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Electrocatalytic Oxidation of Dopamine on Acrylamide Modified Carbon Paste Electrode : A Voltammetric Study

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The preparation of acrylamide modified carbon paste electrode and its electrocatalytic oxidation to dopamine (DA) in 0.2 M phosphate buffer (PBS) at 7.4 pH were presented. Several parameters such as DA concentration, scan rate variation and pH were investigated by the cyclic voltammetric technique (CV). The peak currents were proportional to the concentration of DA with a detection limit of 3.5×10^{-7} M. The concentration effect of modifier in the carbon paste electrode also reveals that the change in the electrode interface which would lead to the formation of anionic charge on the surface of the electrode could enhance the cationic charged dopamine. The stability and repeatability of the electrode for the determination of DA were also investigated.

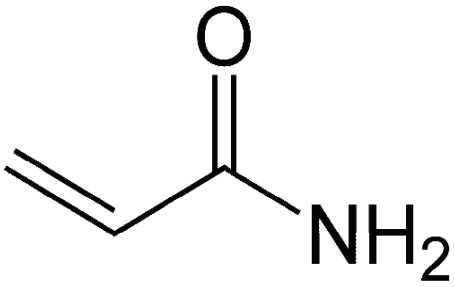
Keywords: Chemically modified electrode, Dopamine, Carbon paste electrode, Electrocatalytic oxidation, Cyclic voltammetry

1. INTRODUCTION

DA is one of the naturally occurring catecholamine, which acts as an important neurotransmitter in mammals. A loss of DA containing neurons may result in some serious diseases such as parkinsonism. A low level of DA has been found in the patient with Parkinson's disease [1]. People with parkinson's disease have depleted levels of dopamine, which causes tremor, muscle stiffness or rigidity, slowness of movement (bradykinesia) and loss of balance. Nevertheless, elevated levels of dopamine also cause adverse reaction such as nausea, vomiting and cardiac arrhythmias [2,3]. DA also acts as a biogenic amine, which functions as neurotransmitters in the brain and nervous system of mammals. Dopamine hydrochloride salt is widely used in the treatment of bronchial asthma, hypertension, heart failure and renal failure associated with shock episodes [4]. The very low

concentration of DA in the "extracellular fluid" of the caudate nucleus provides a large challenge for detection of DA [5]. DA is widely applied to the treatment of circulatory collapse syndrome caused by myocardial infraction, trauma, renal failure, cardiac surgery, or congestive cardiac failure [6]. The concentration of neurotransmitters in biological samples varies from species to species, in a wide range of from 10^{-7} to 10^{-3} M [7]. Therefore the determination of the concentration of this neurochemical is important The development of voltammetric sensors for the detection of neurotransmitters in the extra cellular fluid of the central nervous system has received much attention in the past few decades [8,9]. The electrochemical methods have more advantages over the other because of the advantage of the electrode in sensing the neurotransmitters in living organisms [10]. DA and other catecholamines are easily oxidizable compounds makes their detection possible by electrochemical methods based on anodic oxidation [11]. The electrochemical sensors based on chemically modified electrodes (CMEs) have widely been used for the detection of these biologically important compounds and various modified electrodes have been constructed for this purpose [12–25].

Because of the simple preparation and easy renewal of the surface, carbon has been used extensively as a working electrode for a variety of electrochemical applications. It has also been shown that carbon tends to be more compatible with biological tissues than other commonly used electrode materials [26]. Among the carbon electrodes, the carbon paste electrode (CPE) is of particular importance. The ease and speed of preparation and of obtaining a new reproducible surface, the low residual current, porous surface and low cost of carbon paste are some advantages of CPEs over all other carbon electrodes. Therefore, the CPE can provide a suitable electrode substrate for preparation of modified electrodes.



Scheme 1. Structure of acrylamide

Acrylamide (Scheme.1), an industrially produced α, β- unsaturated (conjugated) reactive molecule, is used worldwide to synthesize polyacrylamide. Polyacrylamide has found numerous applications as a soil conditioner, in wastewater treatment, in the cosmetic, paper and textile industries and in the laboratory as a solid support for the separation of proteins by electrophoresis.

As a part of our research work on the development of modified electrodes, we extended our work on the detection of dopamine [27-33]. In this work acrylamide modified carbon paste electrode was fabricated and characterized by cyclic voltammetry. The acrylamide modified electrode showed

good electrocatalytic oxidation of dopamine. On the basis of the electrochemical response of dopamine the acrylamide modified carbon paste electrode can be used for the development of sensor.

2. EXPERIMENTAL

2.1. Reagents and Chemicals

Acrylamide, potassium ferrocyanide [$K_4Fe(CN)_6$], graphite powder, dopamine, potassium chloride, perchloric acid were obtained from Himedia, sodium dihydrogen phosphate, di-sodium hydrogen phosphate were used for the preparation of 0.2M PBS solution. All chemicals and reagents were prepared with double distilled water. pH of the solution was monitored by a digital pH meter fabricated by systronics.

2.2. Apparatus and Procedure

Cyclic voltammetry (CV) was performed on Model EA-201 Electroanalyser (EA- 201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The carbon paste electrode was prepared as fallows 70 % graphite powder (particle size 50 mm and density is 20 mg/100 ml) 30 % silicone oil were mixed by hand to produce a homogeneous carbon paste electrode. The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothened on a weighing paper.

3. RESULTS AND DISCUSSION

3.1 Preparation of acrylamide modified carbon paste electrode

Acrylamide modified carbon paste electrode was prepared by grinding the 2 mg of acrylamide with 70 % graphite powder of 50 mm particle size and 30 % silicon oil in an agate mortar by hand mixing for about 30 minute to get homogeneous acrylamide modified carbon paste. The paste was packed into the cavity of homemade CPE of 3 mm in diameter and smoothened on weighing paper.

3.2 Electrochemical characterization of acrylamide

The characterization of acrylamide modified carbon paste electrode was investigated with standard [$K_4Fe(CN)_6$] by using CV technique. Fig.1 shows the typical cyclic-voltammogram for 1mM [$K_4Fe(CN)_6$] at both BCPE and acrylamide modified carbon paste electrode. The electrochemical reduction was carried out with 1M KCl as supporting electrolyte.

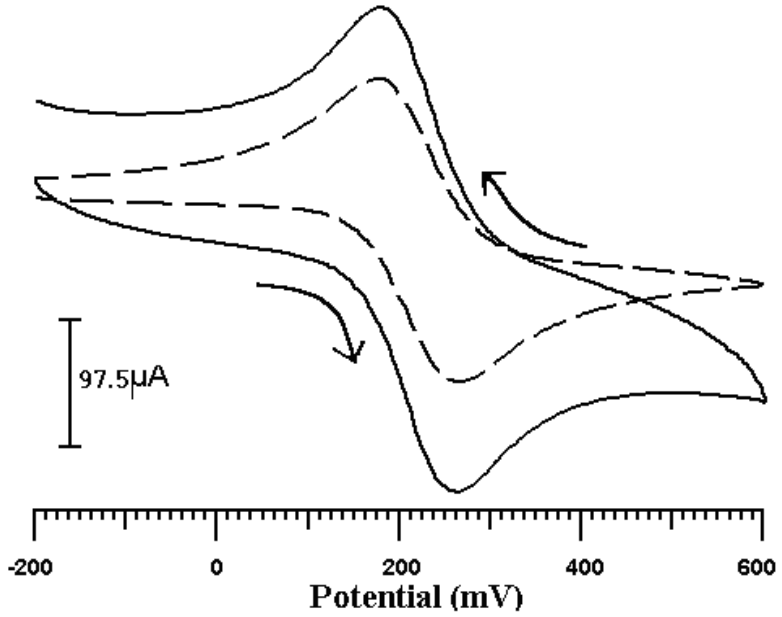


Figure 1. Cyclic Voltammogram of 1mM $[K_4Fe(CN)_6]$ at BCPE (dotted line) and ACRYLAMIDE MCPE (Solid line) in 1M, KCl Scan Rate: 50 mVs^{-1}

Reversible voltammogram was observed for $[K_4Fe(CN)_6]$ at BCPE with small cathodic peak current (Ipc) and anodic peak current (Ipa)(dashed line). The cathodic peak potential and (Epc) and anodic peak potential (Epa) were located at 179 mV and 256 mV respectively. The potential difference of two reversible peaks (ΔEp) was found to be 77 mV. On modification with acrylamide the voltammogram has shown enhancement in both Ipc and Ipa (solid line). The Epa and Epc were found at 239 mV and 178 mV and ΔEp was 61 mV which was on accordance with a Nernst reversible behaviour.

3.3. Effect of acrylamide as modifier.

Acrylamide is used as a modifier in the preparation of modified carbon paste electrode. The characterization of acrylamide modified carbon paste electrode was investigated by using cyclic voltammetric technique. It was prepared of different ratio by adding different amount of acrylamide. By increasing the concentration of acrylamide in the carbon paste electrode, the electrochemical redox peak current goes on increasing in 1 M KCl and 1 mM Potassium ferrocyanide as an analyte. Figure.2 shows the calibration plot of acrylamide sensitivity tendency towards the dopamine. Lower the concentration of the modifier lower is the current response; by increasing the concentration of acrylamide the peak current increases gradually upto 2 mg of acrylamide and then starts to decrease. Hence 2mg concentration of acrylamide was used for the preparation of modified electrode.

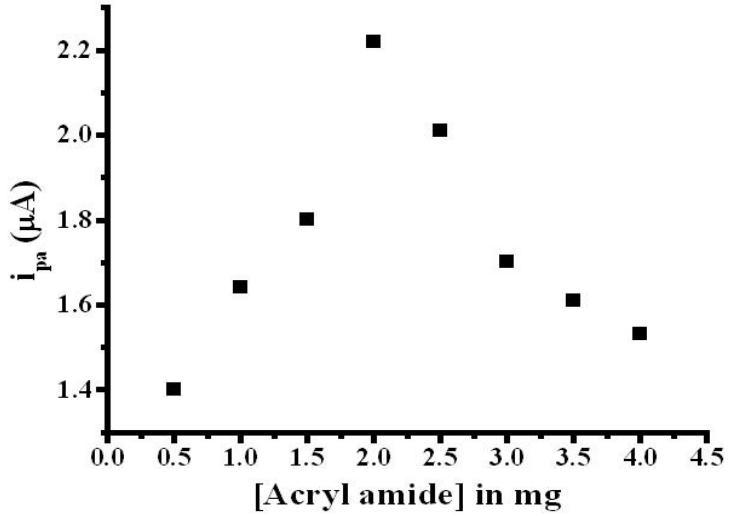


Figure 2. Effect of concentration of acrylamide on anodic peak current of 1 mM $[K_4Fe(CN)_6]$ in 1 M KCl, Scan Rate: 50 mVs^{-1}

3.4. Cyclic voltammograms of DA at Acrylamide modified carbon paste electrode.

Figure 3a shows CVs of DA at bare carbon paste electrode and an acrylamide modified carbon paste electrode.

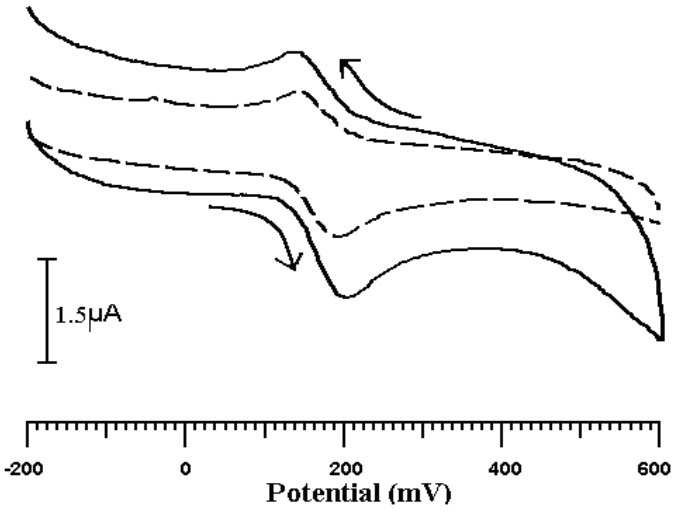


Figure 3. Cyclic voltammogram in a 0.2 M phosphate buffer solution at pH 7.4 at BCPE (dashed line) and ACRYLAMIDE MCPE (solid line) in the presence of $0.5X10^{-4}$ M DA with a scan rate of 50 mVs^{-1}

DA exhibited poor electrochemical response at the bare carbon paste electrode. The peak potential separate value (ΔEp) between the anodic peak potential (Epa189 mV) and the cathodic potential (Epc146 mV) was 43 mV. But at the modified electrode, DA exhibited good electrochemical

response and the voltammograms show one cathodic peaks and one anodic peak at 142 mV and 201 mV respectively. So the peak potential separate value (ΔE_p) was 59 mV.

It can be seen that the oxidation peak potential of DA shifted positively from 189 mV at the bare carbon paste electrode to 201 mV at the acrylamide modified carbon paste electrode. These results indicate that the acrylamide modified carbon paste electrode is able to accelerate the rate of DA electron transfer.

3.5. Effect of scan rate.

Cyclic voltammograms for DA at acrylamide modified carbon paste electrode in different scan rate were shown in Fig.4a. The acrylamide modified carbon paste electrode has shown increase in the peak current with increase in scan rate (50 mV/s to 350 mV/s) for $0.5X10^{-4}$ DA in 0.2 M PBS at pH 7.4.

The graph of current Ipa vs. scan rate (ν) and square root of scan rate ($\nu^{1/2}$) were plotted. The graph obtained were nearly straight line as shown in Fig.4b, and Fig.4c. In the range from 50 mV/s to 350 mV/s the anodic peak currents were proportional to the scan rate (ν) and also the to the square root of scan rate ($\nu^{1/2}$) with correlation coefficient 0.99978 and 0.98882 for Ipa vs. ν and Ipa vs. $\nu^{1/2}$ respectively. This indicates that, the electrode transfer reaction was both adsorption and diffusion controlled.

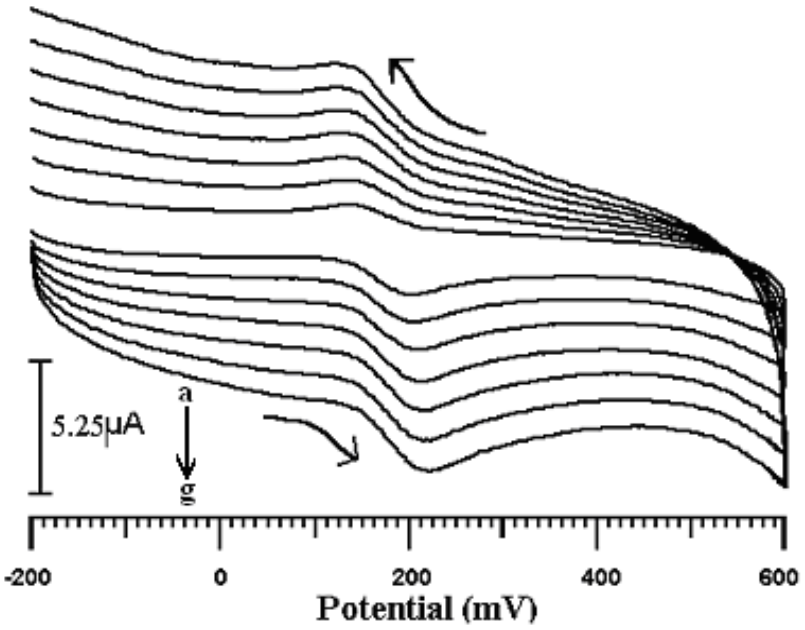


Figure 4a. Cyclic voltammogram of different scan rate in the presence of $0.5X\ 10^{-4}$ M DA and 0.2M phosphate buffer solution at pH 7.4, scan rate 50 mVs^{-1} - $350mVs^{-1}$

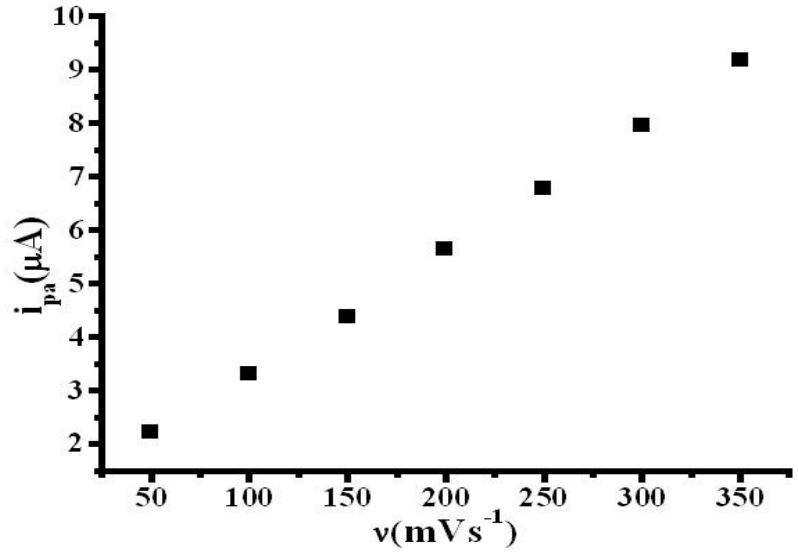


Figure 4b. The dependence of peak current of $0.5X10^{-4}$ M DA at different scan rate at an acrylamide MCPE in a 0.20M phosphate buffer solution at pH 7.4

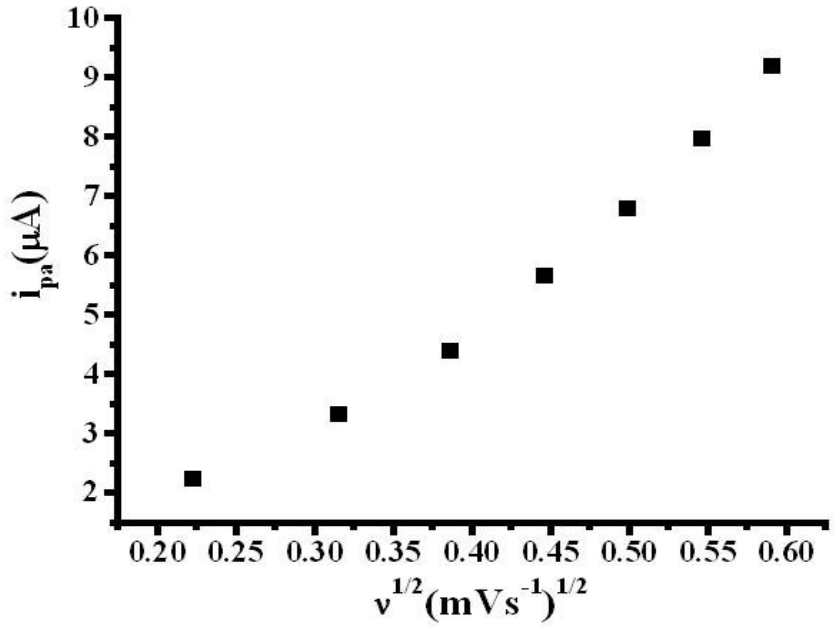


Figure 4c. The dependence of peak current of $0.5X10^{-4}$ M DA on square root of scan rate at an acrylamide MCPE in a 0.2M phosphate buffer solution at pH 7.4

3.6. Effect of concentration of DA.

The cyclic voltammogram of different concentration of dopamine has shown in the Figure.5a which shows the increase in both the anodic peak current and cathodic peak current due to vary the

concentration of DA from $0.4X10^{-4}$ to $2.4X10^{-4}$ M. Figure. 5b shows the linear relationship between the Ipa and the concentration. The correlation coefficient value was found to be 0.9993.

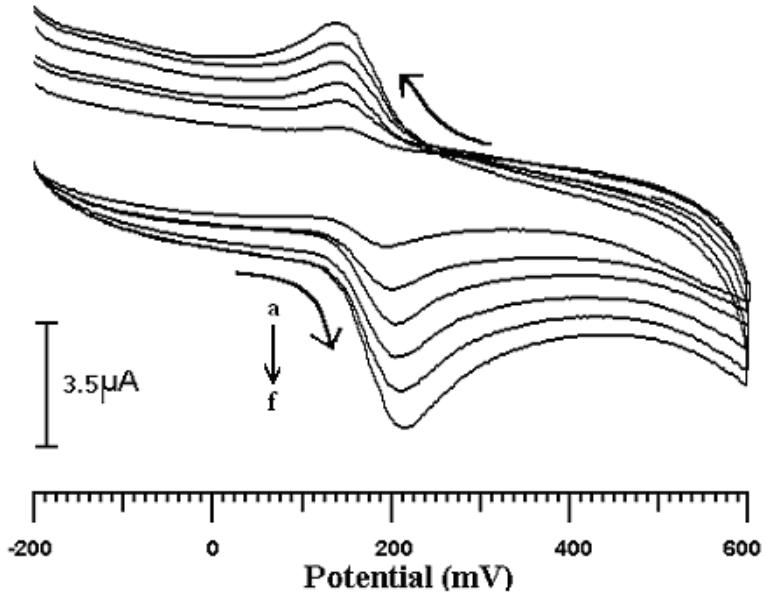


Figure 5a. Cyclic voltammogram of DA at different concentration at ACRYLAMIDE MCPE in 0.2 M PBS of pH 7.4. (a – f; $0.4X10^{-4}$ M, $0.8X10^{-4}$ M, $1.2X10^{-4}$ M, $1.6X10^{-4}$ M, $2\ X10^{-4}$ M, $2.4X10^{-4}$ M)

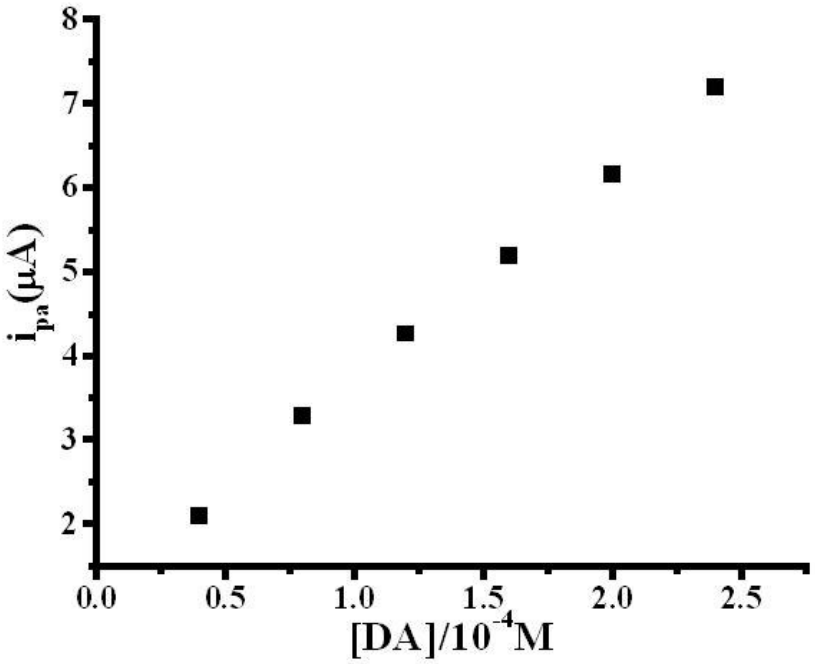


Figure 5b. Graph of current vs concentration of DA.

3.7. Effect of pH variation.

The effect of the solution pH on the response of DA was investigated over the range of 5-9. The observation shows that the anodic peak current increased with increasing solution pH until it reached 7.4. When the pH>7.4, the anodic peak current decreased. Since pH 7.4 is the physiological pH value and it was chosen for the supporting electrolyte in the electrochemical detection of DA. Figure 6 shows the relationship between the Epa of DA and pH of PBS solution.

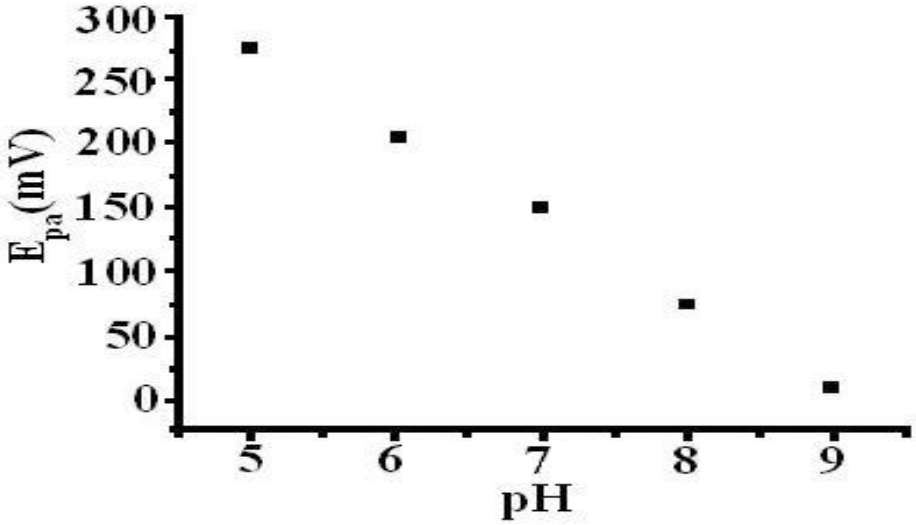


Figure 6 . Effect of pH variation of $0.5X10^{-4}$ M DA at ACRYLAMIDE MCPE, supporting electrolyte 0.2M PBS, at scan rate $50mVs^{-1}$

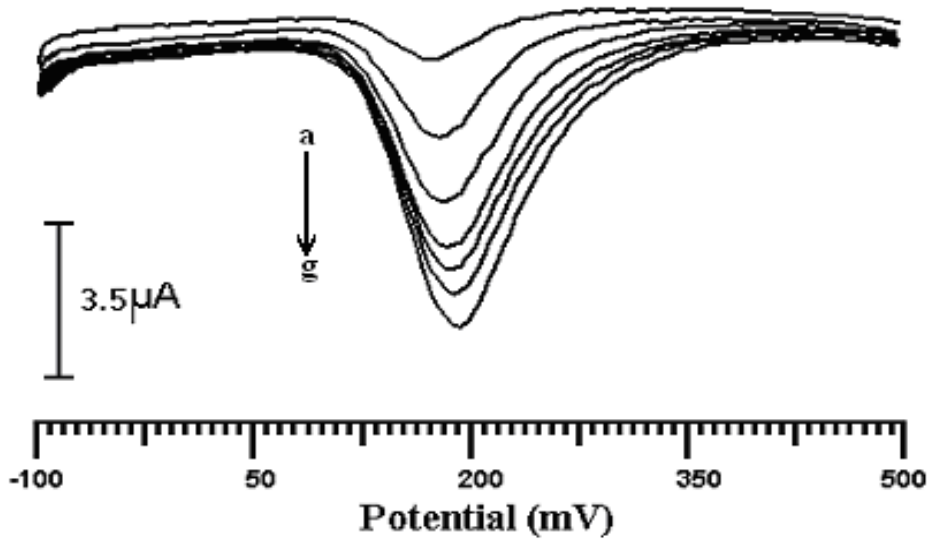


Figure 7. Differential pulse voltammograms of DA at ACRYLAMIDE MCPE in 0.2 M pH 7.4 PBS. [DA] is from a-f. a-0.5;b-1;c-1.5;d-2;e-2.5;f-3;g-3.55 $X10^{-4}$ M DA ; scan rate 20 mVs^{-1}

3.8. Detection limit and reproducibility

DPV was used to determinate the amount of DA. The current response of different concentrated DA was obtained and the results were shown in Fig. 7. The anodic peak current was proportional to the concentration of DA over a range of $0.5X10^{-4}$ to $3.5X10^{-4}$ M. The detection limit was calculated by DPV method and it was fund to be 3.5×10^{-7} M at ACRYLAMIDE MCPE.

4. CONCLUSIONS

In this work, chemically modified carbon paste electrode acts as a good sensor, exhibited strong promoting effect and stability towards the electrochemical oxidation of potassium ferrocyanide in KCl solution and dopamine at pH 7.4 in PBS. With its low cost and easy of preparation, high sensitivity, surface regeneration of the modified electrode and the reproducibility of the voltammetric response make the prepared modified system very useful in the construction of simple devices for the determination of dopamine in clinical and pharmaceutical preparations.

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