

Full Paper

Selective Determination of Norepinephrine at SAOS/MWCNT/MCPE: A Voltammetric Study

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Abstract- A simultaneous determination of Norepinephrine (NE) using Sodium alpha olefin sulfonate/multi-walled carbon nanotube modified carbon paste electrode was developed by voltammetric techniques. The modified electrode shows excellent electrocatalytic activity towards the oxidation of NE in phosphate buffer solution (PBS) of pH 6.8. The electrochemical studies of scan rate, reveals the overall electrode process for NE was controlled by adsorption and for Epinephrine was diffusion. The pH studies confirm that an equal number of protons and electrons were involved in the electrochemical detection of NE. The lower limit of detection of NE and EP was discussed. The interference studies showed that the modified electrode exhibits excellent selectivity in the presence of large excess of Epinephrine (EP). The separation of the oxidation peak potentials for NE–EP was about 0.203 V. This peak difference was large enough to determine NE and EP individually and simultaneously. This method offers a simple and easy approach to selectively detect various bioactive molecules.

Keywords- Sodium alpha olefin sulfonate, Multi-walled carbon nanotube, Norepinephrine, Epinephrine, Selective, Electrochemical sensor

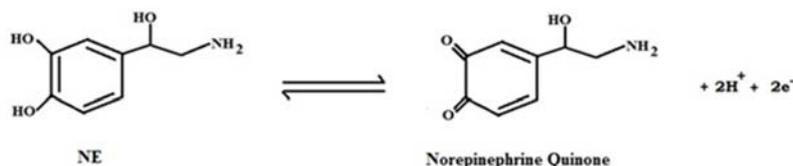
1. INTRODUCTION

Epinephrine (I) and norepinephrine (II) are two major endogenous catecholamines in the human body having complementary actions [1]. Norepinephrine (NE) also called

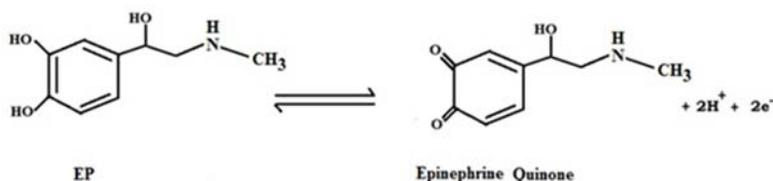
noradrenaline is an organic chemical in the catecholamine family that functions in the brain and body as a hormone and neurotransmitter [2]. NE undergoes oxidation to give norepinephrine quinone (Scheme 1). NE is secreted in the adrenal medulla and maintains important physiological functions in the central nervous system (CNS). It affects muscle and tissue control, stimulates arteriole contraction, decreases peripheral circulation and activates lipolysis in adipose tissue [3-4]. It is also critical in the neurological disease such as heart failure, diabetes and HIV [5-6]. Epinephrine (EP) also known as adrenaline exists as an organic cation [7], which is about nmolL^{-1} in human serum [8]. It belongs to the family of inhibitory/catecholamine neurotransmitters in mammalian CNS and which plays an important role in the transmission of nerve impulse and is associated with a large variety of physiological processes and illnesses [9]. Monitoring the concentration of EP gains great attention since the changes in its concentrations resulted in many diseases such as Parkinsonism [10], Schizophrenia [11], and Huntington's disease [12] as well as drug addiction. It is a hormone synthesized by the adrenal medulla of the adrenal glands [13], it stimulates a series of actions of the sympathetic nervous system called "fight or flight" response [14]. EP controls the performance of the nervous system, and its abnormal levels affect the regulation of the blood pressure, heart rate, and glycogen metabolism [7,15]. EP undergoes oxidation to give epinephrine quinone (Scheme 2). It has been used as a common healthcare medicine, for instance, EP drugs are used to treat anaphylactic shock, bronchial asthma and organic heart disease [16]. Both the neurotransmitters are oxidized at the same potential which results in broad voltammetric responses, it is difficult to distinguish in the binary mixture [17-18]. The number of analytical techniques is used to resolve the problem of interference through fluorimetric, spectrophotometric, radioenzymatic, Ultra performance liquid chromatography-tandem mass spectrometry, GC and HPLC-MS, Chromatography techniques for qualitative and quantitative analysis of NE and EP have been reported and well-reviewed [19-24]. Hence, it is very necessary to develop sensitive, simultaneous and practically reliable methods for the direct detection of the level of NE for monitoring physiological activities and diagnosing diseases [25-27]. Very less literature found on the simultaneous detection of these neurotransmitters [18,28,29]. Therefore, a simultaneous determination of EP and NE has become increasingly significant. Carbon nanotubes (CNTs) are an important class of materials due to their unique electronic, mechanical, and structural characteristics. The physical and catalytic properties make CNTs ideal for use as chemical sensors and for electrochemical detection [30]. These remarkable results suggest that MWCNT possesses properties such as high electrical conductivity, larger surface-active groups to-volume ratio, chemical stability and significant mechanical strength, as a consequence, MWCNT can serve as excellent substrates for the development of biosensor devices [31]. From 1996 the application CNTs in electrochemistry increased severely towards detection of biological analytes and gases using sensors or biosensors. The surfactants play

the very important role especially in electrochemistry and these are the active ingredients in personal hygiene products. There are four classes (cationic, anionic, amphoteric and non-ionic) based on the ionic charge (if present) of the hydrophilic portion of the surfactant in an aqueous solution [32]. These surfactants have an inherent tendency to accumulate at interfaces depending upon the nature of the interface and that of the surfactants. Accordingly, the properties which depend on the interfacial character of a system exhibit alteration in the presence of such surfactants [33,34]. Hu's group has introduced surfactants to electro analytical chemistry to improve the detection limits of some important biomolecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactant types [35]. Sodium alpha olefin sulfonate is an anionic surfactant is produced by the direct reaction of olefins with strong sulfonating agents, such as sulfur trioxide.

In the present work, the Sodium alpha olefin sulfonate/Multi walled carbon nanotube modified carbon paste electrode (SAOS/MWCNT/MCPE) was applied for the simultaneous detection of NE and EP at pH 6.8 PBS solution gives two well-defined oxidation peaks at 0.285 V and 0.082 V respectively. The modified electrode shows good electrocatalytic activity, sensitivity, and minimization in over potential for both NE and EP.



Scheme 1. Electrochemical oxidation mechanism of NE



Scheme 2. Electrochemical oxidation mechanism of EP

2. EXPERIMENTAL SECTION

2.1. Materials

L-Norepinephrine (NE) and Epinephrine (EP) was purchased from Fluka analytical. The stock solution 25×10^{-4} M NE and 25×10^{-4} M EP was prepared in 0.1 M perchloric acid and

double distilled water. The phosphate buffer solutions (PBS) with different pH levels were prepared by mixing the same ionic strength (0.2 M) solutions of Na_2HPO_4 and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ solutions at different ratios. The pH levels were adjusted by adding 0.1 M CH_3COOH and/or 0.1 M NaOH solution and PBS of pH 6.8 was used as a supporting electrolyte. Graphite powder of 50 μm particle size and multi walled carbon nanotube were purchased from Merck and silicone oil from Himedia was used to prepare Carbon Paste Electrode (CPE). All the chemicals mentioned were the entire analytical grade used as received without any further purification.

2.2. Apparatus

The electrochemical experiments were carried out using a CH Instrument model 660 c. The electrode system containing the working electrode consisted of a carbon paste electrode (3 mm in diameter), a platinum counter electrode and a saturated calomel reference electrode. All the redox potential of analytes were reported versus SCE.

2.3. Preparation of bare carbon paste electrode and Multi Walled Carbon Nanotube modified carbon paste electrode

The bare CPE was prepared by hand mixing of 70% graphite powder and 30% silicone oil in an agate mortar for about 45 min until a homogeneous paste was obtained. The paste was then packed into a cavity of PVC tube of 3 mm internal diameter and smoothed on a tissue paper. The Multi walled carbon nanotube (MWCNT) modified carbon paste electrode was prepared by grinding 35% MWCNT along with 45% graphite powder and 20% silicone oil in an agate mortar for about 45min until a homogeneous paste was obtained. The electrical contact was provided by a copper wire connected to the end of the tube.

2.4. Preparation of SAOS/MWCNT/MCPE

SAOS solution (10 μL) was added by using micropipette on the surface of the MWCNT-MCPE and allowed it for about 5 min at room temperature. The electrode was later thoroughly rinsed with distilled water to remove unadsorbed SAOS to get SAOS/MWCNT/MCPE.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization of SAOS/MWCNT/MCPE using standard potassium ferrocyanide system

The freshly prepared stock solutions of 1 mM potassium ferrocyanide and 1 M KCl as supporting electrolyte were placed in an electrochemical cell. The Fig. 1 shows the cyclic

voltammograms recorded for the 1 mM potassium ferrocyanide at BCPE (dashed line), MWCNT/MCPE (dotted line) and SAOS/MWCNT/MCPE (solid line) at the scan rate 0.05 Vs^{-1} . The corresponding anodic peak currents were $1.25 \times 10^{-5} \text{ A}$, $1.89 \times 10^{-5} \text{ A}$ and $3.72 \times 10^{-5} \text{ A}$ for the BCPE, MWCNT/MCPE and SAOS/MWCNT/MCPE respectively, and the redox peak potential difference (ΔE_p) for BCPE, MWCNT/MCPE and SAOS/MWCNT/MCPE were 118 mV, 96 mV and 45 mV respectively. The low redox peak currents and high peak potential difference response were obtained at BCPE, MWCNT/MCPE but in the same condition SAOS/MWCNT/MCPE exhibited stable enhancement of redox peak currents, minimization in over potential and also it shows the fast rate of electron transfer kinetics. The result obtained greatly improved the voltammetric response of potassium ferrocyanide at SAOS/MWCNT/MCPE. This suggests that the surface property of the modified electrode has been significantly changed. And also the result proves that the electrocatalytic activity of the SAOS/MWCNT/MCPE towards the potassium ferrocyanide. The total active surface area available for the reaction of species in solution can be estimated by the Randles-Sevcik equation (1) [38-40].

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_0 \nu^{1/2} \quad (1)$$

Where I_p is the peak current in A. C_0 is the concentration of the electroactive species (mol cm^{-3}), n is the number of electrons exchanged, D is the diffusion coefficient in $\text{cm}^2 \text{ s}^{-1}$, ν is the scan rate (Vs^{-1}) and A is the electroactive surface area (cm^2). For SAOS/MWCNT/MCPE the electroactive surface area is maximum (0.0484 cm^2) as compared with MWCNT/MCPE (0.0317 cm^2), BCPE (0.02892 cm^2).

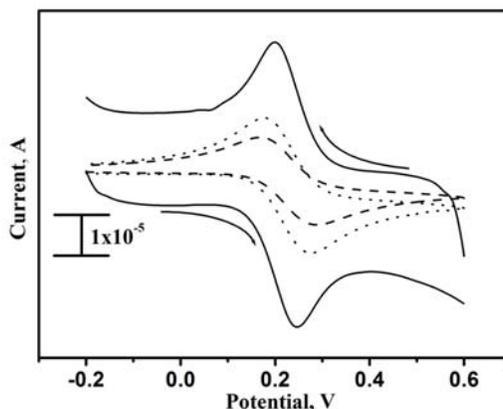


Fig. 1. Cyclic voltammograms of BCPE (dashed line), MWCNT/MCPE (dotted line) and SAOS/MWCNT/MCPE (solid line) at in the presence 1 mM potassium ferrocyanide at scan rate of 0.05 Vs^{-1}

3.2. Electrocatalytic oxidation of NE at the BCPE and the MCPE

The electrochemical responses of 10×10^{-5} M NE in 0.2 M phosphate buffer solution of pH 6.8 at the BCPE and at the MCPE prepared with MWCNT and SAOS/MWCNT were measured at a scan rate of 0.05 Vs^{-1} . The corresponding anodic peak currents were 9.63×10^{-7} A, 1.99×10^{-6} A and 1.635×10^{-5} A for the bare CPE, the MCPE prepared from MWCNT and SAOS/ MWCNT respectively, has been shown in Fig. 2 (A)–(C). The inset Fig. 2 voltammogram B(solid line) and C(dashed line) was for the MWCNT/MCPE and bare CPE respectively. The result showed both MWCNT/CPE and SAOS/MWCNT/CPE which exhibited good electrocatalytic activity than BCPE. Among them, SAOS/MWCNT/CPE ($\Delta E_p=29 \text{ mV}$) exhibited enhanced current response with minimization in over Potential than the MWCNT/CPE($\Delta E_p=60 \text{ mV}$). This indicated that the MCPEs prepared from SAOS/MWCNT/CPE exhibited good electrocatalytic activity towards the detection of NE.

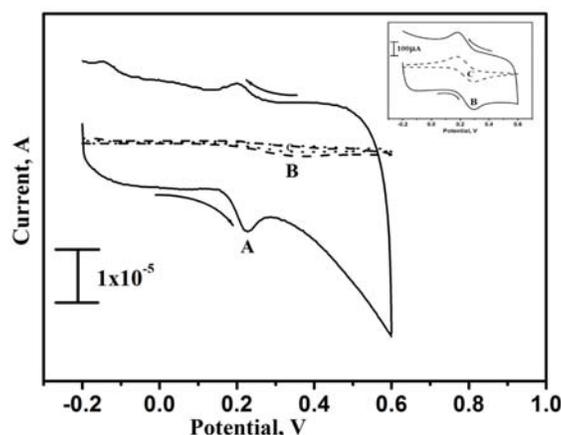


Fig. 2. Cyclic voltammograms of BCPE (dotted line), MWCNT/MCPE (dashed line) and SAOS/MWCNT/MCPE (solid line) in the presence of 10×10^{-5} M NE in 0.2 M phosphate buffer solution of pH 6.8 at scan rate of 0.05 Vs^{-1}

3.3. The effect of scan rate on peak current of NE

The effect of variation of scan rate from 0.05 to 0.50 Vs^{-1} for 10×10^{-5} M NE in 0.2 M PBS of pH 6.8 was examined by cyclic voltammetric (CV) technique at SAOS/MWCNT/MCPE as shown in the Fig. 3A. The experimental results obtained at SAOS/MWCNT/MCPE showed an increase in the redox peak currents with an increase in the applied scan rate and they are proportional to each other according to Randles-Sevcik equation. The observation shows that there is a shifting of anodic peak potential (E_{pa}) to the more positive side and cathodic peak potential (E_{pc}) to the negative side. In order to confirm the electrode process, the graph of logarithmic anodic peak current ($\log I_{pa}$) vs logarithmic scan rate ($\log v$) was

plotted for SAOS/MWCNT/MCPE as shown in Fig.3B. The determined slope was 0.9394 was a close agreement with the theoretical value of 1 for adsorption controlled process [41].

The heterogeneous rate constant (k^0) values were determined from the experimental peak potential difference (ΔE_p) data's; equation (2) was used for such voltammograms whose ΔE_p values are greater than 10 mV [42-43].

$$\Delta E_p = 201.39 \log(v/k^0) - 301.78 \quad (2)$$

From the experimental ΔE_p values as shown in Table 1 and equation (2); the values of the k^0 for the NE oxidation was determined. The values of k^0 obtained from the scan rate 0.05 to 0.50 Vs^{-1} for the SAOS/MWCNT/MCPE exhibited by increasing the Scan rate the heterogeneous rate constant decreases.

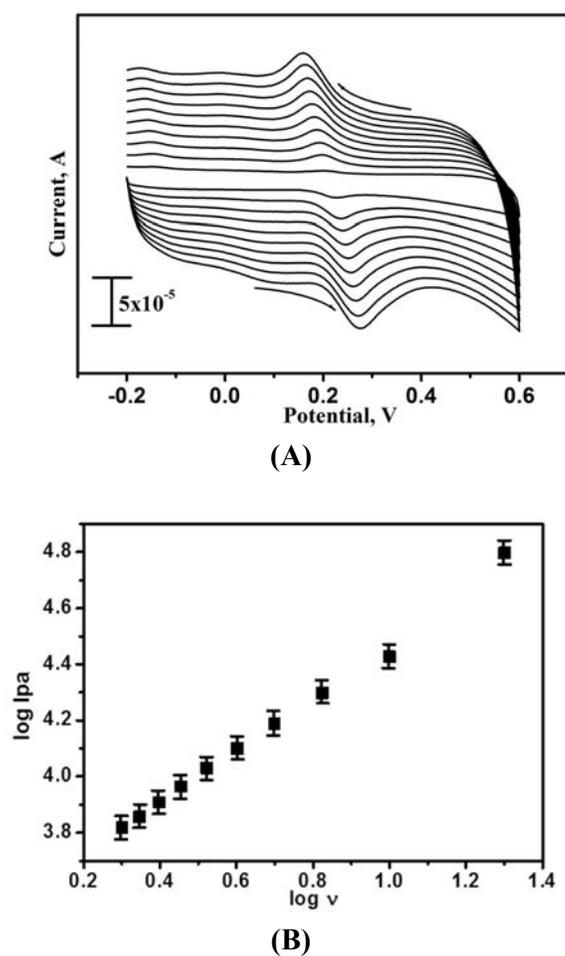


Fig. 3. (A) Cyclic voltammograms of different scan rate in the presence of 10×10^{-5} M NE and 0.2 M phosphate buffer, in pH 6.8 Scan Rate: 0.05 Vs^{-1} -0.5 Vs^{-1} ; (B) Graph of the $\log I_{pa}$ vs $\log v$

This is in support for SAOS/MWCNT/MCPE controlled by adsorption towards the detection of NE. All the parameters are tabulated in Table 1.

Table 1. Variation of the voltammetric parameters gathered from the plots shown in Fig. 3A as a function of the potential scan rate

| v / Vs^{-1} | $\Delta E_p / \text{V}$ | k^0 / s^{-1} |
|----------------------|-------------------------|-----------------------|
| 0.05 | 0.028 | 0.6345 |
| 0.1 | 0.038 | 0.3172 |
| 0.15 | 0.046 | 0.2114 |
| 0.20 | 0.059 | 0.1585 |
| 0.25 | 0.068 | 0.1268 |
| 0.30 | 0.079 | 0.1056 |
| 0.35 | 0.087 | 0.0905 |
| 0.40 | 0.098 | 0.0792 |
| 0.45 | 0.105 | 0.0704 |
| 0.50 | 0.118 | 0.0634 |

3.4. Effect of NE concentration

The electrochemical oxidation of NE was carried out by varying its concentration at SAOS/MWCNT/MCPE. The Fig. 4A shows by increasing the concentration of NE from $0.2 \times 10^{-4} \text{ M}$ to $2.0 \times 10^{-4} \text{ M}$, the I_{pa} and I_{pc} goes on increasing with shifting E_{pa} towards more positive and E_{pc} towards the less negative side. The graph of I_{pa} vs. concentration of NE was plotted in Fig. 4B and it shows two linear relationships ranges $0.2 \times 10^{-4} \text{ M}$ to $1.0 \times 10^{-4} \text{ M}$ and $1.0 \times 10^{-4} \text{ M}$ to $2.0 \times 10^{-4} \text{ M}$ with the linear regression equations as $I_{pa}(10^{-5} \text{ A}) = 0.1445(C_0 10^{-4} \text{ M/L}) + 7.56 \times 10^{-6}$, ($N=5$, $r^2=0.9987$) and $I_{pa}(10^{-5} \text{ A}) = 0.0827(C_0 10^{-4} \text{ M/L}) + 1.341 \times 10^{-5}$, ($N=3$, $r^2=0.9987$) respectively. The decrease of sensitivity (slope) in the second linear range is likely to be due to kinetic limitation [44,45]. The detection limit in the lower concentration range for NE was $6.6 \mu\text{M}$ for the SAOS/MWCNT/MCPE and the result was compared with found literature [18,48,49] as shown in Table 2 and limit of quantification was $2.2 \times 10^{-5} \text{ M}$ was calculated by using the formulas (3) and (4) [46,47], where S is the standard deviation and M is the slope obtained from the three calibration plots.

$$\text{LOD} = 3S/M \quad (3)$$

$$\text{LOQ} = 10S/M \quad (4)$$

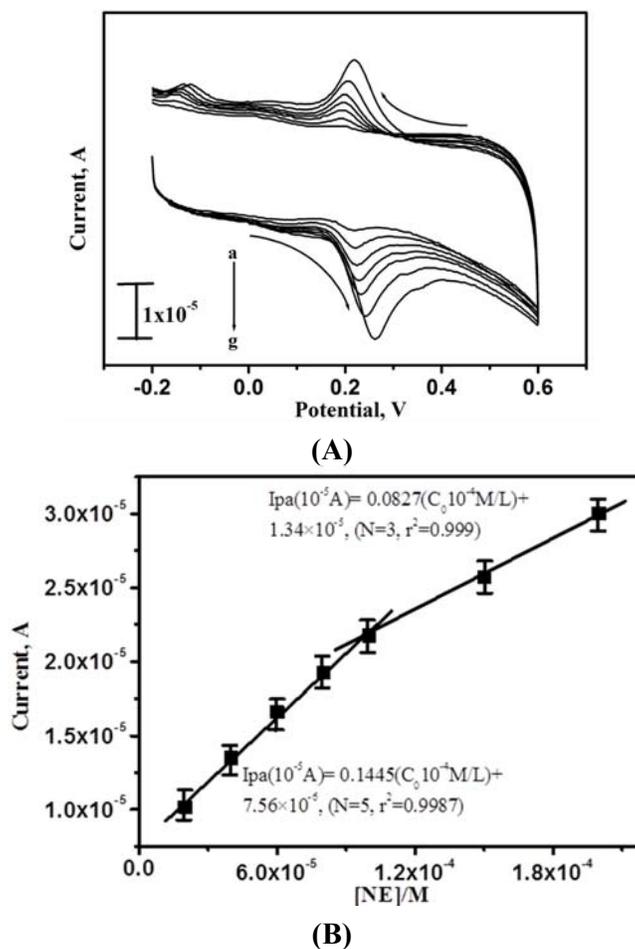


Fig. 4. (A) Cyclic voltammogram of variation of concentration of NE from 0.2×10^{-4} M to 2.0×10^{-4} M in presence of phosphate buffer solution at pH 6.8 at 0.05 Vs^{-1} ; (B) Graph of the anodic peak current versus the concentration of NE in the analyzed range 0.2×10^{-4} M to 2.0×10^{-4} M

Table 2. Comparison of NE detection limits at different modified electrodes

| Electrode | Detection limit | Techniques | Ref. |
|------------------|---------------------|------------|------------|
| Nanotubes/ EPPGE | 9 nM | SWV | [18] |
| TTAB/CPE | $0.016 \mu\text{M}$ | DPV | [48] |
| (TLA/Au) | $2.0 \mu\text{M}$ | CV | [49] |
| TX-100/CPE | $5.0 \mu\text{M}$ | CV | [50] |
| SAOS/MWCNT/MCPE | $6.6 \mu\text{M}$ | CV | This paper |

3.5. Effect of pH value on the determination of NE at SAOS/MWCNT/MCPE

The effect of pH on the determination of NE in PBS at the SAOS/MWCNT/MCPE was investigated in the pH range of 5.8–7.8. The cyclic voltammograms of 10×10^{-5} M NE were

recorded at 0.2 M PBS of 5.8–7.8 solutions. Both anodic and cathodic peak potentials shifted to less positive potentials with increasing the pH from 5.8-7.8 as shown in Fig. 5(A). Graphs of I_{pa} vs the pH of the solution shows that the anodic peak current (I_{pa}) of NE increases with an increase the pH value from 5.8-6.8 after that the anodic peak current decreases with increasing the pH value from 6.8-7.8 and E_{pa} (V) versus the pH of the solution shows that the anodic peak potential (E_{pa}) of NE decreased with an increase in the pH value. A linear regression equations obtained was $E_{pa}(\text{V}) = -0.06268\text{pH} + 0.7076$ ($n=5$, $r^2=0.9946$) for SAOS/MWCNT/MCPE are shown in Fig. 5(B) with a slope of 62 mV/pH. This result confirms that the equal number of protons and electrons were involved in the electrochemical oxidation of NE [46] and I_{pa} increases indicated that the electrode showed good sensitive at pH.6.8 compared to other pH solutions which have been clearly shown in Fig. 5(B) and for further studies pH.6.8 was selected for NE.

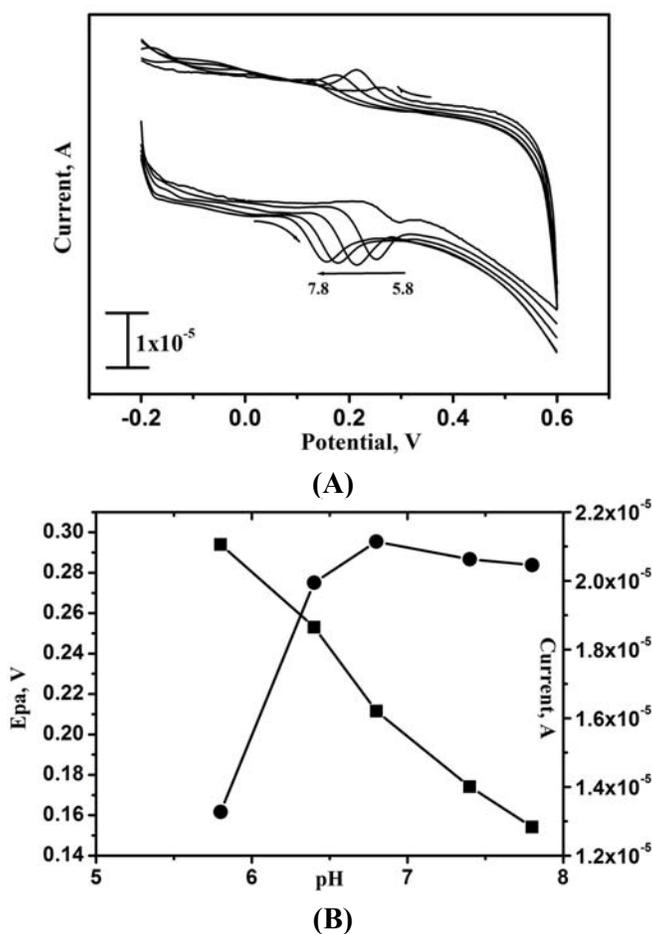


Fig. 5. (A) Cyclic voltammograms of 10×10^{-5} M NE for variation of pH from 5.8 to 7.8 at 0.2 M PBS Solution at SAOS/MWCNT/MCPE, Scan rate: 0.05 Vs^{-1} ; **(B)** The Graph of anodic peak potential v/s pH and anodic peak current v/s pH from 5.8 to 7.8

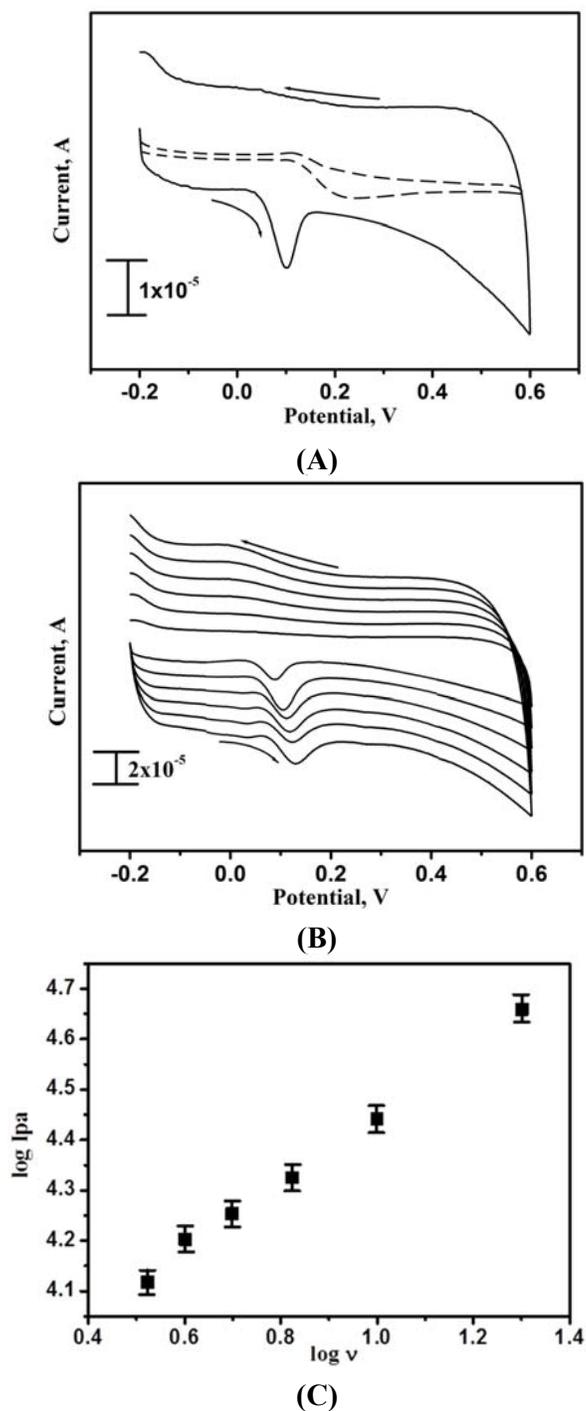
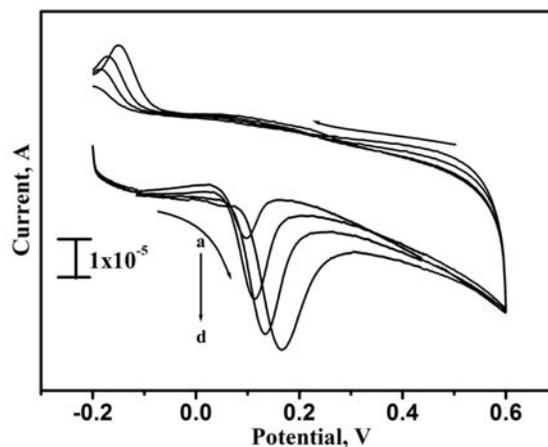


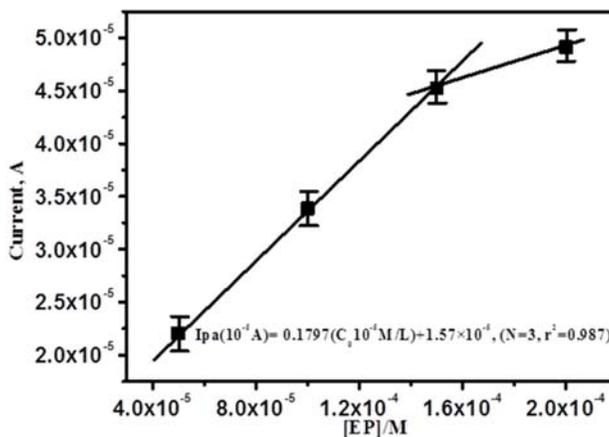
Fig. 6. (A) Cyclic voltammograms of BCPE (dashed line) and SAOS/MWCNT/MCPE (solid line) in the presence of 0.5mM EP in 0.2 M phosphate buffer solution of pH 6.8 at scan rate of 0.05 Vs^{-1} ; **(B)** Cyclic voltammograms of different scan rate in the presence of 0.5 mM EP and 0.2 M phosphate buffer, in pH 6.8 Scan Rate: 0.05 Vs^{-1} - 0.3 Vs^{-1} ; **(C)** Graph of $\log I_{pa}$ vs. $\log v$

3.6. Electrochemical response of EP at SAOS/MWCNT/MCPE

Fig. 6A shows the cyclic voltammograms recorded for 0.5 mM EP at BCPE (dashed line) and SAOS/MWCNT/MCPE (solid line) in 0.2 M PBS solution of pH 6.8 with the scan rate 0.05 Vs^{-1} . It is noticed that voltammogram obtained at BCPE was less sensitive and E_{pa} was located at 0.21 V. However, at SAOS/MWCNT/MCPE showed a significant increment in oxidation peak current and E_{pa} was located at 0.11 V with the peak potential shift towards more negative side this indicates the electrocatalytic nature with fast electron transfer. By this result, it shows the SAOS/MWCNT/MCPE acts as a good electrochemical sensor for EP.



(A)



(B)

Fig. 7. (A) Cyclic voltammogram of variation of concentration of EP from $0.5 \times 10^{-4} \text{ M}$ to $2.0 \times 10^{-4} \text{ M}$ in presence of phosphate buffer solution at pH 6.8 at 0.05 Vs^{-1} ; **(B)** Graph of the anodic peak current versus the concentration of EP in the analyzed range $0.5 \times 10^{-4} \text{ M}$ to $2.0 \times 10^{-4} \text{ M}$

The effect of scan rate was also studied for 0.5 mM EP in 0.2 M PBS of pH 6.8 in the scan range from 0.05 to 0.3 Vs^{-1} at SAOS/MWCNT/MCPE as shown in Fig. 6B. The graph of $\log I_{pa}$ versus $\log v$ was plotted in the range from 0.05 to 0.3 Vs^{-1} (Fig. 6C). The graph obtained was linear line with the slope of 0.6718 was a close agreement with the theoretical value of 0.5 for diffusion controlled process [41].

3.7. Effect of EP concentration

The cyclic voltammograms recorded for the oxidation of EP in 0.2 M PBS of pH 6.8 at SAOS/MWCNT/MCPE with the scan rate 0.05 Vs^{-1} by varying the concentration from 0.5×10^{-4} M to 2.0×10^{-4} M as shown in the Fig. 7A. This shows the increase in anodic peak current due to increase in the concentration of EP. The plot shown in the Fig. 7B shows the linear relationship between I_{pa} and the concentration of EP with the linear regression equation $I_{pa}(10^{-5} A) = 0.1797(C_0 10^{-4} M/L) + 1.579 \times 10^{-5}$, $r^2 = 0.967$, $N = 4$. The detection limit of the lower concentration range for EP was 6.3×10^{-5} M for the SAOS/MWCNT/MCPE and the result was compared with found literature [18,28,29] as shown in Table 3 and limit of quantification was 2.11×10^{-4} M [46].

Table 3. Comparison of EP detection limits at different modified electrodes

| Electrode | Detection limit | Techniques | Ref. |
|--|-------------------------|------------|------------|
| Nanotubes/ EPPGE | 0.15 nM | SWV | [18] |
| Carbon nanotube paste electrode of 2-(4-oxo-3-phenyl-3,4-dihydro-quinazolinyl)-N ¹ -phenylhydrazinecarbothioamide | 9.4 nM | SWV | [29] |
| MWCNT/Fe ₃ O ₄ /2,3-Nc, | 1.23×10^{-5} M | DPV | [28] |
| SAOS/MWCNT/MCPE | 6.3×10^{-5} M | CV | This paper |

3.8. Simultaneous electroanalysis of NE in excess concentration of EP

The NE and EP always exist together in the biological environment and simultaneous analysis of these molecules was difficult at bare carbon paste electrode [47]. The concentrations of EP were much greater than that of NE. Moreover, the oxidation potential of EP was nearly same as that of NE results in an overlapped poor voltammetric response at

BCPE. The Fig. 8A shows the cyclic voltammetric response of 0.1×10^{-4} M NE in presence of high concentration of 1.5×10^{-3} M EP in 0.2 M PBS of pH 6.8 at the scan rate of 0.05 Vs^{-1} at both BCPE and SAOS/MWCNT/MCPE.

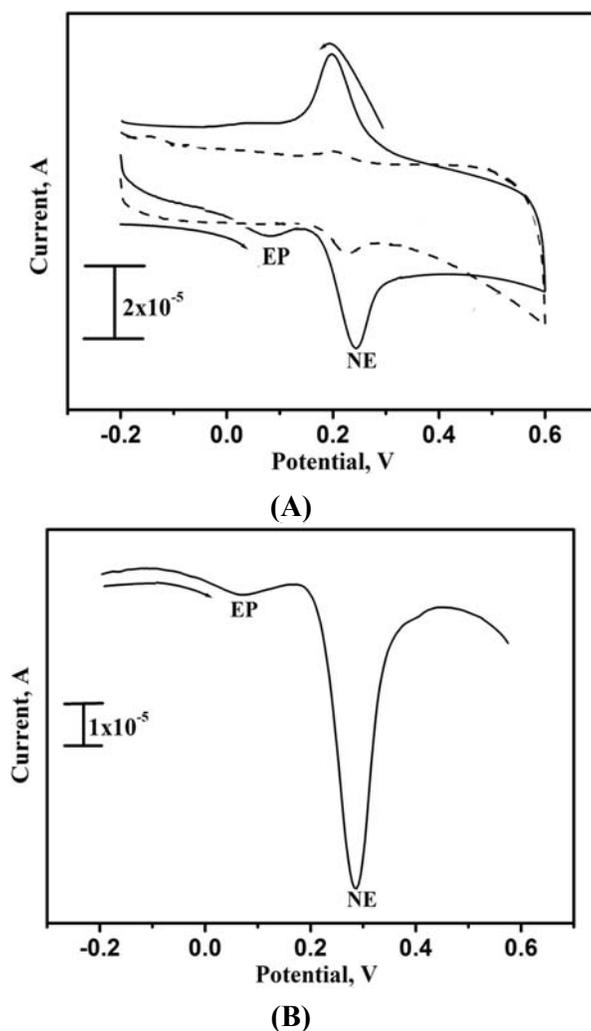


Fig. 8. (A) Cyclic voltammograms for 0.1×10^{-4} M NE and 1.5×10^{-3} M EP at pH 6.8 PBS at a scan rate of 0.05 Vs^{-1} in BCPE (dotted line) and SAOS/MWCNT/MCPE (solid line); (B) Differential pulse voltammogram for 0.1×10^{-4} M NE and 1.5×10^{-3} M EP at pH 6.8 PBS at a scan rate of 0.05 Vs^{-1} in BCPE (dotted line) and SAOS/MWCNT/MCPE (solid line)

The cyclic voltammograms obtained for the mixture of NE and EP at BCPE was broad, less sensible and gives overlapped potential. This leads to their individual identification impossible (dashed line). However, the SAOS/MWCNT/MCPE has an ability to overcome this difficulty and solve the problem of interference of both the analytes in the reaction mixture. Two well-defined peak potential of NE and EP at different potentials are located at 0.248 V and 0.082 V respectively (solid line). The peak to peak separation of NE-EP was

0.166 V. This result was more enough to identify and determine NE in the presence of high concentration of EP at SAOS/MWCNT/MCPE.

Differential pulse voltammetry (DPV) was employed for the analysis of NE and EP at SAOS/MWCNT/MCPE due to its higher current sensitivity and absence of background current. The Fig. 8B shows the simultaneous determination of 0.1×10^{-4} M NE and 1.5×10^{-3} M EP in 0.2 M PBS of pH 6.8 with well separated voltammetric signals corresponding to their oxidation at SAOS/MWCNT/MCPE. The oxidation potential of NE and EP was situated at 0.285 V and 0.082 V respectively. The peak to peak separation between NE-EP was 0.203 V.

4. CONCLUSION

A sensitive and selective electrochemical method was developed for the electroanalysis of NE using SAOS/MWCNT/MCPE. The SAOS/MWCNT/MCPE shows excellent electrocatalytic activity towards the oxidation of NE in phosphate buffer solution at pH 6.8 by cyclic voltammetric and differential pulse voltammetric techniques. The SAOS/MWCNT/MCPE exhibits less heterogeneous rate constant at 0.5 Vs^{-1} towards NE and this confirm the modified electrode adsorbed by NE species. The detection limit in the lower concentration range for NE was $6.6 \mu\text{M}$ for the SAOS/MWCNT/MCPE and quantification limit was 2.2×10^{-5} M. The pH studies reveal that the equal number of electrons and protons involved in the detection of NE. The scan rate variation for EP confirms that the modified electrode controlled by the diffusion process. The SAOS/MWCNT/MCPE shows excellent sensitivity and electrocatalytic activity for NE and good electrochemical signal separation between NE and EP. The oxidation peak to peak separation between NE-EP was 0.2 V individually and simultaneously. This result was large enough to analyze NE in presence of large excess of EP. Therefore, the present method can be extended to various bioactive molecules in the field of electroanalytical chemistry and development of electrochemical sensors.

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