Full Paper

Electrocatalysis of Dopamine by Alizarin and Triton-X 100 Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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Abstract-The electrocatalytic oxidation of dopamine at alizarin and Triton X-100 modified carbon paste electrode has been studied by means of cyclic voltammetric technique in 0.2 M acetate buffer solution at pH 7.0. This suggests the effectively of surface modification of carbon paste electrode by Triton X-100 a non–ionic surfactant. Cyclic voltammetric investigations demonstrated the improved responses of dopamine. The modified electrode exhibited strong promoting effect and stability towards the detection of dopamine in mobilization and immobilization methods of surfactant. The presence of Triton-X 100 on the alizarin modified carbon paste electrode showed excellent electrocatalytic effect towards the detection of dopamine.

Key words- Dopamine, Alizarin, Modified Carbon Paste Electrode, Electrocatalytic Oxidation, Triton X-100, Cyclic Voltammetry

1. INTRODUCTION

Dopamine (DA) is one of the most significant catecholamines and belongs to thefamily of inhibitory neurotransmitters that exists in the mammalian central nervous system [1]. Since

its discovery in 1950s, DA has been of interest of neuroscientists and chemists. The loss of DA in the human body may result in some serious diseases such as Parkinsonism [2,3]. Therefore DA is currently the subject of intense research focus to neuroscientists and chemists and it is essential to develop rapid and simple methods for the determination of the concentration of DA. DA can be determined by electrochemical methods because it is an electrochemically active compound. So it is important to establish a fast, sensitive and selective method for the detection of DA [4]. DA is generated in various parts of central and peripheral nervous system and has an agonist action on β adrenoceptors. DA has positive chronotropic and ionotropic effects on myocardium which stimulates cardiac contractility and enhances heart beat rate [5].

It is associated with proper functioning of several organs such as the heart, brain, and suprarenal glands. The determination of DA is a subject of great clinical significance for investigating its physiological functions and diagnosing nervous diseases resulting from DA abnormal metabolism, such as epilepsy and senile dementia [6]. There were many methods for the detection of DA, such as titrimetry [7], spectrophotometry [8], chemiluminescence[9], potentiometery [10] and voltammetric methods have been developed for this purpose. Electrochemical techniques have proved to be significantly advantageous to the biosciences. The DA is electroactive and can be detected electrochemically. However, the direct electroanalysis of DA at a bare electrode often suffers from the interferences of other commonly coexisting electroactive substances. The oxidation peak potential of AA is close to that of DA and the working electrode is often fouled owing to the accumulation of oxidized product [11,12]. In order to overcome these problems, different kinds of modifications were done to carbon paste electrode for the determination of DA.

Alizarin is an interesting compound for investigation in electroanalytical chemistry due to formation of conductive, electro-active films which make it as a key constituent, used for modification of electrodes [13]. Alizarin is an anthraquinone derivative, mordant vegetable dye (Scheme 1) and the detailed electrochemical investigation of alizarin by cyclic voltammetric method was reported [27,28].

Surfactant belongs to a class of molecules with surface active properties. This behaviour is due to their amphiphilic structure, which contains both a polar or hydrophilic head and non-polar or hydrophobic tail [14,15]. Surfactants are normally classified according to the head group type [16]. Micellar effects in electrochemistry are a subject of substantial current interest. Adsorption of surfactants on the electrode surface and solubilization of electrochemically active compounds in micellar aggregates might significantly change the redox potential, charge transfer coefficients and diffusion coefficients of electrode processes [17-19]. The addition of trace surfactants to the working solutions could effectively improve the signals of these substances. The applications of surfactants in electrochemistry and electroanalytical chemistry have been widely reported [20-29]. The cetyl trimethyl

ammonium bromide, a cationic surfactant was immobilized on carbon paste electrode and induced iron phthalocyanin modified carbon paste electrode for simultaneous determination of dopamine with ascorbic acid and uric acid by our group [30,31].

In this work, the adsorption of Triton X-100 (TX-100) at chemically modified alizarin carbon paste electrode (TX-100/AZMCPE) was explored by cyclic voltammetric technique which might be able to explain the enhancement effects of surfactants in electroanalytical chemistry. The results revealed not only the adsorptive behavior of TX-100 but also the influences of TX-100 adsorption on the surface of the electrode interface and the redox reactions in solution.
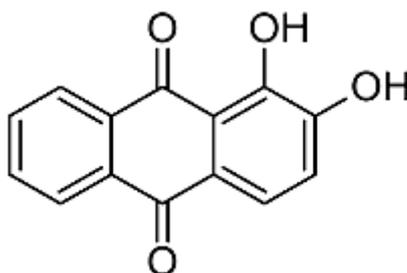
Scheme 1. Structure of Alizarin

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Alizarin (AZ), Dopamine (DA) and Triton-X 100 (TX-100) were obtained from Himedia chemical company and of analytical grade used without further purification. 25 mM DA stock solution was prepared in 0.1 M perchloric acid. Graphite powder of 50mm size was purchased from Loba and silicon oil was purchased from Himedia. TX-100 surfactant was dissolved in double distilled water to get 1×10^{-5} M. The acetate buffer (0.1 M pH 7.0) was used as optimum measurments. Sodium hydroxide and acetic acid were used for increasing and decreasing the pH of the buffer. The water used in all the measurements was double distilled.

2.2. Apparatus

Cyclic Voltammetry (CV) was performed in a model EA-201 Electroanalyser (EA-201 Chemilink system). 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 (BCPE) and alizarin modified carbon paste electrode (AZMCPE)

The carbon paste electrode was prepared as fallows, 70% graphite powder and 30% silicone oil were mixed by hand about 45 minutes to produce a homogeneous bare carbon paste electrode (BCPE). The paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper. The alizarin modified carbon paste electrode (AZMCPE) was prepared by grinding different percentage of AZ (0.21, 0.41, 0.62 and 0.83%) along with 70% graphite powder and 30% silicone oil.

3. RESULTS AND DISCUSSION

### 3.1. Effect of AZ as a modifier towards the detection of DA

AZ is a derivative of anthraquinone mordant vegetable dye used as a modifier in the preparation of AZMCPE. The characterization of AZMCPE was investigated by using cyclic voltammetric technique. AZMCPE was prepared of different ratio by adding different percentage of AZ. By increasing the percentage of AZ from 0.21% to 0.62% in the carbon paste electrode, the electrochemical redox peak current of 50 µM DA goes on increasing in 0.2M acetate buffer as supporting electrolyte. Further increase of AZ the current signal of DA decreases. The graph of anodic peak current vs. different percentage of AZ in carbon paste electrode was plotted and shown in Fig. 1. Maximum current signal was noticed in 0.62 % AZMCPE, so we have chosen 0.62% AZMCPE as optimum for the study of all other parameters.

3.2. Electrochemical response of DA at AZMCPE

Fig. 2 shows the cyclic voltamogramms of 50 µM DA at BCPE and AZMCPE in 0.2 M acetate buffer solution at pH 7 and scan rate 100 mV s^{-1}. At the BCPE the cyclic voltammogram of DA (dotted line) shows an oxidation peak potential at 155 mV and reduction peak potential at 100 mV with low current signals. The electrochemical response of DA at AZMCPE showed a well defined redox wave of DA with strong increase of the redox peak current (solid line). The oxidation peak potential occurs at 162 mV and reduction peak potential at 104 mV respectively, with the peak potential separation (ΔE_p) 58 mV. The value of i_{pa}/i_{pc} was about 1.15, and negligible shift in the redox peak potentials, shows the characteristics of the reversible natured voltammogram. The modified electrode exhibited strong promoting effect and high stability towards the electrochemical oxidation of DA. It was observed that the peak currents enhanced at the AZMCPE, which provides more evidence for asserting that the AZ in the CPE possessed high electrocatalytic activity towards the DA detection.
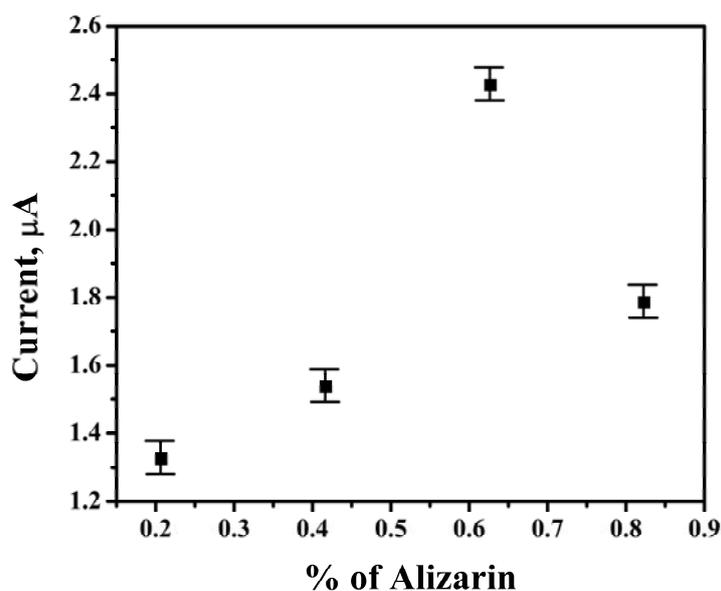
**Fig. 1.** Effect of percentage of AZ on anodic peak current in 50 μM DA and 0.2 M acetate buffer solution scan rate: 100 mV s^{-1}
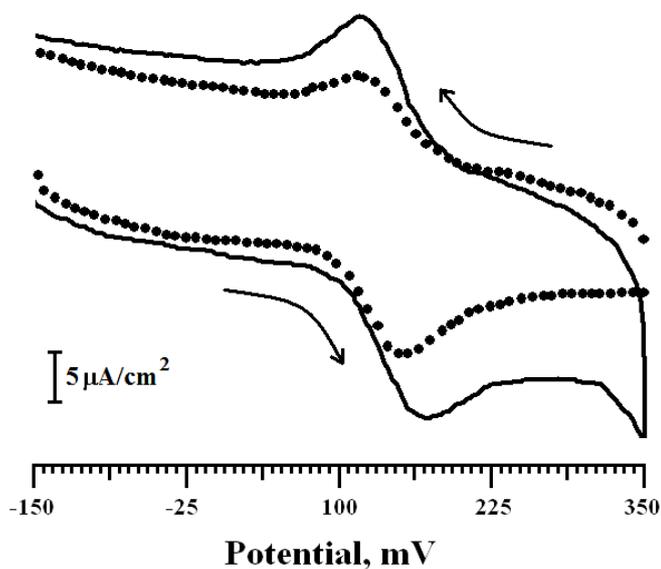
Fig. 2. Cyclic voltammograms of BCPE (dotted line) and AZMCPE (Solid line) in the presence of 50 μM DA and 0.2 M acetate buffer, in pH 7.0 scan rate: 100 mV s^{-1}

3.3. Effect of TX-100 Surfactant

Initially, cyclic voltammogrames were recorded for TX-100/AZMCPE in a solution containing DA (50 μM) in 0.2 M acetate buffer solution at pH 7.0. The TX-100/AZMCPE was calibrated by varying the immobilization time interval from 5 min to 25 min. The graph

of i_{pa} *vs.* different time in minutes was plotted (Fig. 3). The higher current signal was obtained at 10min time intervals. Hence, the 10min time gap was fixed for further investigation. The effect of immobilization study was done by varying the concentration of TX-100 in μL (5 μL to 25 μL) on to the surface of AZMCPE with the immobilization time interval 10 min.
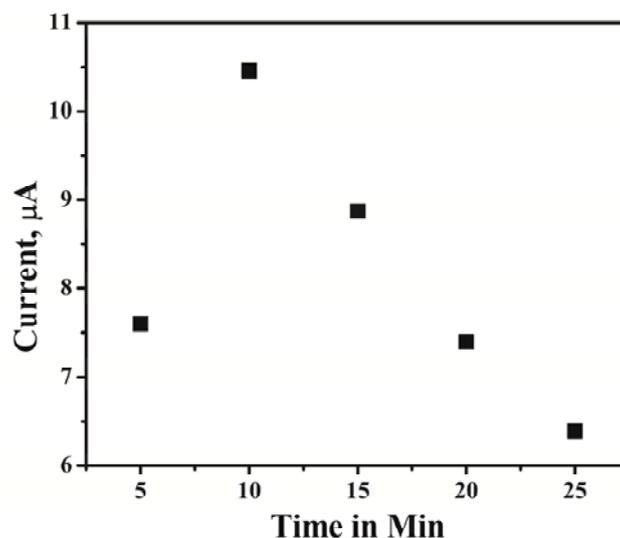

Fig. 3. Graph of i_{pa} *vs.* time in min at 10 μL of 1×10^{-5} M TX-100 on to the surface of AZMCPE in presence of 50 μM DA and 0.2 M acetate buffer at scan rate: 100 mV s^{-1}
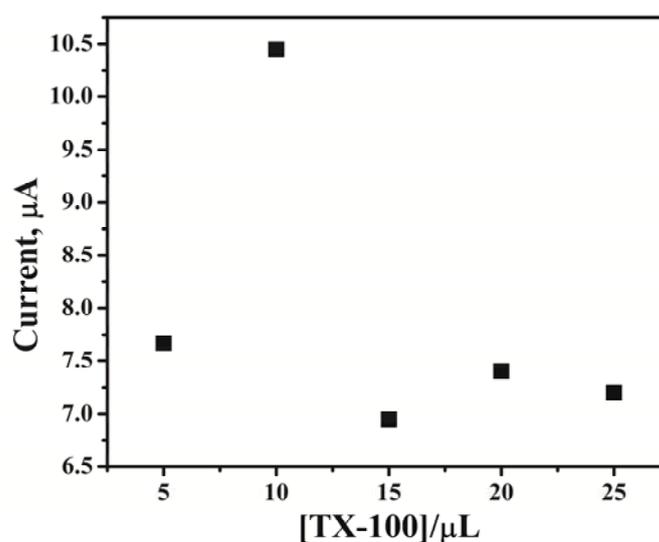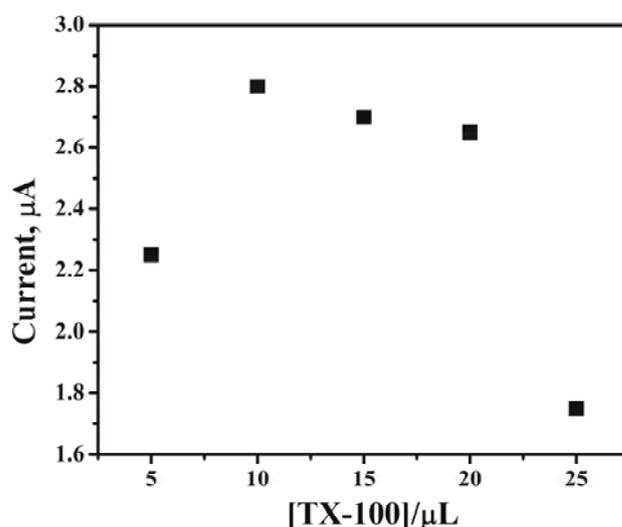

Fig. 4. Graph of i_{pa} *vs.* different concentration of 1×10^{-5} M TX-100 in μL on to the surface of AZMCPE in presence of 50 μM DA and 0.2 M acetate buffer at pH-7.0 scan rate: 100 mV s^{-1}

The graph of i_{pa} *vs.* different concentration of TX-100 was plotted (Fig. 4). The experimental results revealed that the 1×10^{-5} M TX-100 with 10 µL concentration with 10 min time gap showed good electrocatalytic activity towards the detection of DA.

The Fig. 5 shows the comparison of bare CPE (dotted line), AZMCPE (dashed line) and TX-100/AZMCPE(solid line) towards the detection of DA. Among all the TX-100/AZMCPE showed the excellent electrocatalytic activity for detection of DA. The mobilization effect of TX-100 towards the electrtocatalytic oxidation of DA was studied by addition of different concentration of TX-100 in µL (5 µL–25 µL) directly in to the solution containing the DA (50 µM) in 0.2 M acetate buffer solution as supporting electrolyte. However, the better redox current signal was obtained at 10 µL addition of TX-100 which could be seen in Fig. 6. The results show the effect of surfactant concentration into the solution that is mobilization method also catalyzes the oxidation of DA. When the surfactant concentration is below 10 µL, the CMC of surfactant at room temperature, both i_{pa} and i_{pc} increases rapidly with the increase of surfactant concentration. The concentration of the surfactant was increased from 5 µL to 25 µL into the solution and onto the surface that is both mobilization and immobilization method as shown in Fig. 6 and Fig. 4 respectively. The redox current signal for DA was superior in immobilization when compared to mobilization method. From this overall we can say that immobilization is more favorable than mobilization method [32].
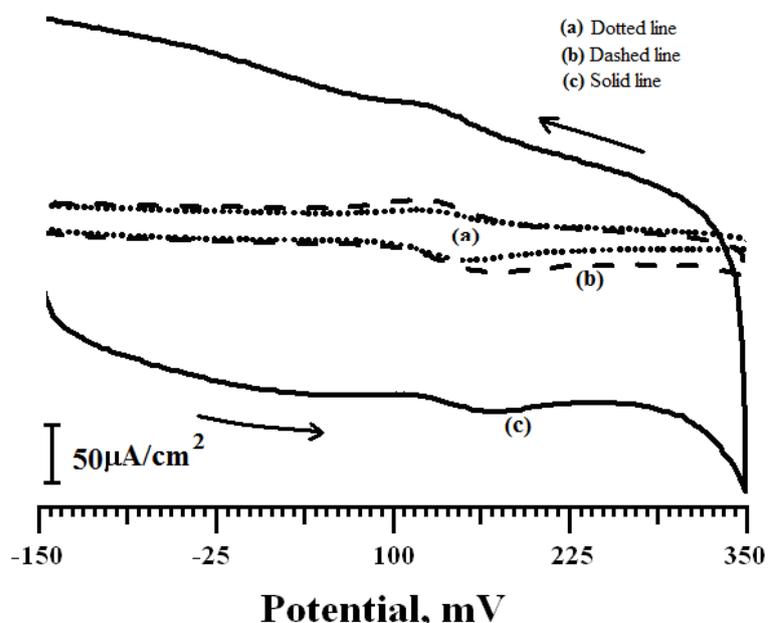
Fig. 5. Cyclic voltammogram of 50 µM DA at a) BCPE (dotted line) b) AZMCPE (dashed line) c) 10 µL TX-100 (solid line) immobilized AZMCPE in 0.2 M acetate buffer solution (pH 7.0) at scan rate:100 mV s^{-1}

Fig. 6. Graph of i_{pa} *vs.* different concentration of 1×10^{-5} M TX-100 into the solution of AZMCPE in presence of 50 μM DA and 0.2 M acetate buffer at pH-7.0. scan rate:100 mV s^{-1}

4. CONCLUSION

The incorporation of TX-100 as a non-ionic surfactant on the AZMCPE is introduced as a new and very efficient method for enhancement in electrocatalytic effect. From the results of comparative study of BCPE, AZMCPE, TX-100/AZMCPE suggests that TX-100/AZMCPE showed the excellent electrocatalytic activity for detection of DA. The comparative results from the mobilization and immobilization methods, immobilization is more favorable than mobilization method for the detection of dopamine at carbon paste electrode. The experimental results revealed that the 1×10^{-5} M TX-100 with10 μL concentration with 10min time gap showed significant electrocatalytic activity towards the detection of DA. Hence this modified electrode can be applied for the detection of other neurotransmitters.

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