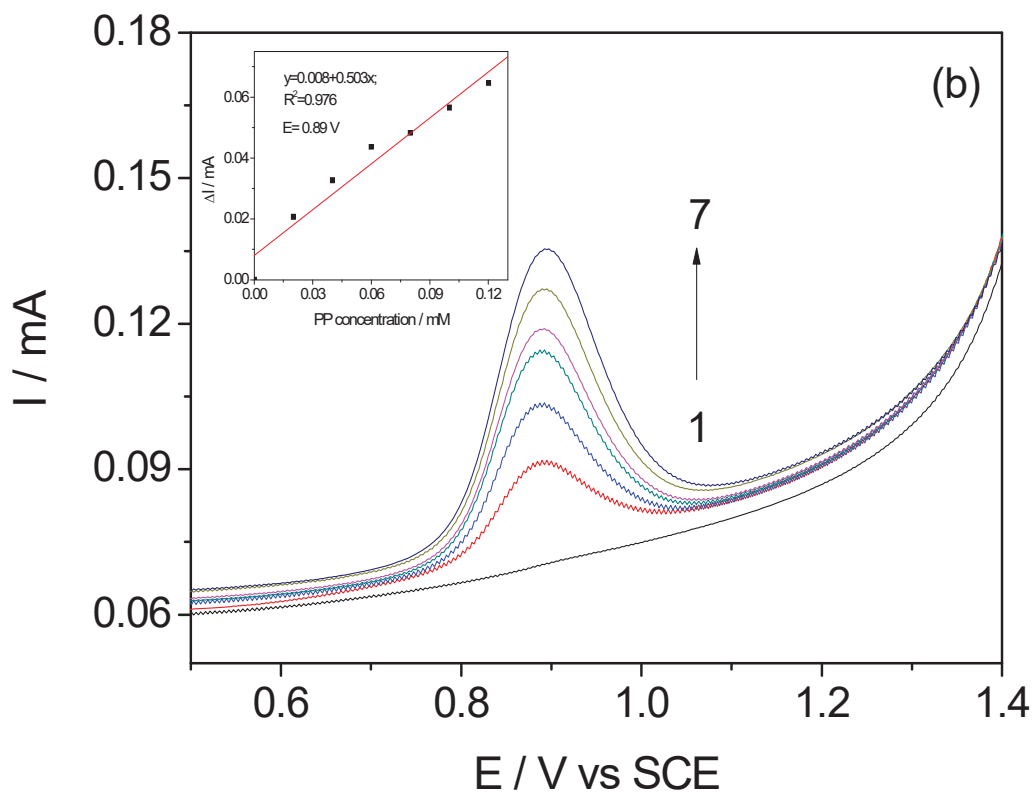

Fig. 4 CVs recorded in the acetate buffer (1) and in the presence of (2) 0.10 mM PP; (3) 0.14 mM PP and (4) a mixture of 0.14 mM PP and 0.04 mM MP, at a scan rate of 50 mV·s⁻¹

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

(b)

Inset:
y=0.008+0.503x;
R^2=0.976
E= 0.89 V
ΔI / mA vs PP concentration / mM

(c)

Inset:
y=0.014+0.884x;
R^2=0.9089
E=0.85 V
ΔI / mA vs PP concentration / mM

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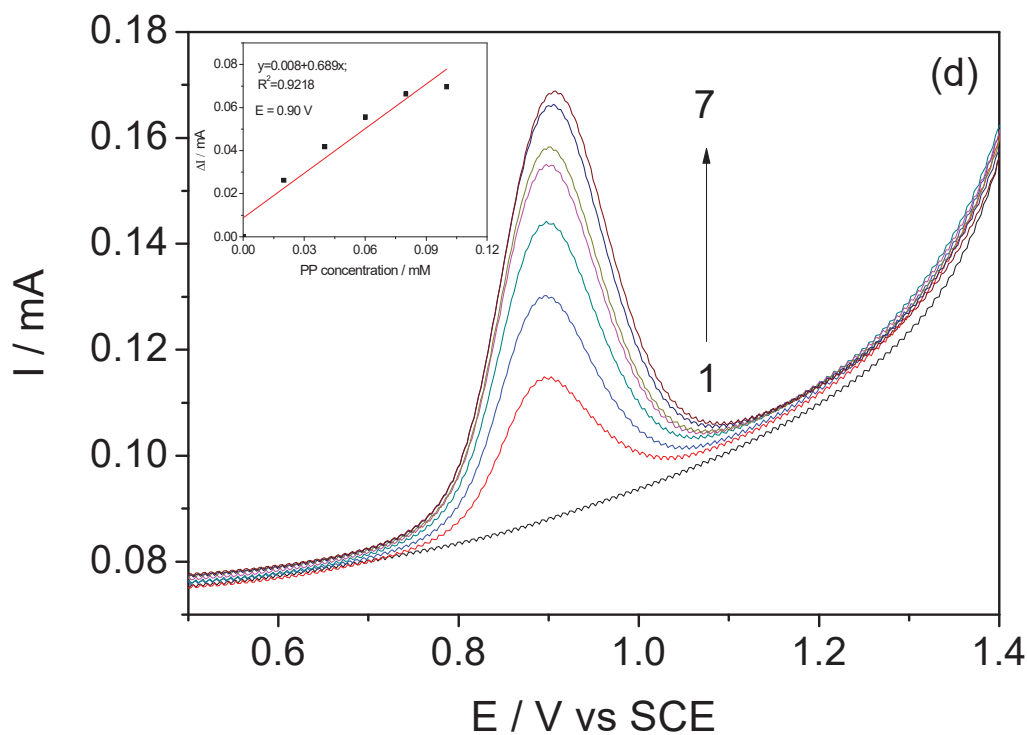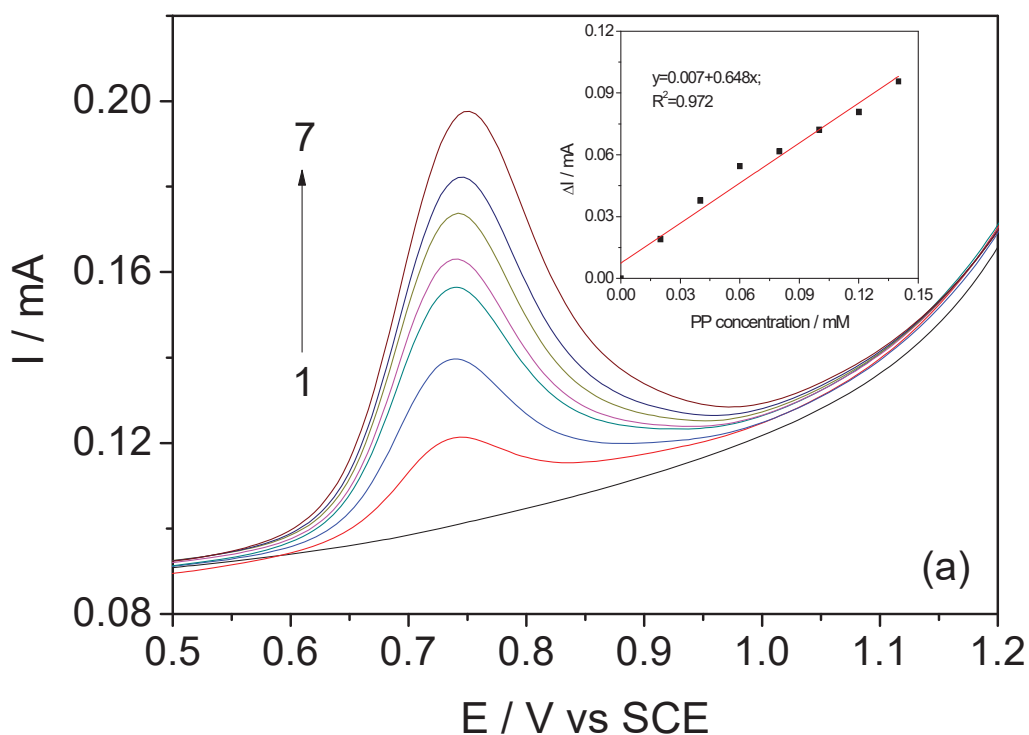International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

Fig. 5 Square wave voltammograms recorded on CNF-Ep electrode in acetate buffer (1) and in the presence of different PP concentrations: 1-0 mM; 2-0.02 mM; 3-0.04 mM; 4-0.06 mM; 5-0.08 mM; 6-0.10 mM; 7-0.14 mM; potential range: $0 \, V \rightarrow +1.5 \, V$ vs. SCE, scan rate of 50 mV·s^{-1} and various operational parameters: (a) F=10 Hz, SP= 5 mV; A=50 mV; (b) F=20 Hz; SP=2.5 mV; A=50 mV; (c) F=20 Hz, SP=2.5 mV; A=100 mV; (d) F=30 Hz; SP=25 mV; A=50 mV, Insets: calibration plots of anodic peak current vs. PP concentration

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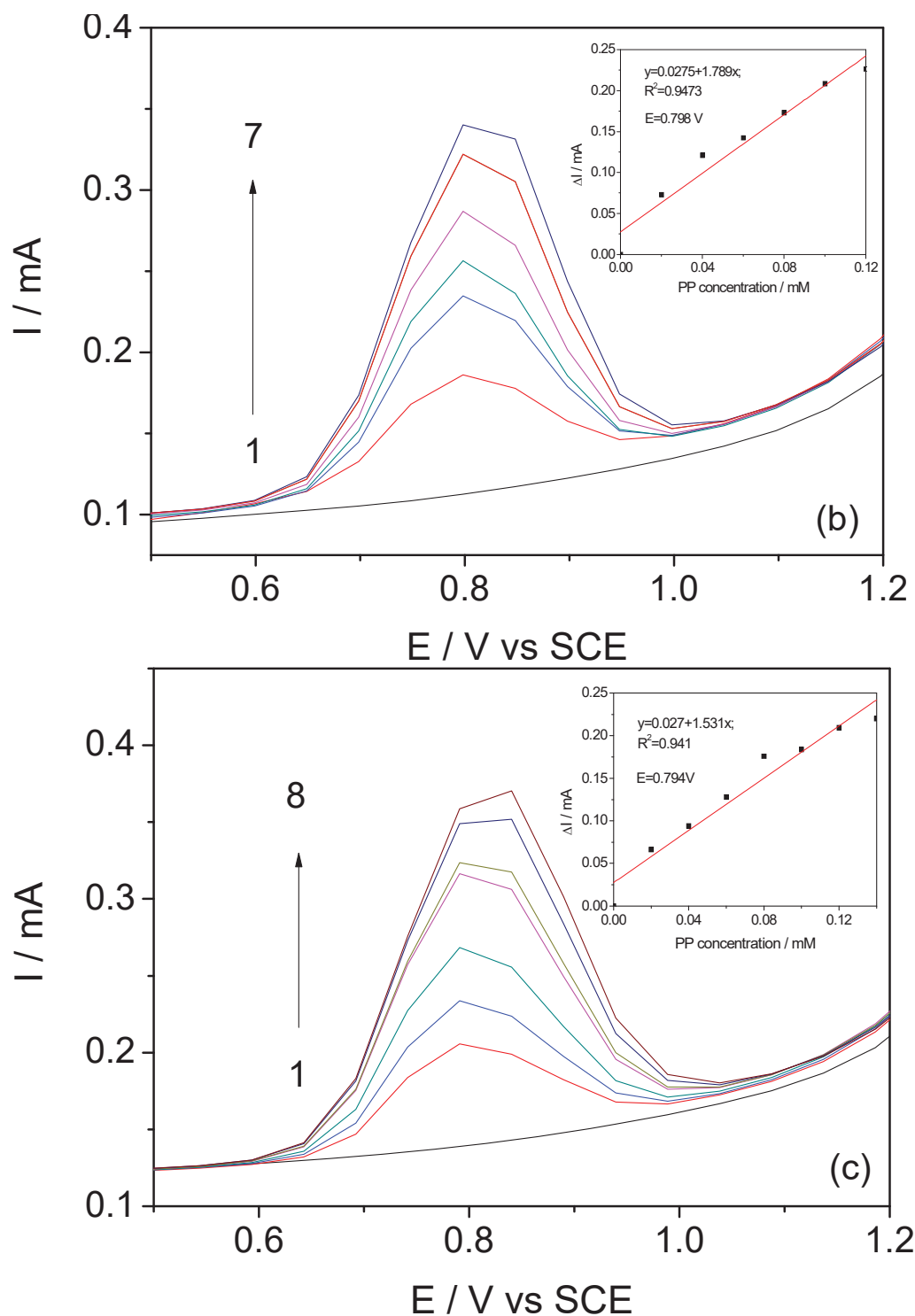International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

Fig. 6 Differential pulsed voltammograms recorded on CNF-Ep electrode in acetate buffer (1) and in the presence of different PP concentrations: 1-0 mM; 2-0.02 mM; 3-0.04 mM; 4-0.06 mM; 5-0.08 mM; 6-0.10 mM; 7-0.12 mM; 8-0.14 mM; potential range: 0 V → +1.5 V vs. SCE, MA=200 mV and various operational parameters: (a) t=0.1 s; SP=5 mV; v=50 mV/s; (b) t=1 s; SP=50 mV; v=50 mV/s; (c) t=0.5 s; SP=50 mV; v=100 mV/s

Another applied voltammetric technique was the differential-pulsed voltammetry (DPV). For this technique, the scan rate (v) and SP were varied and the modulation time (Mt) was kept constant at 50 ms, and modulation amplitude (MA) at 200 mV, in order to achieve optimum condition for PP detection. In Fig. 6, a well-defined peak recorded at the potential values 0.75 V/SCE (Fig. 6 (a)) and 0.79 V/SCE (Figs. 6 (b), (c)) for PP oxidation can be observed. The operational parameters and electrochemical performances are gathered in Table I. The best electroanalytical performances

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

were recorded for the DPV performed with a scan rate of 50 mV/s, with a SP of 50 mV and MA of 200 mV. The sensitivity recorded with this technique was the best of all tested voltammetric techniques, i.e., 1.789 mA/mM and a LOD of $2 \cdot 10^{-4}$ mM. Also, the peak shifted to less positive value is a notable advantage achieved for PP determination in the selected acetate buffer supporting electrolyte.

In comparison with the reported results of other commercial carbon fiber based electrode tested for parabens detection, the detection peak was shifted to less positive values from 1.05 V vs Ag/Ag Cl [15] to 0.75 V vs. SCE in this paper, by applying the DPV technique in the optimized operational conditions.
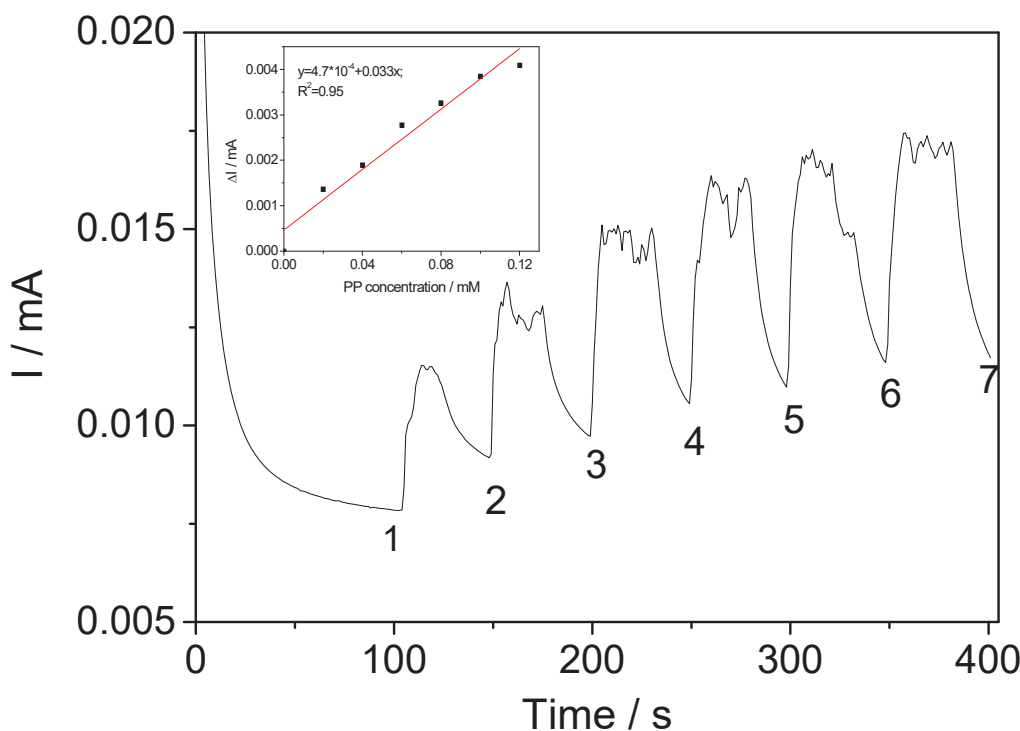
Fig. 7 Chronoamperogram recorded on CNF-Ep electrode in acetate buffer (1) and after successive addition of PP concentrations: 1- 0 M; 2- 0.02 mM; 3-0.04 mM; 4-0.06 mM; 5-0.08 mM; 6-0.10 mM; 7-0.12 mM, Inset: The calibration plots of the currents recorded at 0.9 V/SCE vs. PP concentration

TABLE I
ELECTROANALYTICAL PERFORMANCES RECORDED FOR PP DETECTION

Technique	Parameters	E_p / V	Sensitivity (mA/mM)	LOD (mM)	LOQ (mM)
CV s1	v= 50 mV·s⁻¹	0.93	0.455	0.0047	0.0158
SWV	F=10 Hz SP=5mV A=50mV	0.76	0.803	0.0007	0.0025
SWV	F=20Hz SP=2.5mV A=50mV	0.89	0.503	0.0005	0.0017
SWV	F=20Hz SP=2.5mV A=100mV	0.85	0.884	0.0006	0.0021
SWV	F=30Hz SP=2.5mV A=50mV	0.90	0.689	0.0016	0.0054
DPV	MA=200mV SP=5mV v= 50 mV·s⁻¹ **MA=200mV SP=50mV**	0.75	0.648	0.0015	0.0050
DPV	**v=50mV/s** MA=200mV SP=50mV	**0.79**	**1.789**	**0.0002**	**0.0007**
DPV	v=100 mV·s⁻¹	0.79	1.531	0.0011	0.0038
BIA	0.90 V	0.90	0.033	0.0195	0.0648

Amperometric techniques were tested for their simplicity and suitability for practical application. The PP oxidation potential determined by CV was the applied potential in CA through batch injection analysis (BIA). PP was continuously added to acetate buffer supporting electrolyte in the concentration range between 0.02 to 0.14 mM. The recorded results were inferior to the one recorded by voltammetric techniques in terms of sensitivity and LOD. For practical application, an *in-situ* cleaning step of the electrode surface is required along amperometric measurements, in order to enhance the useful signal.

IV. CONCLUSION

The application of the CNFs based composite electrode can be successfully used in the detection of parabens for individual or simultaneous quantification as a "paraben index". The use of acetate buffer supporting electrolyte at a pH of 5.6 represent an important advantage to the previous reported papers [5], [15] where the detection potential for the paraben oxidation was recorded at more positive potentials. The high stability, sensitivity, accuracy, time saving and simplicity of the pulsed voltammetric techniques using "in-lab" made carbon based

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:9, 2016

sensor in the optimal determined condition, opens perspectives for further practical application for the quantitative determination of parabens as emerging pollutants into environment.

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