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Poly(amoxicillin) Modified Carbon Paste Electrode for the Determination of Dopamine: A Cyclic Voltammetric Study

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Abstract- The carbon paste electrode (CPE) was modified by electropolymerisation of amoxicillin in 0.2 M acetate buffer solution (ABS) of pH 5.0 by using cyclic voltammetric (CV) technique. The modified electrode was used for the electrochemical determination of dopamine (DA). The poly(amoxicillin) modified CPE showed excellent electrocatalytic activity towards the oxidation of DA. The study of variation in concentration and scan rate shows that the electrode process was diffusion-controlled. Further the modified electrode was used for the simultaneous determination of DA and ascorbic acid (AA) by CV technique.

Keywords- Dopamine, Electropolymerisation, Carbon paste electrode, Cyclic voltammetry

1. INTRODUCTION

In recent years the design, fabrication and application of novel electrochemical sensor has of considerable interest [1]. Particularly the development of voltammetric sensors for the determination of neurotransmitters, such as dopamine (DA) and other catecholamine's has received a lot of interest. Among the families of catecholamine's DA received much interest, because the change in DA levels gives clear information regarding understanding of brain functions, such as learning and memory formation, physiological and pathological process of

parkinson's disease [2]. As a result of this, catecholamine drugs are now widely used in various clinical fields such as, treatment of bronchial asthma, hypertension, parkinson's disease, myocardial infarction and cardiac surgery etc. There are various techniques have been proposed for the qualitative and quantitative determination of DA in the diagnosis. A major problem was the coexistence of probable interference AA, which is also present in biological fluids at relatively hundred times higher in concentration compared to DA [3]. It is well known that the direct anodic oxidation of DA and AA is irreversible, requires high over potential, and suffers from fouling effect at bare working electrodes [4-5]. Due to the accumulation of the oxidized products the result obtained was least selective and less sensitive. Therefore, for the determination of DA so many methods are proposed [6-13]. Among these methods, usage of electropolymerised working electrode is the recent trend. In the literature so many methods are proposed for the modification of the bare working electrodes to achieve the simultaneous and sensitive determination of DA and AA. Such as, poly(phenosafranine) [14], N,N-dimethylaniline [15] hippuric acid [16] sulfosalicylic acid [17] styrene sulfonic acid [18] amino benzoic acid [19] aniline [20] cobalt hexacyanoferrate [21] 3,4-ethlenedioxy thiophene [22] eriochrome black-T [23] L-methionine [24] toludine blue [25] DL-alanine [26]. In the present work, amoxicillin was electropolymerised on the surface of bare carbon paste electrode (BCPE) by cyclic voltammetric technique. The amoxicillin is an antibiotic drug used in the treatment of bacterial infections. The chemical structure of amoxicillin contains d-4-hydroxyphenylglycine side chain attached to 6-aminopenicillanic acid moiety. The fabricated poly(amoxicillin) modified carbon paste electrode (MCPE) was used for the determination of DA. The result shows the fabricated electrode can be employed for the analysis of DA in the biological fluids.

2. EXPERIMENTAL

2.1. Apparatus and reagents

Cyclic voltammetric studies were conducted with a model EA-201 Electroanalyzer (Chemilink Systems) connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three electrode cell. The BCPE or poly(amoxicillin) MCPE was used as a working electrode, platinum wire as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. All potentials reported were versus the SCE. Dopamine hydrochloride (DA) and ascorbic acid (AA) were obtained from Himedia chemicals and were used as received. All other chemicals were of analytical grade. An acetate buffer solution (ABS) was prepared by mixing standard stock solutions of 0.2 M CH_3COOH and 0.2 M CH_3COONa and adjusting the pH with 0.1 M NaOH. All the solutions were prepared with double distilled water.

2.2. Preparation of bare carbon paste electrode

The BCPE was prepared by hand mixing of 70% graphite powder and 30% silicon oil in an agate mortar for 45 minutes to form a homogenous mixture. The prepared carbon paste was tightly packed into a PVC tube of 3 mm internal diameter and the electrical contact was provided by a copper wire connected to the end of the tube.

2.3. Fabrication of poly(amoxicillin) MCPE

The paste packing procedure was same as that at BCPE. Electropolymerisation of amoxicillin at the carbon paste electrode was carried out by using cyclic voltammetric technique. The aqueous solution containing 1 mM amoxicillin in 0.2 M ABS of pH 5.0 was taken in an electrolytic cell. The electropolymerisation was achieved by the formation of a thin film that grew between -0.1 V and +1.5 V at a scan rate of 50 mVs^{-1} for 15 cycles as shown in Figure 1. After the electropolymerisation the electrode was washed thoroughly with double distilled water and used for the electroanalysis.

During the process of electropolymerisation, the voltammograms increased at first indicating the growth and formation of polymer film on the surface of carbon paste electrode. After the 15 cycles the increase in the voltammograms tends to be almost constant, suggesting the growth and formation of a polymer film reached the level of saturation [27-28].

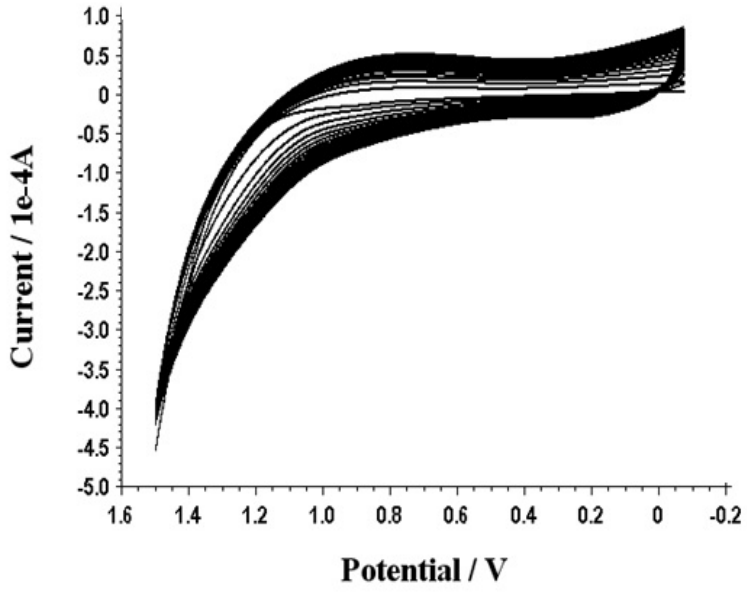

Fig. 1. Cyclic voltammograms obtained during the electropolymerisation of amoxicillin on the surface of BCPE

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical investigation of potassium ferrocyanide at poly(amoxicillin) MCPE

The Figure 2 shows the electrochemical response of 1mM solution of potassium ferrocyanide at BCPE (dashed line) and poly(amoxicillin) MCPE (solid line) in 1 M KCl at the scan rate of 50 mVs^{-1}. The poly(amoxicillin) MCPE shows increase in the redox peak current when compared with the BCPE. The difference between the anodic and cathodic peak potential (ΔEp) is 0.054 at poly(amoxicillin) MCPE, which is attributed to the reversible electrode process, The results obtained greatly improved the voltammetric response of potassium ferrocyanide at poly(amoxicillin) MCPE. This suggests that the surface property of the modified electrode has been significantly changed.

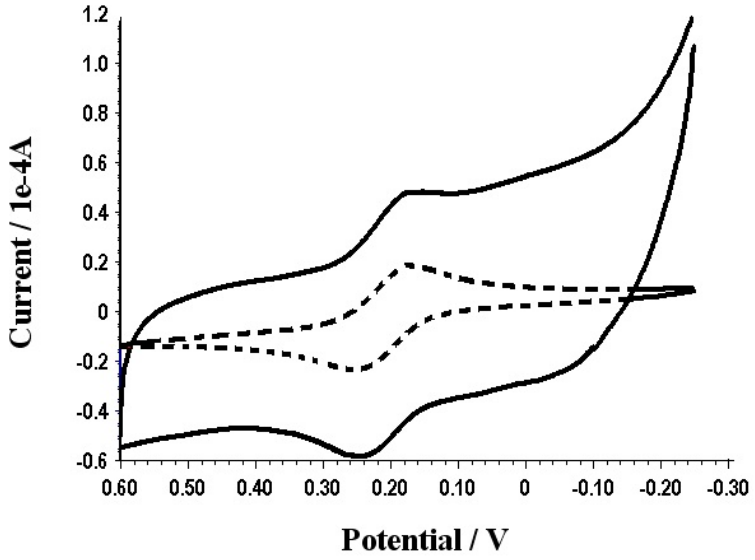

Fig. 2. Cyclic voltammograms obtained for the electrochemical response of 1mM $K_4[Fe(CN)_6]$ at BCPE (dotted line) and poly(amoxicillin) MCPE (solid line) in 1 M KCl at scan rate of 50 mVs^{-1}

3.2. Electrochemical response of dopamine at the poly(amoxicillin) MCPE

Figure 3 shows the cyclic voltammograms obtained for the electrochemical response of 1.0 mM DA at poly(amoxicillin) MCPE (curve c), BCPE (curve a) and in absence of DA (curve b) in 0.2 M ABS of pH 5.0. At BCPE the oxidation of DA was with less sensitivity and oxidation potential was located at 0.265V (Versus SCE). Under the same condition the poly (amoxicillin) MCPE shows significant increment in the peak currents and oxidation potentials was observed at 0.275 V. This remarkable enhancement of peak current confirms the electrocatalytic effect of poly(amoxicillin) MCPE.

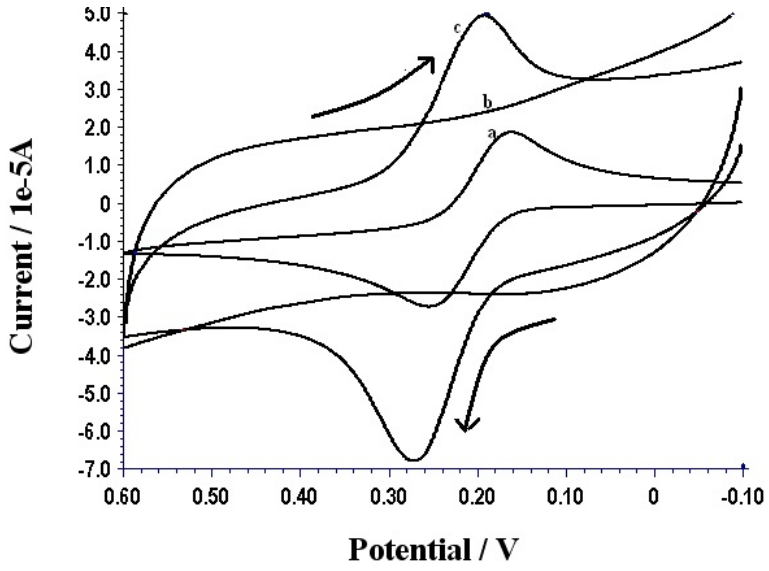

Fig. 3. Cyclic voltammograms recorded for the oxidation of 1.0 mM DA at BCPE (curve a) and poly(amoxicillin) MCPE (curve c) in 0.2 M ABS of pH 6.0. In the absence of DA (curve b)

3.3. Effect of scan rate on the peak current of dopamine

Figure 4 shows the cyclic voltammograms of 1 mM DA at poly(amoxicillin) MCPE at different scan rates. This was carried out in order to investigate the kinetics of the electrode reactions and verify whether diffusion is the only controlling factor for mass transport. The observation shows that with the increased scan rate the redox peak current also increased gradually (Figure 4).

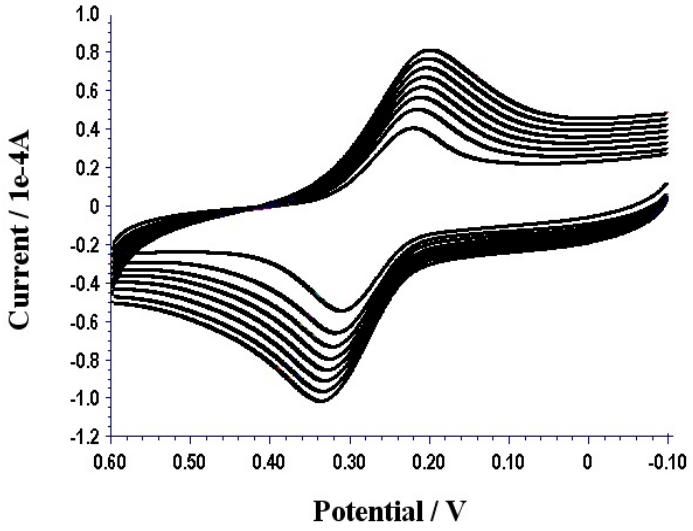

Fig. 4. Cyclic voltammograms of 1.0 mM DA at poly(amoxicillin) MCPE at different scan rates (a–h: 50, 60, 70, 80, 90, 100, 110, 120, mVs^{-1}) in 0.2 M ABS of pH 5.0

The relationship between the peak currents with square root of scan rate was shown in the Figure 5 in the range from 50 to 120 mVs^{-1}. The redox peak currents were proportional to the square root of the scan rate ($v^{1/2}$) indicating the electrode process was controlled by the diffusion of the analytes.

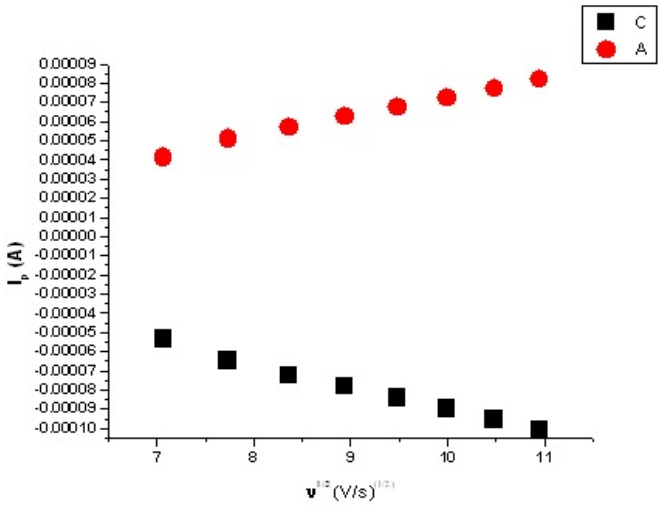

Fig. 5. Graph of peak current versus square root of scan rate

3.4. Effect of pH

Cyclic voltammetry was used to investigate the effect of solution pH value in the determination of DA at the poly(amoxicillin) MCPE. Figure 6 shows the cyclic voltammograms obtained for the oxidation of 0.1 mM DA at a scan rate of 50 mVS^{-1} at the poly(amoxicillin) MCPE in 0.2 M ABS of varying pH.

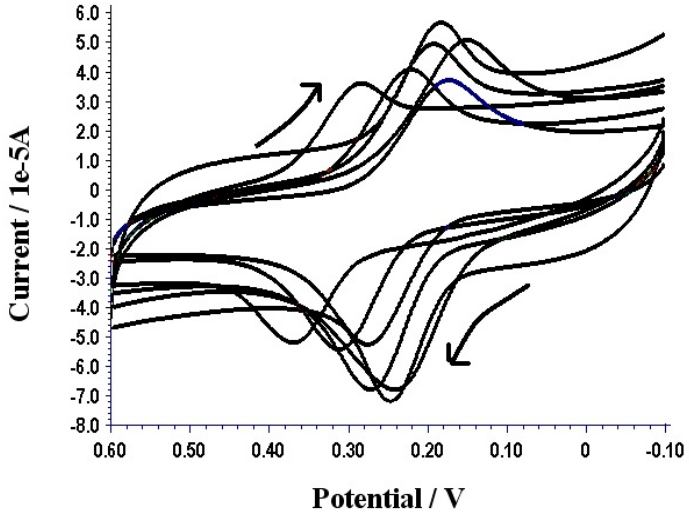

Fig. 6. Cyclic voltammograms obtained for the oxidation of 1.0 mM DA at poly(amoxicillin) MCPE in 0.2 M ABS of different pH values with the scan rate of 50 mVs^{-1}

As shown in the Figure 7 the anodic and cathodic peak potentials of DA were shifted to a less positive potential with the increase of pH values. The plot of E^o versus solution pH gives an almost straight line with a slope of 0.053 V/pH in the pH range from 4 to 9. The obtained slope in a good agreement with the theoretical value of 0.059 V/pH for equal number of proton and electron transfer process [27-29].

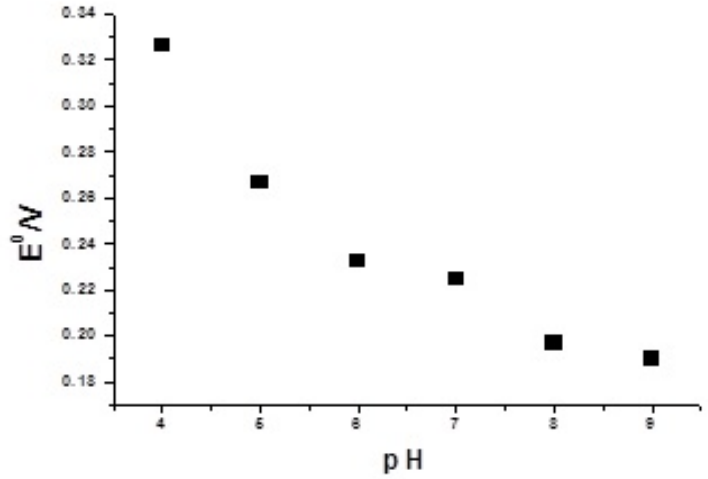

Fig. 7. Graph of peak potential of DA versus pH values

3.5. Electrochemical behavior of ascorbic acid at poly(amoxicillin) MCPE

Figure 8 shows the cyclic voltammograms obtained for 6.0 mM AA in 0.2 M ABS of pH 6.0 at BCPE and poly (amoxicillin) MCPE at the scan rate of 50 mVS^{-1}. At BCPE the AA shows irreversible behavior nature, the oxidation potential was located at 0.21 V.

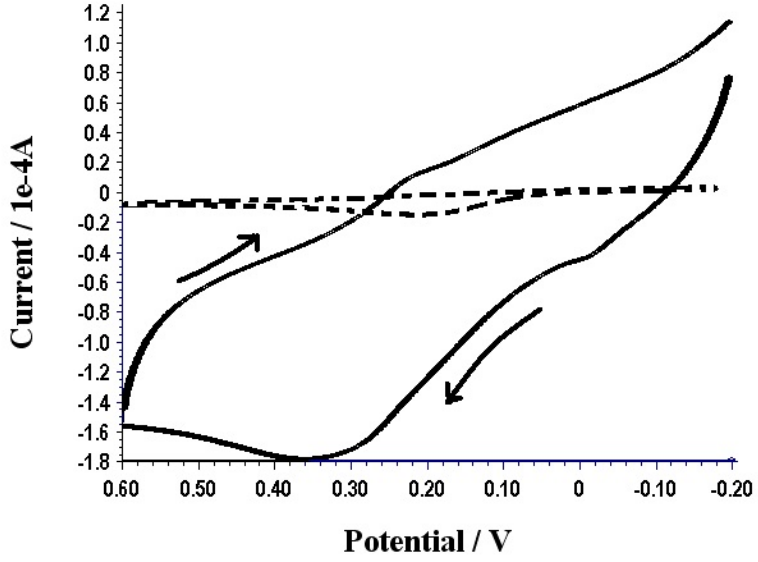

Fig. 8. Cyclic voltammograms obtained for the oxidation of 6.0 mM AA at BCPE (dashed line) and poly(amoxicillin) MCPE (solid line) in 0.2 M ABS (pH 6.0) at a scan rate 50 mVs^{-1}

However, at poly(amoxicillin) MCPE the oxidation was observed at -0.080 V. This improvement of current signal and minimization of over potential confirms the electrocatalytic activity of the poly(amoxicillin) MCPE towards the oxidation of AA. Since the oxidation potential of AA was shifted to the negative side leads to the elimination of interference in the oxidation of DA [27].

4. CONCLUSION

The electropolymerisation of amoxicillin on the carbon paste electrode was achieved by CV technique. The fabricated electrode was used to study the redox behaviors of DA. The poly(amoxicillin) MCPE shows enhanced current response compared to BCPE. The oxidation potential of AA was shifted to the negative side leads to the absence of interference in analyzing the DA. Overall the fabricated electrode can be used for the determination of DA in physiological and pharmaceutical samples.

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