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Electrosensitive Determination of Paracetamol Using a Poly (glycine) Film Coated Graphite Pencil Electrode: A Cyclic Voltammetric Study

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Abstract- The poly (glycine) film was deposited on the surface of graphite pencil electrode (GPE) by cyclic voltammetric technique. The modified film coated graphite pencil electrode exhibits excellent electrocatalytic activity towards the detection of paracetamol at pH 7.0. The scan rate effect was found to be diffusion controlled electrode process. The concentration effect of paracetamol was linear with current. This developed method can also be applied for some neurotransmitters.

Keywords- Electropolymerisation, Poly(glycine), Paracetamol, Graphite pencil electrode, Cyclic voltammetry

1. INTRODUCTION

Paracetamol, (N-acetyl-p-aminophenol) known as acetaminophen, is a pain killer that is popular throughout the world because it is remarkably safe to the stomach. Paracetamol (PC) was firstly introduced into medicine as an antipyretic/analgesic by Von Mering in 1893. Prior to this cinchona bark, which was also used to make the anti- malaria drug quinine, had been used to treat fevers. paracetamol is one of the most commonly used analgesics in

pharmaceutical formulations, for the reduction of fever and also as a pain killer for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain in adults and children. It is the most used medicine after acetylsalicylic acid in many countries as an alternative to aspirin and phenacetin [1-5].

The graphite pencil electrode (GPE) has been successfully acting as a biosensor in modern electroanalytical field. A porous composite is consisting of graphite particles, poly meric binder and other additives such as clay. Due to high electrochemical reactivity, electrical conductivity, good mechanical rigidity, low cost, electrochemical reactivity, ease of modification, renewal, low background current and miniaturization, the GPE has good application in the analysis of neurotransmitter and in the detection of traces of metal ions [6-9]. GPE has a larger active electrode surface area and is therefore able to detect low concentrations and or volume of the analyte [10]. This type of electrode has been successfully applied to design various biosensors [11-14].

Electropolymerisation is a good approach to immobilize polymers to prepare polymer modified electrodes (PME's) as adjusting the electrochemical parameters can coated film thickness permeation and charge transport characteristics. Polymer-modified electrodes have many advantages in the detection of analytes because of its selectivity and homogeneity in electrochemical deposition, strong adherence to electrode surface and chemical stability of the film [15-17].

Surfactants, due to their favorable physicochemical properties are extensively used in many fields of technology and research, i.e. in pharmacy, in cosmetics, textile industry, agriculture, biotechnology. Normally surfactant is a linear molecule with a hydrophilic (attracted to water) head and a hydrophobic (repelled by water) end. Surfactants, a kind of amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other, have been widely applied in electrochemistry to improve the property of the electrode solution interface and also improve the detection limits of some bimolecular. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactants [18-21].

In the present work, it describes the electrochemical investigation of paracetamol on poly (glycine) modified graphite pencil electrodes. Many of the analytes have been detected by cyclic voltammetric technique by our research group [22-24]. The aim of the work reported here was to investigate the electrochemical properties of paracetamol on graphite pencil electrode and SDS/GPE as well as the electrochemical characterization of electrodes by cyclic voltammetric technique. It can be applied to routine investigations of pharmaceutical preparations in the form of tablets by using the cyclic voltammetric technique.

2. EXPERIMENTAL SECTION

2.1. Reagents

The pencil-lead rods were HB 0.5 mm in diameter and 6 cm length purchased from local bookstore. Sodium dodecyl sulphate, Sodium dihydrogen orthophosphate dihydrate, di-sodium hydrogen phosphate anhydrous was obtained from Merck. Glycine and Paracetamol obtained from Hi-media, 25×10^{-4} M Glycine and 25×10^{-4} M paracetamol and 0.2 M phosphate buffer solution (PBS) solutions all stock solutions were prepared with double distilled water. All experiments were performed at room temperature.

2.2. Apparatus

The electrochemical experiments were carried out using a CHI-660 c (CH Instrument-660 electrochemical workstation). All the experiments were carried out in a conventional three electrochemical cell. The electrode system contained a working electrode was bare GPE and poly(glycine) modified GPE (0.5 mm in diameter), a platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE.

2.3. Preparation of poly (glycine) modified GPE

The poly (glycine) modified GPE was prepared by 1 mM glycine solution was placed in the electrochemical cell with 0.2 M PBS. The GPE was scanned by immersing 3 mm length in that solution. Electropolymerisation was achieved by the formation of film that grew between –100 mV to 1600 mV at a scan rate of 50 mVs^{-1} for 10 cycles by using cyclic voltammetry [25,26].

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymerization of Glycine on GPE

The Fig. 1 shows the cyclic voltammograms for electro polymerization of glycine on the surface of GPE in the range from –100 to 1600 mV at the sweep rate of 50 mVs^{-1} at 10 multiple cycles. For 10 cycles the glycine was deposited on the surface of GPE by electropolymerization. After electropolymrization, the modified electrode was carefully rinsed with double distilled water and was used for electrochemical analysis.

3.2. Electrochemical characterization of poly (glycine) modified GPE

Cyclic voltammetric technique was used for the estimation of electroactive surface of the modified electrode. Fig. 2 shows the cyclic voltammograms of 1 mM $K_3[Fe(CN)_6]$ at bare GPE (dashed line) and at poly(glycine) modified GPE(solid line) in 1 M KCl at scan rate of 50 mVs^{-1}. Well defined oxidation and reduction peaks due to the $Fe^{2+/}Fe^{3+}$ redox couple were observed. A comparison between the anodic and cathodic peaks for ferricyanide shows that (ΔEp), is 60 mV for poly (glycine) modified GPE and 97 mV for bare GPE. As

ΔEp is a function of the rate of electron transfer, the lower ΔEp, shows the higher electron transfer rate.

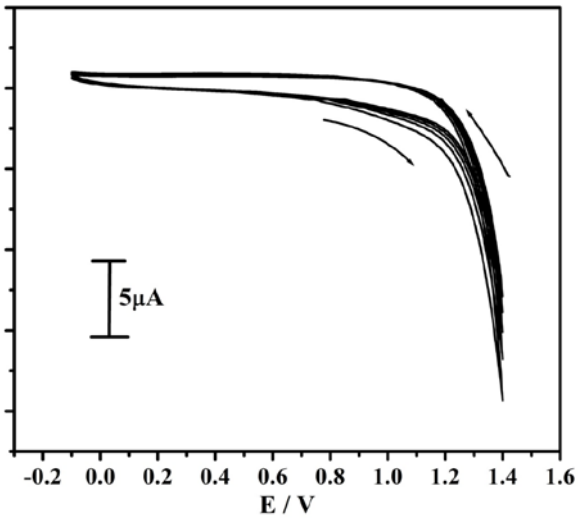

Fig. 1. Cyclic voltammogram for the electrochemical polymerization of glycine at the Graphite pencil electrode

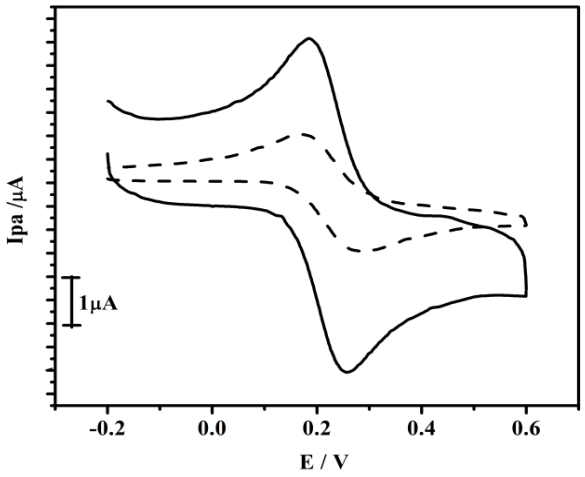

Fig. 2. Cyclic voltammograms for the electrochemical responses of $K_3[Fe(CN)_6]$ at bare (dotted line) and poly(glycine) modified GPE (solid line) in 1 M KCl containing1 mM $K_3[Fe(CN)_6]$ at scan rate 50 mVs^{-1}

The results obtained greatly improved the voltammetric response of potassium ferricyanide at poly(glycine) modified GPE reflected by the enlargement of peak current and the decline of peak potential. This indicates that the surface property of the modified electrode has been significantly changed. Based on the above observations the poly(glycine) modified GPE had

favorable and stable electrochemical behavior. It might be used as a chemically modified electrode to explore electrochemical sensor applications.

3.3. Electrochemical oxidation of paracetamol at poly (glycine) modified GPE

Electrochemical study of paracetamol was studied by using cyclic voltammetric technique. Fig. 3 shows the cyclic voltammograms of 2 mM paracetamol in PBS (pH 7) at scan rate of 50 mVs^{-1} at bare GPE (curve b), poly (glycine) modified GPE (curve c) and blank solution (curve a**)**. Fig. 3 shows that there is no characteristic peak of the modifier in the blank PBS solution and exhibited the redox nature of the paracetamol in the PBS solution. At bare GPE, for paracetamol shows significant increases of oxidation peak currents. At the poly (glycine) modified GPE for paracetamol shows increase in oxidation peak currents as compared to bare. This results shows that poly (glycine) modified GPE good catalytic effect and is irreversible electrode.

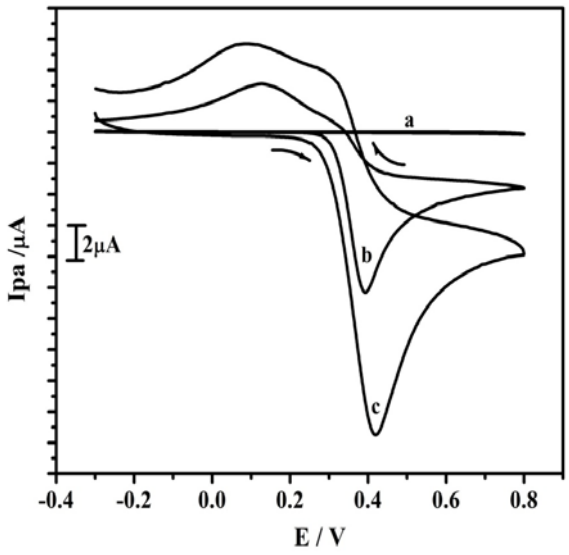

Fig. 3. Cyclic voltammograms of 2×10^{-4} M paracetamol obtained at the bare GPE (curve b), Poly (glycine) modified GPE (curve c) and in the absence of paracetamol at bare GPE (curve a) in 0.2 M PBS (pH.7.0) at scan rate 50 mVs^{-1}

3.4. Effect of scan rate

Investigation of the effect of scan rate on the electrochemical oxidation of paracetamol at poly (glycine) modified GPE by using cyclic voltammetric technique. Fig. 4(A) shows the scan rate was increased from 50 to 300 mVs^{-1} the anodic peak current was increased with increase in scan rate. The graph of I_{pa} *vs.* scan rate was plotted in Fig. 4(B) the correlation co-efficient was found to be 0.99309 and Fig. 4(C) shows the graph of I_{pa} *vs.* square root of scan rate was plotted. The resulted graph shows good linearity with the correlation coefficient was found to be 0.99965. Suggested that the electrode process was controlled by diffusion [27].

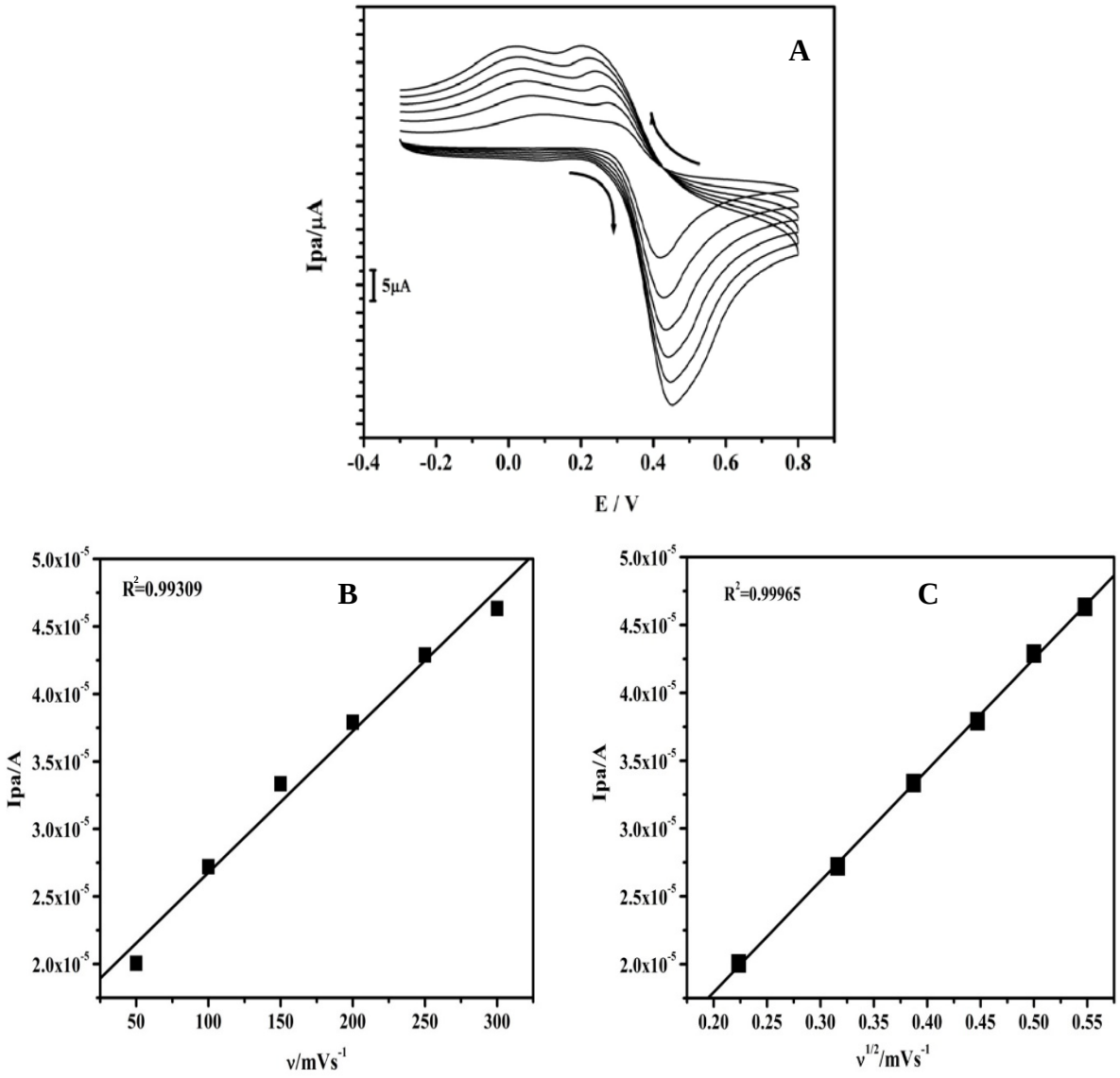

Fig. 4. A) Cyclic voltammograms of 2×10^{-4} M paracetamol on the Poly(glycine) modified GPE at different scan rates (a–f: 50, 100, 150, 200, 250, 300 mVs^{-1}) in 0.2 MPBS (pH 7.0); B) shows the plot of the anodic peak current versus scan rate; C) shows the plot of the anodic peak current versus square root of scan rate

3.5. Effect of surfactant

The Fig. 5 shows the graph of anodic peak current of paracetamol *vs.* concentration of SDS. The electrochemical response of paracetamol at SDS mobilized GPE at pH 7. The SDS/GPE was mobilized by adding 5 μL-50 μL at 50 μL shows high current signal as the SDS concentration increases. This is due to subsequently electrostatic interaction between adsorbed substrate and hydrophobic character at SDS/GPE. This result shows that the method of modification shows maximum increases in the current signals [28,29].

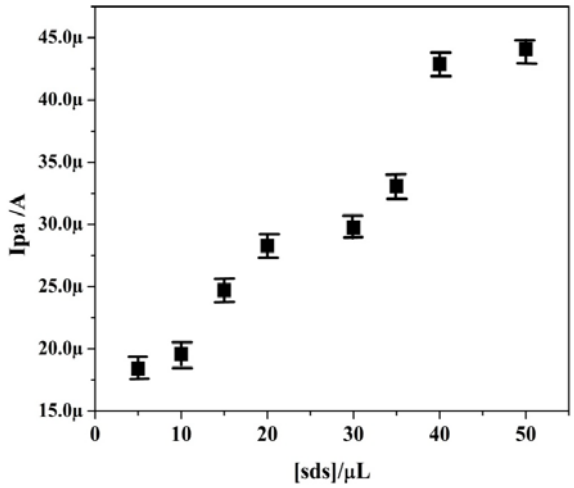

Fig. 5. Plot of anodic peak current versus concentration of SDS at scan rate 50 mVs^{-1}

3.6. Electrochemical response of paracetamol at SDS/ GPE by mobilization method

The Fig. 6 shows the cyclic voltammograms were recorded for a GPE containing 2 mM paracetamol in Phosphate buffer solution of pH 7 at the scan rate of 50 mVs^{-1}. At bare GPE for paracetamol shows low redox peak currents (dashed line) and SDS/GPE (solid line) shows good increase in peak currents for paracetamol. This result shows that SDS(anionic surfactant) exhibited good electrosensing effect in the presence of paracetamol.

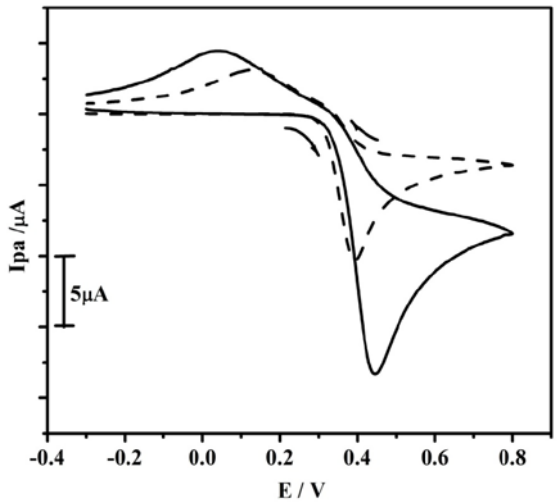

Fig. 6. Cyclic voltammograms of 2×10^{-4} M paracetamol at bare (dotted line) and SDS/GPE (solid line) scan rate 50 mVs^{-1} in 0.2 M PBS pH 7.0

3.7. Effect of concentration of paracetamol

The electrocatalytic oxidation of paracetamol was carried out by varying the concentration at poly(glycine) modified GPE. Fig. 7(A) shows that by increasing the

concentration of paracetamol from 1 mM to 6 mM, the anodic peak current and cathodic peak current goes on increasing with negligible shifting anodic peak potential towards positive and cathodic peak potential towards negative side. The graph of anodic peak current *vs* concentration of paracetamol was plotted and it shows increase in electrochemical peak currents Fig. 7(B). The obtained correlation coefficient was found to be 0.9986 and detection limit for paracetamol in the lower region was found to be 0.45 mM. The detection limit was calculated by using the formulas (1) [30-32], where S is the standard deviation and M is the slope obtained from the three calibration plots. From the data, a lower limit of detection (LOD) can be achieved using the proposed method [33-36].

$$LOD=3S/M \quad (1)$$

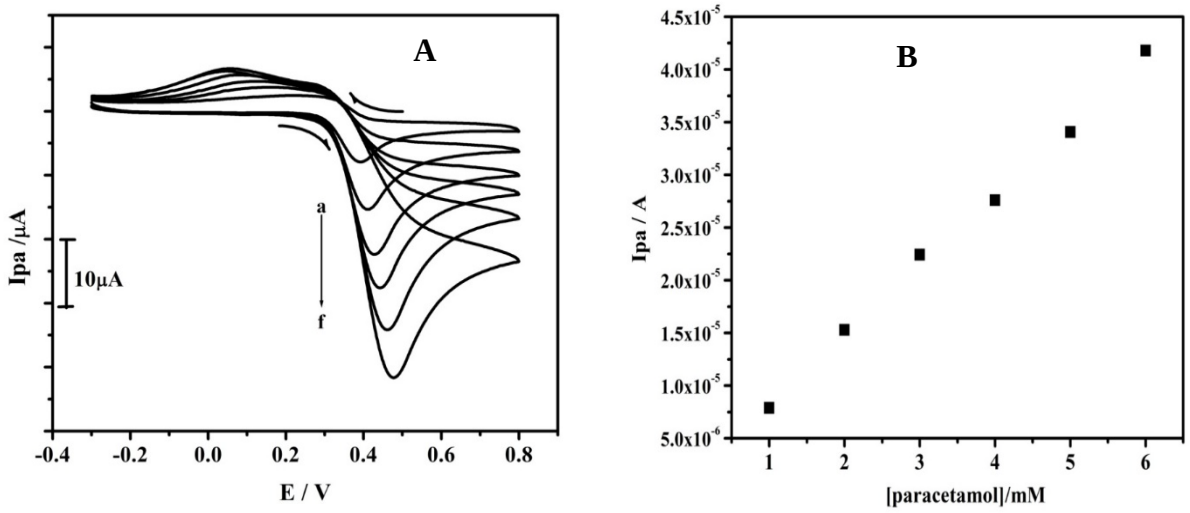

Fig. 7. A) Cyclic Voltammograms of different concentration of paracetamol (a-f: 1 mM to 6 mM) at Poly (glycine) modified GPE in 0.2 M PBS. Scan rate 50 mVs^{-1}; B) Plot of anodic peak current versus concentration of paracetamol.

4. CONCLUSIONS

The modified poly(glycine) GPE shows electrochemical sensor was used for the electrochemical determination of paracetamol. The effect of scan rate and concentration shows overall electrode process was diffusion controlled. The modified electrode shows good sensor application for electrochemical investigation of paracetamol with detection limit 0.45 mM. The surfactant SDS modified electrode shows significant increases for the determination of paracetamol. The proposed modified electrodes shows selectivity, sensitivity and stability towards paracetamol and the same method can also be applied for some bioactive molecule.

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