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Full Paper

Electrochemical Studies of Paracetamol at Poly (Aniline Blue) Modified Carbon Paste Electrode: A Voltammetric Study

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Abstract- The electropolymerziation of aniline blue was carried out in NaOH as a supporting electrolyte by cycling the potential on the carbon paste electrode. The poly (aniline blue) film MCPE used for the votammetric determination of paracetamol at pH 7.2 PBS. Its shows excellent high enhancement and electrocatalytic actvity towards paracetamol at modified carbon paste electrode. The various parameters like effect of scan rate, paracetamol concentration, simulations determination of DA and AA in their sample mixture was analysed by voltammetric technique. The proposed method showed excellent stability and reproducibility.

Keywords- Dopamine, Paracetamol, Aniline Blue, Electropolymerisation, Carbon Paste Electrode

1. INTRODUCTION

Paracetamol (acetaminophen, N-acety p-aminophenol) is an acylated aromatic amide that was first introduced in medicine by Von Mering in 1893 has been used as an analgesic for home modification for over 50 years and is accepted as effective drug for the relief of pain and fever in adults and children [1,2]. It is an effective and safe analgesic agent used for the

relief of mild to moderate pain associated with headache, backache arthritis and postoperative pain. It is also used for the reduction of fevers of viral and bacterial origin. Paracetamol relives pain and fever by inhibiting prostaglandin's synthesis in the central nervous system and sedating hypothalnic heat regulating center [3-5]. Overdose of paracetamol leads to hepatic toxicity and in some cases associated with liver and kidney damage and even death [6,7]. Thus several methods have been used for the determination of AC in pharmaceutical formulations and biological fluids including spectrophotometry, flow-injection and chromatographic methods. Also, AC is an electroactive molecule (AC contains hydroxyl and NH groups on its aromatic rings), and its electrochemical behavior has been studied extensively. The ease of AC oxidation led to development of electrochemical procedures for measuring AC levels at various electrodes and using various electrochemical methods [8–12].

Aniline blue water soluble ($C_{32}H_{25}N_3O_9S_3Na_2$) is kind of anionic triphenylmethane dyes derivate which has application in histological and microbiological staining solutions. In histology, aniline dyes are most widely used as constituent of trichrome stains for demonstration of connective tissue elements. Triphenyle methane dyes derivate belong to a group of molecules called twisted intramolecular change transfer (CTICT) molecules [13]. Aniline blue fluorescence has been widely used in botanical histochemistry, particular to stain callose plug in phloem [14,15].

Dopamine is an important neurotransmitter in the amygdala, a phylogenetically older structure of the brain, which is thought to play a critical role in limbic, cognitive and neuroendocrine functions [16-18]. Abnormalities in DA concentrations may lead to several diseases such as Parkinsonism [19,20] and Schizophrenia [21]. Therefore it is significant to develop sensitive and simple methods for the determination of dopamine. Dopamine can be determined with electrochemical methods because it is an electrochemically active compound [22-29]. Carbon paste electrode was very much attracted towards the determination of biologically active molecules because of the easy preparation of modified electrode, renewability, and low background current and fast response. A number of modified electrodes were developed by using carbon paste, glassy carbon, polymer, metal oxides and nonomaterials for the determination of DA by using voltammetric techniques [30-34]. Similarly, Vitamin C (L -ascorbic acid), a water-soluble vitamin that is widely required for metabolism and consumed on a large scale, is electroactive and has been studied extensively [35-39]. Because AA exist at much higher concentration than that of DA and oxidizes at a near potential with DA on bare carbon electrode surface which result in an overlap of their voltammetric response [40,41]. AA has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS. Up to now, the ability to detect DA with high selectivity and sensitivity is still a major target of electroanalytical research [42-45].

In this work poly (aniline blue) film was fabricated on the surface of carbon paste electrode by cyclic voltammetric technique [46]. Fabricated poly (aniline blue) film on the surface of CPE shows excellent sensitivity for paracetamol and DA. The bare carbon paste electrode was unable to detect both the species but modified electrode shows two well behaved voltammetric peaks.

2. EXPERIMENTAL

2.1. Reagents and Materials

Dopamine hydrochloride, Paracetamol and ascorbic acid were purchased from Sigma-Aldrich. 25 mM DA stock solution was prepared in 0.1 M perchloric acid, 25mM Paracetamol and 25×10^{-4} M AA was prepared in double-distilled water. Graphite powder of 50 mm size was purchased from Loba and silicon oil was purchased from Himedia. The chemicals for preparation of buffer solution were purchased from Merck. Phosphate buffer (0.2 M of pH 7.2) was used as supporting electrolyte.

2.2. Apparatus

Cyclic voltammetry (CV) was performed in a model CHI-660c (CH Instrument-660 electrochemical workstation). All 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 as counter electrode and saturated calomel as reference electrode.

2.3. Preparation of Bare Carbon Paste Electrode

The bare carbon paste electrode was prepared by hand mixing of graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.4. Preparation of Poly (Aniline Blue) Modified Carbon Paste Electrode

The paste packing procedure was same as that at the bare carbon paste electrode. Electrochemical polymerizations of Aniline blue at the carbon paste electrode were carried out by using cyclic voltammetric method in 0.1M NaOH solution containing 1mM Aniline blue

3. RESULTS AND DISCUSSION

3.1. Electropolymerziation of Aniline Blue at Carbon Paste Electrode

1mM of aniline blue was taken in the electrochemical cell in which contains 0.1 M NaOH as supporting electrolyte. Electropolymerzation was achieved by the formation of film that grew between -0.6 to 1.2 at the scan rate of 0.1 Vs^{-1} for 20 cycles by using cyclic voltammetry. Fig. 1 shows that in first cycle a small anodic peak is observed corresponding to the oxidation of aniline blue monomer. While increase the cycle in time the anodic peak descended gradually. This indicates that a thin polymer film of aniline blue was deposited on the surface of carbon paste electrode. After polymerization the electrode was thoroughly washed with distilled water and was used for the electrochemical oxidation of paracetamol.

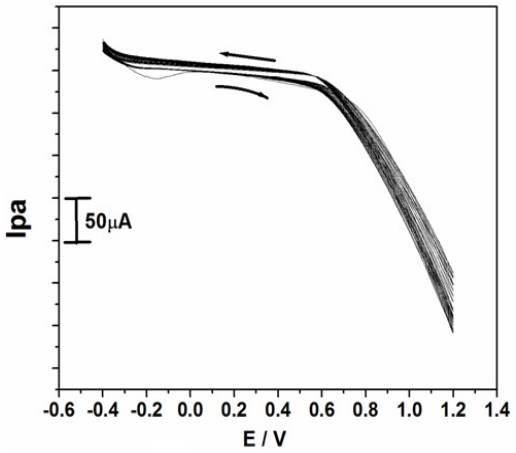

Fig. 1. Electropolymerzation of 1 mM of aniline blue at 0.1M NaOH as supporting electrolyte for 20 cycles with scan rate of 100 mVs^{-1}

3.2. Electrochemical Response of Paracetamol at Poly (Aniline Blue) Film CPE

The cyclic voltammograms of 1×10^{-4} M paracetamol in 0.2 M PBS at pH 7.2 with scan rate 100 mVs^{-1} was shown in Fig. 2. The Fig. 2 showed that at bare carbon paste electrode (solid line) paracetamol shows an irreversible redox behavior with low redox peak current [47] with high peak potential difference [ΔE_p=0.207 V]. In poly (aniline blue) film coated MCPE (dashed line) the anodic and cathodic peak current are significantly increased with reducing the peak potentials difference [ΔE_p=0.129 V] and the anodic peak shift negligibly towards negative side. This shows the modified CPE has fast electron kinetics and also due to large specific area and good conductivity and a large capacitive current [48]. This indicates that our modified shows electrocatalytic activity towards paracetamol.

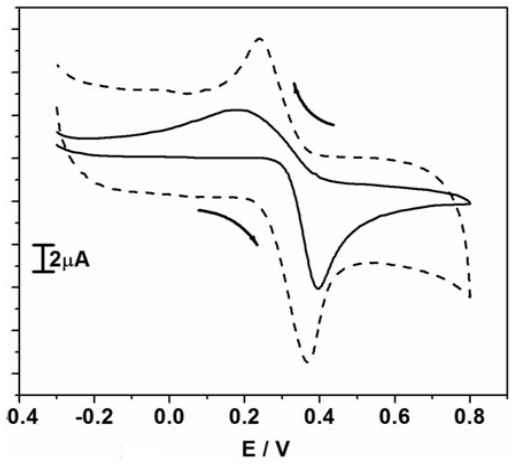

Fig. 2. Cyclic voltmmograms in 0.2 M phosphate buffer solution pH 7.2 at BCPE (solid line) and Poly (aniline blue) MCPE (dashed line) of 1×10^{-4} M paracetamol with scan rate of 100 mVs^{-1}

3.3. Effect of Scan Rate

The cyclic voltammograms of 1×10^{-4} M paracetamol recorded at different scan rate using poly (aniline blue) film coated MCPE at pH 7.2 PBS solution as shown in the Fig. 3a, the anodic peak and cathodic peak current goes on increases with increasing the scan rate from 50-400 mVs^{-1}. The plot of I_{pa} v/s $\upsilon^{1/2}$ Fig. 3b shows linear regression equation Ipa=-$4.5939X10^{-6}$+0.6790 ($\upsilon^{1/2}$) R^2=0.98571. The plot of I_{pa} v/s (υ) Fig. 3c shows linear regression equation I_{pa}=-$8.61314X10^{-8}$+0.07872(υ) R^2=0.99573. This indicates that poly (aniline blue) modified electrode reaction of paracetamol shows diffusion controlled process [49-51].

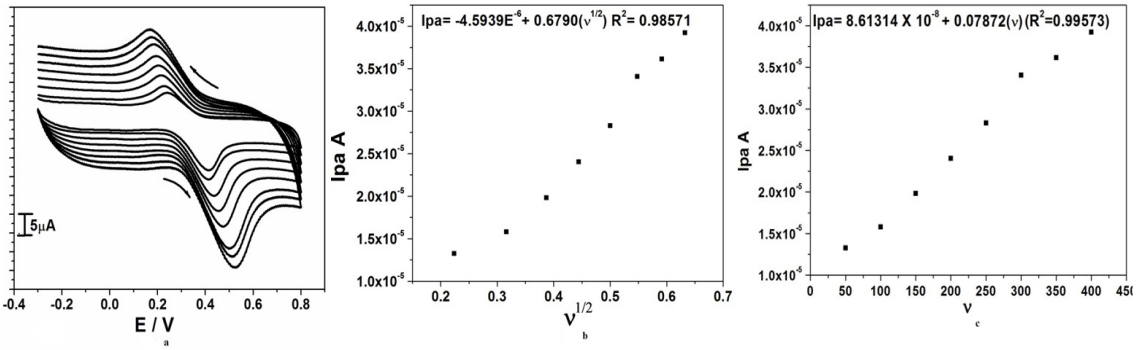

Fig. 3. a. Cyclic voltammograms of paracetamol at different Scan rate at Poly (aniline blue) MCPE in 0.2 M PBS of pH 7.2; **b.** Graph of current V/S Square root Scan rate of 1×10^{-4} M paracetamol at scan rate 100 mVs^{-1} of pH 7.2; **c.** Graph of current V/S Scan rate of 1×10^{-4} M paracetamol at scan rate 100 mVs^{-1} of pH 7.2

3.4. Effect of Paracetamol Concentration

The electrocatalytic oxidation of paracetamol was carried out by varying its concentration at poly (aniline blue) modified CPE (Fig. 4a). The oxidation peak current of paracetamol shifts more towards positive side while increasing the concentration of paracetamol in the range of 0.1–0.8 mM. The plot of I_{pa} V/S paracetamol concentration (Fig. 4b) shows that the anodic peak current goes on increasing with linear regression equation $I_{pa}(\mu A)=52.55\ C(\mu)M/L+10.32\ (\mu A)$ ($R^2=0.9909$). The detection limit for paracetamol was found to be 1.179 nM. The detection limit was calculated by using the formula (1) [52] where S is the standard deviation and M is the slope obtained from the calibration plots.

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

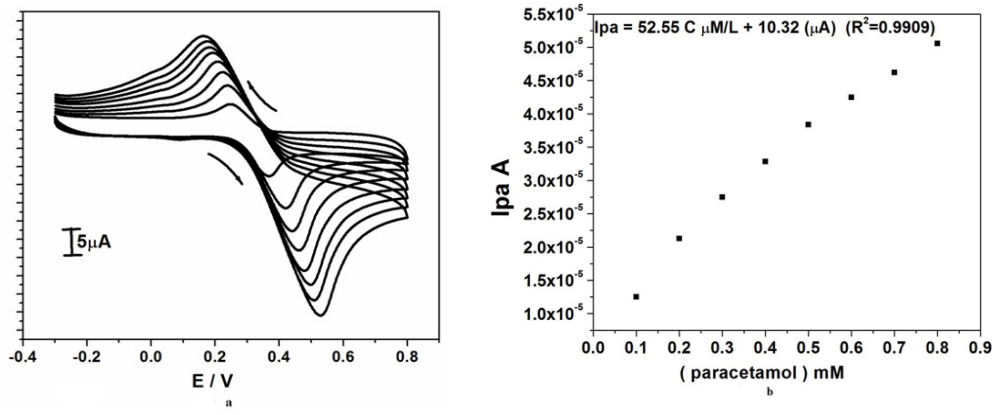

Fig. 4. a. Cyclic voltammogram of at paracetamol different concentration at Poly (aniline blue) MCPE in 0.2 M PBS of pH 7.2; **b.** Graph of current V/S concentration of paracetamol at scan rate 100 mVs^{-1} of pH 7.2

3.5. Simultaneous Study of Dopamine and Paracetamol

The main objective of our present work was the simultaneous determination of DA and paracetamol in PBS solution. Fig. 5 shows that the cyclic voltammograms of simultaneous study of 5×10^{-4} M DA and 1×10^{-4} M paracetamol at pH 7.2 PBS solution. At bare carbon paste electrode (solid line) the oxidation peaks of paracetamol and DA was unable to separate [53]. However at poly (aniline blue) MCPE (dashed line) shows two well defined wave oxidation peak of paracetamol and dopamine and the anodic peak potential of DA and paracetamol 394 mV and 223 mV respectively. This indicates that our modified electrode acts as a good sensor for paracetamol and DA.

Differential pulse voltammogram was used for the determination of 5×10^{-4} M DA, 1×10^{-3} M AA and 1×10^{4} M paracetamol because it has more sensitivity and selectivity [54]. The simultaneous study was carried out in the potential range from -200 to 600 mV at pH 7.2

(Fig. 6) and DPV shows three well defined oxidation of DA, AA and paracetamol at poly (aniline blue) MCPE. The anodic peak potentials of AA, paracetamol, and DA were 0.144, 0.125, and 0.332 V respectively.

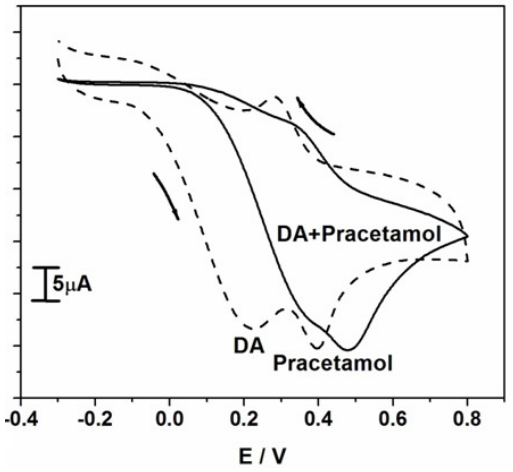

Fig. 5. Cyclic voltammograms obtained for oxidation of DA and paracetamol at bare (solid line) and Poly (aniline blue) MCPE (dashed line) at scan rate of 100mVs^{-1} 0.2 M PBS (pH 7.2)

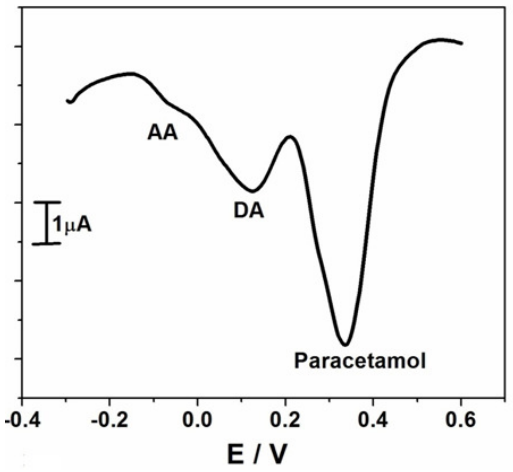

Fig. 6. Differential pulse voltammogram for 1 mM ascorbic acid, 0.5 mM dopamine and 0.1 mM paracetomol at poly (aniline blue) modified carbon paste electrode at 100 mVs^{-1}

4. CONCLUSION

In the present work, the carbon paste electrode was modified with aniline blue by electropolymerisation technique and was used for the electrochemical determination of

paracetamol, DA and some neurotransmitters. The poly (aniline blue) MCPE showed excellent high sensitive current has been proved to be efficient for the electrocatalytic oxidation of paracetamol. On the other hand simultaneous determination of paracetamol and DA in a binary mixture was achieved with good separation.

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