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# Electrochemical behaviorof carbon paste electrode modified with Carbon Nanofibers: Application to detection of Bisphenol A

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**ABSTRACT**
The electrochemical behavior of carbon paste electrode modified with carbon nanofibers has been studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scaning electron microscopy. The response of modified electrodein ferroferricyanidesolutionsshows reversible behavior and significant increment in current value compared to the bare CPE indicating that CNFs act as efficient electron mediator to catalyze reactions at the surface. The modified electrode has been used to study the electrochemical response of bisphenol Ausing different electrochemical techniques such as cyclic voltammetry, linear sweep voltammetry, differential pulse voltammetry and square wave voltammetry. The oxidation peak of BPA was observed at about 0.53 V in phosphate buffer solution at pH 6.7. The oxidation peak current of BPA varied linearly with concentration over a wide range of 5µmol $L^{-1}$ to 400 µmol $L^{-1}$ and the detection limit of this method was found to be 0.55 µmol $L^{-1}$.
*Keywords***:** Carbon nanofibers; electrochemical techniques, bisphenol A; carbon paste electrode

## I. INTRODUCTION

Emerging contaminants such as bisphenol A (BPA) are suspected of possibly causing cancer, as well as disturbing the balance of hormones. So, extensive researches were conducted on detection of such element. Bisphenol A (BPA) is considered as an endocrine disruptor that can alter hormone balance of vertebrates, by interacting directly with hormone receptors. BPA is able to bind to estrogen receptors, the female sex hormones, and mimic their action in the body [1-2]. BPA is found in common consumer products such as bottles, cups, disposable, boxes to store food, sunglasses, toys, etc. It migrates in small amounts in foods and beverages and especially when the container is heated [3]. The acceptable daily intake of BPA was set by European Food Safety Authority (EFSA) is 50µg / kg / day [4].Nowadays, many analytical methods have been proposed for BPA determination, such as high performance liquid chromatography and gas chromatography coupled with mass spectrometry [5–6]. These techniques have high sensitivity and low detection limit, but they are expensive and time-consuming.
In recent years, electrochemical methods have been received considerable attention because of their high sensitivity, excellent selectivity, low cost, fast response, time saving and simple operation [7]. For example, Haixia Fan have fabricated an Electrochemical bisphenol A sensor based on N-doped graphene sheets to determine the concentration of BPA in river water sample, they found a detection limit of 5 x$10^{-9}$M [8]. A novel electrochemical sensor was constructed by Ke-Jing

Huang for the determination of bisphenol A (BPA) based on $MoS_2$and chitosan-gold nanoparticles composites modified glassy carbon electrode, they found a detection limit of 5x$10^{-9}$M[9]. Moreover, many other researchers have also investigated the electrochemical behavior of BPA on the modified electrodes based on various materials with low detection limits and wide linear ranges [10–11]. Though some satisfactory results have been obtained, it is still a challenge to develop new, simpler and more effective methods for BPA determination and also focus on further prevention and control to minimize human exposure.

Carbon nanofibers exhibit extraordinary thermal,mechanical and electrical properties [12]. CNFs are different from carbon nanotubes, they have lots of crystalline carbon wall and structural defects than carbon nanotubes [13]. Their preparation cost is significantly lower than that of carbon nanotubes due to the synthesis techniques used [14]. They are suitable for a range of applications such as reinforcing fillers, the field emitters and nanoelectronics devices. CNFs are chemically inert and cannot create a chemical bond with other elements. It is therefore necessary to modify their surface for any use. For this, several liquid path treatments are possible: ultrasonic, addition of surfactants, or chemical surface treatment [15]. The aim of this work is to elaborate and characterize a new electrode based on carbon paste electrode modified by carbon nanofibers. The carbon nanofibers were used to increase the surface area of the electrode, which leads to the improvement of the oxidation current peak. The

response of bisphenol A (BPA) on the modified electrode will be carefully studied by different electrochemical techniques .

## II. EXPERIMENTAL
### 2.1. Materials
Natural graphite,HCl (37%), $H_2SO_4$ (98%), $HNO_3$ (70%) and NaOH were purchased from Sigma Aldrich, while CNFs were obtained from the university of Dayton USA. BPA (97%) was purchased from CARLO-ERBA.A 0.4 mM stock solution of BPA was prepared by dissolving the right amount of BPA in a minimum amount of 0.1M NaOH and diluting with 0.1 M phosphate buffer solution (PBS). Phosphate buffer solution was used as the supporting electrolyte for all electrochemical experiments. All electrochemical measurements were performed using an instrument of PalmSens linked with PSTrace 4.6 software using a three-electrode configuration. Working electrode, counter electrode and reference electrode were a Carbone paste electrode (4 mm diameter), platinum wire and Ag/AgCl (Cl-) respectively. The amplitude of the sine wave perturbation was 10 mV peak-to-peak and the frequency range was 10 kHz to 0.01 Hz with 5 points per decade of frequency. The surface morphologies and microstructures of the modified electrodes were examined by field emission gun scanning electron microscopy (FEG-SEM) (Zeiss, Supra 55).

### 2.2. Carbon nanofibers dispersion
CNFs are treated with a solution of sulfuric acid ($H_2SO_4$) and nitric acid ($HNO_3$) [16]. 100 mg of CNFs powder was added to 150 ml H2SO4 / $HNO_3$ solution (3:1 by volume ratio) to generate oxygen functionalities on their surface and offer better electrochemical properties [17]. This solution was refluxed under magnetic stirring at 90 °C for 1 h. The carboxylated CNFs were filtered with a 0.2 μm cellulose acetate microfiltration membrane, washed with distilled water until pH increased to natural. The carboxylated CNFs were then dried in a vacuum drying oven at 100 °C for 1 h before further

treatment. CNFs dispersion was obtained by adding dimethylformamide (DMF) to the final powder as the concentration equal to 2 mg / 1mL

### 2.3. Carbon nanofibers modified carbon paste electrode
CPE was prepared by hand mixing the graphite powder with paraffin oilin a mortar until a uniform paste was obtained[18]. A portion of resulting homogeneous paste was carefully packed into electrode cavity (Teflon tube, with an outside diameter of 4mm, and inside diameter of 3mm), the electrical contact was established with a stainless steel rod. The surface of the electrode was polished on a white paper and then activated by cyclic voltammetry in 0.1M HCl during 5scans at a scan rate of 100mV/s. The CNFs modified CPE was prepared by dropping 10 μL (2mg mL$^{-1}$) of the functionalized CNFs suspension on the surface of electrode and then dried at room temperature for 20 min, this electrode was named CPE/CNFs

### 2.4 Electrochemical Detection of Bisphenol A
The response of bare and modified carbon paste electrode towards bisphenol was then studied using different electrochemical techniques, Cyclic voltammetry (CV), Differential pulse voltammetry (DPV), square wave voltammetry (SWV). All bisphenol experiments were done in phosphate buffer. Different concentrations varying from 5 μM to 400μM of BPA were prepared and their SWV were used to plot the calibration curve and calculate the detection limit. All SWV experiments were done at room temperature at amplitude 50 mV and a frequency of 25 Hz.

## III. RESULTS AND DISCUSSION
### 3.1. Electrode surface morphology
Scannigelectronmicroscopy (SEM) can provide useful information concering the electrode surface morphology. The morphology of the surfaces of CPE andCPE/CNFs have been characterizedby scanning
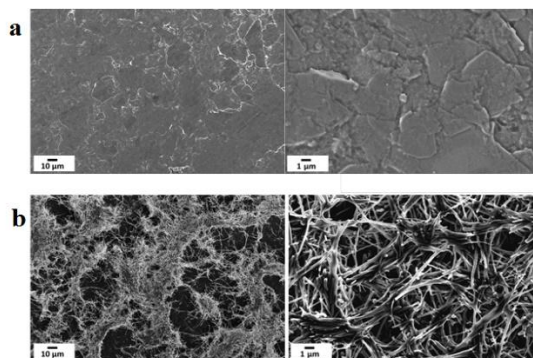


**Figure 1:** SEM images of bare CPE(a) and CPE/CNFs electrode (b)

electron microscopy. Figure1.a. shows the flakes of carbon graphite on bare electrode.Figure1.b shows surface morphological images of CNFs modified electrode. The SEM image shown in Figure1.b is a detailed structure of CPE/CNFs, on which the high density of carbon nanofibers can be observed. It also can be seen that the nanofibers appear to be hightly dispersed and homogenously distributed as reported also by others authors [19 ].

## 3.2. Electrochemical characterization of CNFs modified CPE

Electrochemical behavior of bare and modified CPE was investigated using $Fe(CN)_6]^{3-}$/[Fe LAV$(CN)_6]^{4-}$ as a redox probe by cyclic voltammetry. Figure.2 shows the cyclic voltammograms of 1 mM[Fe$(CN)_6]^{3-/4-}$containing 0.1M KCl in potential range of -0.2 to 0.6 V/ECS at CPE and CPE/CNFs The cyclic voltammogram of

bare CPE shows a pair of well-defined voltammetric peaks with cathodic peak potential ($E_{pc}$) of 0.08 V and anodic peak potential ($E_{pa}$) of 0.36 V.The peak-to-peak separation ($\Delta$Ep) is 284 mV. The cyclic voltammogram of CPE/CNFs shows that $E_{pc}$ is about 0.17 V and$E_{pa}$appears at 0.26 V giving a $\Delta$Ep of 91.2mV. Compared with bare CPE, the peak currents of CPE/CNFs increased and the peak-to-peak separation decreased. The results indicated that CNFs modifiedCPE could greatly increase the electron transfer rate.

The anodic and cathodic peakscurrentof [Fe$(CN)_6]^{3-/4-}$at CPE/CNFs were alsohigher (Ipa= 34.85 µA and Ipc=-34µA) than CPE (Ipa=25.71µA and Ipc=µA) which implied that the electron transfer rate at CPE/CNFs was significantly improved.This behavior can be attributed to a larger surface area and high conductivity of CNFs.
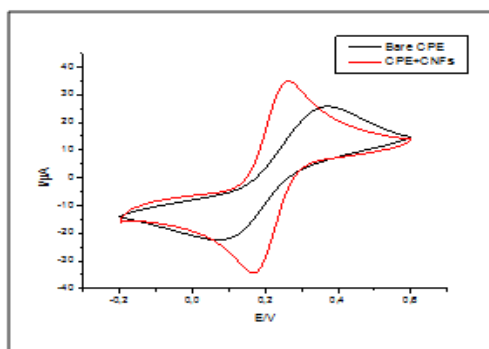


**Figure.2:**Figure 2 : Cyclic voltammograms of bare electrode and modified electrode in 1 mM [Fe$(CN)_6]^{3-}$/ [Fe $(CN)_6]^{4-}$ (pH 6.7) at a scan rate of 50 mV / s.
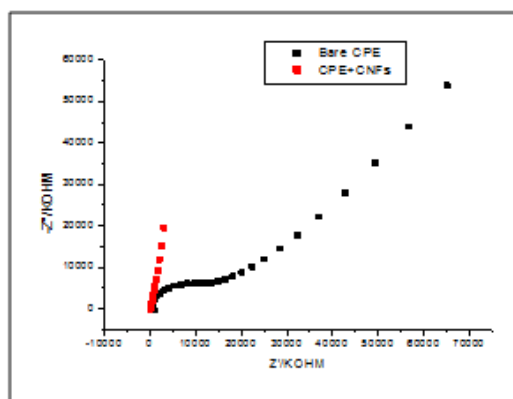


**Figure.3:** Electrochemical impedance spectroscopy of bare electrode and modified electrode in 1 mM Fe (CN) 6]3-/[Fe (CN) 6]4-(pH6.7)

Electrochemical impedance spectroscopy is a frequency domain measurement method, which can be measured over a wide frequency range. Thus, we can get more information about the dynamics and the electrode interface structure compared with conventional electrochemical methods. A typical Nyquist plot includes a semicircle portion and linear portion. The semicircle portion corresponds to the

electron-transfer resistance (Ret) at higher frequency whereas a linear part at lower frequency representsthe diffusion limited process.The impedance measurements were performed in [Fe$(CN)_6]^{3-/4-}$ 1 mM and KCl 0.1 M solution, at 400mV. The Nyquist plots shows a semicircle portion at high frequencies corresponding to the electron-transfer-limited process and a linear part at

low frequency range representing the diffusion-limited process (Fig.3).

The values of the charge transfer resistance (Rct) and the interfacial capacitance (Cdl) can be evaluated by fitting the impedance data. The results shows that (Rct) valueobtained at the bare is equal to 17970Ω. After modification of the electrode by CNF, the Ret decreased to 696Ω, which may be attributed to the excellent electrocatalytic activity and large specific surface area of CNFs. This results are in agreement with the previous results obtained of glassy carbone electrode and glassy carbon electrode modified with graphene. [20]

### 3.3. Electrochemical oxidation of Bisphenol A

In order to evaluate the performance of the CPE/CNFs for bisphenol oxidation,themodified electrode has beenstudied in 0.1 molL$^{-1}$ phosphate solution containing 0.4 mmol L$^{-1}$ Bisphenol by different electroanalytical techniques such as cyclic voltammetry (CV), linear voltammetry (LSV), differential pulse (DPV) and square wave voltammetry (SWV).The oxidation peak currents intensity were found to be superior on CPE/CNFs.

### 3.3.1. Cyclic and Linear Sweep Voltammetry

The oxidation of BPA phenol groupsis irreversible, the oxidation peak appeared at 0.53V. By continuous cycling, the current decrease and this

can be explained by the polymerization of these groups at the surface of the electrode [21]. The formed film blocks the electrode surface which explains the decrease in current peak as reported to the literature. So, our study will be focused only on the first scan of bisphenol.Fig.4.a shows the cyclic voltammograms of 0.4mmol L$^{-1}$ bisphenol A in a phosphate buffer solution 0.1M (pH = 6.7) between 0V and 1V, at scan rate of 50 mV/s on bare and modified electrodes. The oxidation peakwas observed at both bare and modified electrode with currents of 9.3µA and 47.17µA respectively. A sighinificant enhancement was observed at CPE/CNFs. The same behavior was observed when using linear scan voltammetry (Fig.4.b.).The curves show a well-defined oxidation peak on the modified electrode, in which anodic peak potentials are about 0.53V. The oxidation peak current increased from 9.2µA on bare CPE to 40.3µA on CPE/CNFs.

### 3.3.2. Differential Pulse Voltametry

In order to improve the response of the electrode, The electrochemical behavior of 0.4mM of bisphenol A in 0.1M of phosphate buffer (pH 6.7) on CPE and CPE/CNFs was also examined using differential pulse voltammetry (DPV). The obtainedvoltammogramsare shown in Fig.4.c.
The enhancement of oxidation peak current was
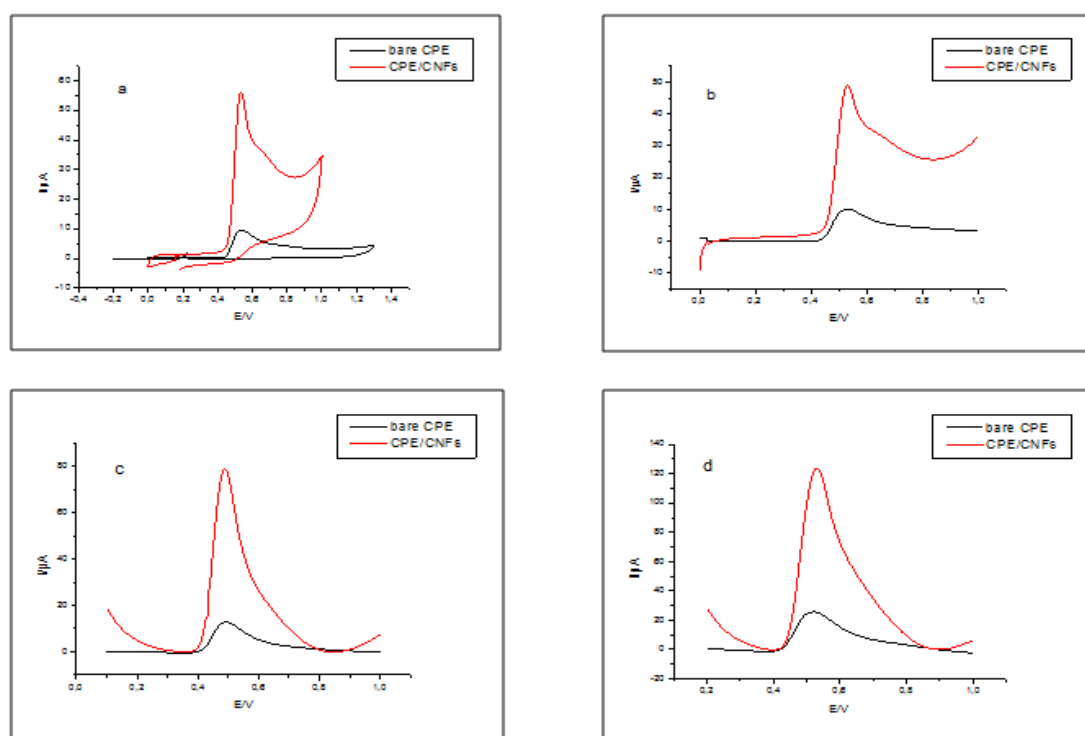


**Figure 4:** electrochemical respnoce of 0.4 mM BPA in a phosphate buffer solution 0.1M (pH = 6.7) on bare and modified electrode obtained by (a) cyclic Voltammetry (CV), (b) linear voltammetry (LSV) between 0V and 1V, at scan rate of 50 mV /s, (c) differential pulse voltammetry response(DPV) between 0V and 1V; at scan rate 50mV/ pulse time 0.05s and pulse amplitude of 50mV.(d) Square waves voltametry (SWV) between 0V and 1V, at an amplitude of 50 mV and a frequency of 25 Hz.

observed. The current increased from 15.2µA on bare CPE to 78.6 µA on modified electrode (CPE/CNFs).

The percentage of increasing current is equal to 450%.(Calculated from equation 1).

### 3.3.3. Square Wave Voltammetry
The response of bisphenolwere also recordedby using square wave volatmetryusing optimized parameters of SWV(fig.4.d.). On scanning the potential from 0V to 1V s at an amplitude of 50 mV and a frequency of 25 Hz, a well-defined oxidation peak is obtained at potential 0.53V with a current of 27.4µA at bare CPE and 124µA at CPE/CNFs. The percentage of increasing current is 414%.

Peak currents obtained with electrodecontaining CNFs increased due to the interesting properties of nanoparticles such as large surface area, high electrical conductivity, and good stability. Using this modifier well dispersed on the surface of the paste enhances the electrode response towards Bisphenol. Therefore, the application of carbon nanofibers in electrochemical detection of Bisphenol can lead to desired sensors with appropriate characteristics. Table1summuriaze the obtained results by different techniques on both electrodes. The percentage of increaseof current( given by equation 1) is also reported.The percentage of increase current is calculated by the following equation:

(1)    % increase = $( I_{CPE/CNFs} - I_{CPE} / I_{ICPE} )$ x100

**Table 1.** The percentage of increase current obtained from different used techniques

|     | $I_a$ (CPE) | $I_a$ (CPE/CNFs) | % increase |
|-----|-------------|------------------|------------|
| CV  | 10.6µA      | 56.2µA           | 405%       |
| LSV | 9.2µA       | 40µA             | 334%       |
| DPV | 15.2 µA     | 78.6µA           | 417%       |
| SWV | 27.4µA      | 127µA            | 414%       |

From these results, it turns out that the best results in term of current are those obtained by the SWV technique. The SWV will be used in the further work.

### 3.4. Calibration curve
Under the chosen conditions, a calibration curve for the determination of Bisphenol was constructed for a
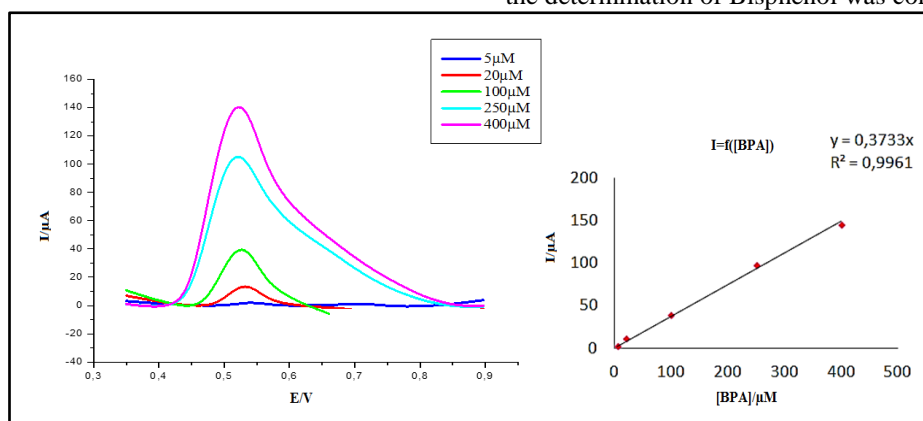


**Figure5:** Square wave voltammograms and calibration curve of different concentrations of BPA performed at amplitude of 50 mV and a frequency of 25 Hz.

**Table2:**The detection limits of BPA obtained when using other electrodes by others groups

| Electrode | Modifier | Detection limit M | pH | References |
|-----------|----------|-------------------|-----|------------|
| GCE | Carrbonnantubes and NiO | $5.9x10^{-8}$ | 6 | [22] |
| DE | Boron doped diamond electrode | $2.1 x10^{-7}$ | 6 | [23] |
| EGE | None | $7.6x10^{-7}$ | 10 | [24] |
| GCE | stacked graphene nanofibers/gold nanoparticles composite | $3.5x10^{-8}$ | 6 | [25] |
| GCE | Molecularly imprinted polypyrrol/graphene quantum dots composit | $4x10^{-8}$ | 7 | [26] |
| CPE | Carbon nanofibers | $5.5x10^{-7}$ | 6.7 | This work |

concentration range from 5 to 400 μM using SWV techniques.The calibration plot shows a linear relationship with a correlation coefficient of 0.9961in a concentration range of 5μM to 400 μM. The formula 3σ/slope was employed to calculate detection limit, where σ is the standard deviation of the blank. Under the optimized conditions, the detection limit of this method was found to be 0.55 μM.The modified electrode demonstrated high sensitivity and a low detection limit. The analytical performances have been compared with other sensors reported previously in the literature for bisphenol determination (Table.2).

## IV. CONCLUSION

In this work, a very simple approach based on modification of the surface of carbon paste electrode (CPE) by carbon nanofibers (CNFs) for the detection of bisphenol A (BPA) is reported. The surface of the electrode was characterized by cyclic voltammetry, impedance spectroscopy and scanning electrode microscopy. Then the response of Bisphenol was studied using different electrochemical techniques. The carbon nanofibers increase the surface area of the electrode, which leads to the enhancement of the oxidation current peak of Bisphenol.This electrode can be used for determination of BisphenolA using Square wave voltammetry with a limit of detection of 0.55μM.

## ACKNOWLEDGEMENTS

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