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Research Article

Voltammetric Studies of Trimethoprim at Sodium Dodecyl Sulphate Modified Carbon Paste Electrode

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Abstract

Sodium dodecyl sulphate (SDS) surfactant immobilized carbon paste electrode has been proposed for investigation and determination of trimethoprim by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electro analytical determination of trimethoprim was carried out in phosphate buffer solution at pH 3.0. The analyte showed one well-resolved irreversible oxidation peak at around 1141 mV, which served as the analytical response. The variation of pH, scan rate, concentration of trimethoprim has been studied. The limit of detection (LOD) and limit of quantification (LOQ) of trimethoprim were found to be 0.14µM and 0.48µM, respectively. From the studies of scan rate effect the overall electrode process was found to be diffusion controlled. SDS modified carbon paste electrode showed good electro catalytic effect towards the detection of trimethoprim.

Keywords: Cyclic voltammetry, Trimethoprim, Sodium dodecyl sulphate, Differential pulse voltammetry and Carbon paste electrode.

1. Introduction

Trimethoprim (2,4-diamino-5-(3,4,5-trimethoxybenzyl) pyrimidine) (TMP) is a well-known antibacterial agent as shown in Figure-1. It is widely used in the treatment of a number of bacterial infections[1-3] and also used in the treatment of trachoma and ocular toxoplasmosis, tract infections for HIV-affected patients prophylaxis treatment and urinary[4].

Several analytical methods are used for the determination of TMP from liquid chromatography [5,6] spectrophotometry[7-9], potentiometry[10], capillary zone electrophoresis and capillary electrophoresis with amperometric detection at carbon electrodes[11,12], NMR[13] and electroanalysis[14]. In the earlier electrochemical methods the determination of TMP was achieved by polarographic reduction in acidic solutions[15].

Surfactants are a kind of amphiphilic ions or molecules with a hydrophilic head compatible with water on one side and long hydrophobic tail compatible on the other side. They have been widely used in electrochemical and electro analysis chemistry field [16-18] to change the electrochemical process through adsorption at interfaces or aggregation into supramolecular structure. Adsorption of surfactant aggregates on the electron transfer, gently enhance the peak current, change the redox potential or charge transfer coefficients or diffusion coefficients as well as alter the stability of electro generated intermediates or electrochemical products [19].

In this work, a simple, rapid and sensitive electrochemical procedure for the determination of TMP at a carbon paste electrode in the presence of surfactant SDS was proposed. The experimental results showed that the surfactant SDS had a distinct enhancement effect on the electrochemical responses of TMP at the carbon paste electrode. Electrochemical parameters of the TMP oxidation were investigated.

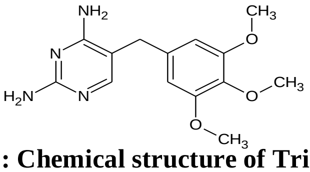

Figure-1: Chemical structure of Trimethoprim

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2. Experimental section

2.1. Reagents

Trimethoprim (TMP) was purchased from Himedia chemicals and all other chemicals were of analytical grade. Stock solutions of TMP with a concentration within the 1×10^{-3} mol dm^{-3} level were prepared in methanol, stored at 4 ^{0}C. Supporting electrolytes, phosphate buffer (Na_2HPO_4 and NaH_2PO_4) was prepared with deionised water (Millipore water) and the pH was adjusted with 0.1 N NaOH solutions. Other chemicals used were of analytical grade except for spectroscopically pure graphite powder. All Solutions were prepared with deionised water (Millipore water).

2.2. Apparatus

Electrochemical measurements were carried out with a model-201 electrochemical analyzer (EA-201 chemlink systems) in a conventional three-electrode system. The working electrode was carbon paste electrode, having cavity of 3 mm diameter. The counter electrode was platinum electrode with a saturated calomel electrode (SCE) as a standard reference electrode completing the circuit.

2.3 Modification procedure

2.3.1. Preparation of bare carbon paste electrode (BCPE)

The bare carbon paste electrode was prepared by hand mixing of graphite powder 70% and silicon oil 30% in an agate mortar for about 30 min to get homogenous carbon paste. The paste was then packed into the cavity of a teflon tube electrode (3 mm diameter). Before measurement, the modified electrode was smoothened on a piece of transparent paper to get a uniform, smooth and fresh surface.

2.3.1. Preparation of modified carbon paste electrode

The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothed out on a weighing paper. SDS modified carbon paste electrode (SDS/MCPE) was prepared by immobilizing 10 µL of SDS on the surface of the carbon paste electrode for 10 mins.

3. Result and Discussion

3.1. Electrochemical response of potassium ferrocyanide at SDS modified carbon paste electrode

Figure 2 shows the electrochemical response of potassium ferrocyanide in 1M KCl at bare carbon paste electrode (dashed line curve in **Figure-2**) and at SDS modified carbon paste electrode (solid line curve in **Figure-2**). Solid line curve shows the electrochemical response of BCPE having the cathodic peak current (I_{pc}) 33.7 µA and anodic peak current (I_{pa}) 41.9 µA. The electrochemical cathodic peak potential (E_{pc}) 170 mV and anodic peak potential (E_{pa}) 270 mV. After modification with SDS/MCPE shows enhancement of both electrochemical anodic peak current (I_{pa}) 57.5 µA and cathodic peak current (I_{pc}) 44.6 µA anodic peak potential (E_{pa}) 251 mV and cathodic peak potential (E_{pc}) 188 mV. The effective area of the modified electrode was found to be 0.0355 cm^2.

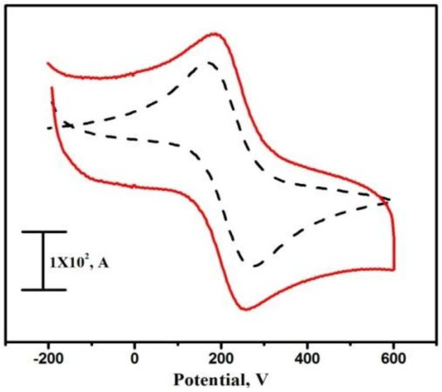


Figure-2: Comparison of $K_4[Fe(CN)_6]$ in KCl solution at SDS/MCPE (solid line) and BCPE (dashed line)

3.2. Electrochemical behavior of Trimethoprim (TMP) at SDS modified CPE

Figure 3 shows cyclic voltammograms of Trimethoprim at pH 3.0 in phosphate buffer at bare CPE (dashed line) and at SDS modified CPE (dotted line) and at blank solution of SDS modified CPE (solid line). Above studies showed that only one oxidation peak at 1209 mV and a anodic peak current of 220.2 µA at bare CPE, whereas an oxidation peak at 1141 mV and a anodic peak current of 343 µA at the SDS modified CPE, in the potential range +400 to +1400 mV. No reduction peak was observed in the reverse scan, suggesting that the electrochemical reaction is a totally irreversible process and the oxidation peak at the bare CPE is broad due to slow electron transfer, while the response was considerably improved at the SDS modified electrode and the peak potentials shifted to negative direction, the shape of the peak turns sharper and the peak current increased significantly.

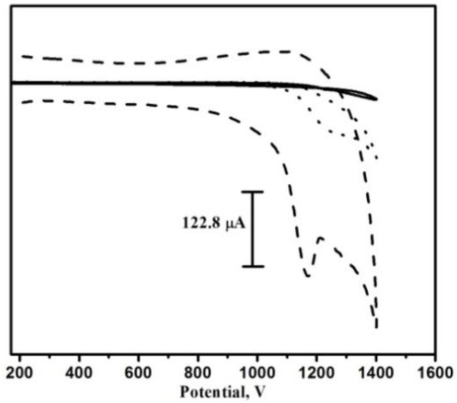
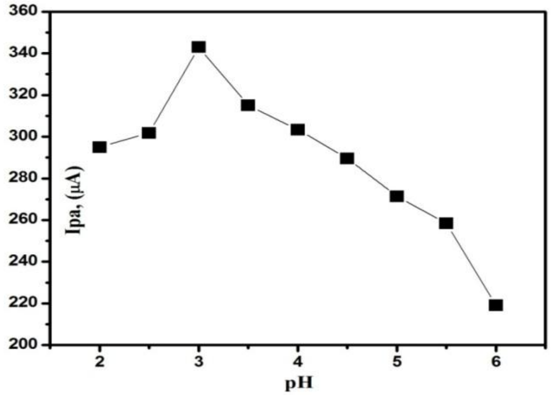


Figure-3: Comparison of TMP at SDS modified CPE (dotted line), Bare CPE (dashed line) and Blank Solution in Phosphate buffer (solid line) at 50 mVs^{-1}

3.3. Effect of pH

The pH influence was investigated by cyclic voltammetric measurement at different pH values between 2.0 and 6.0 as shown in **Figure-4a**. The maximum response current was observed at pH 3.0. In order to obtain the maximum bioactivity and optimal sensitivity, phosphate buffer of pH 3.0, 50 mVs^{-1} was selected for our experiments. The oxidation peak current increases with increase of pH from 2 to 3.0 and becomes maximum and peak potential shifted negatively. While pH beyond 3.0, a great decrease of the oxidation peak current could be observed, then it decreased gradually with the further increasing the pH of solution as shown in **Figure-4a** and the oxidation peak potential decrease with increase of pH as shown in **Figure-4b**. Linear relationship was obtained between the anodic peak potential and pH of the solution in the range 2 – 6.

The linear regression equation was given by:



$$Ep\mathit{a}\ (\text{mV}) = 1187.7111 - 54.233\ \text{pH} \quad (R = 0.99826),$$

Figure-4a: Plot of anodic peak current versus pH of TMP at SDS/MCPE.

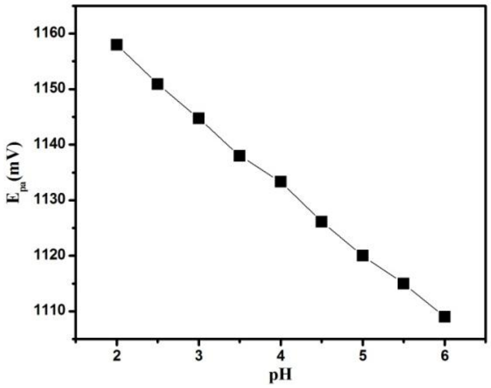
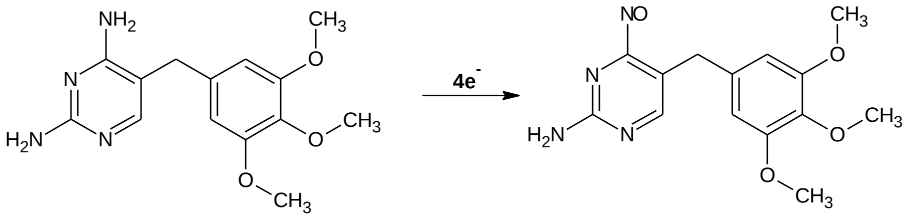


Figure-4b: Plot of anodic peak potential versus pH of TMP at SDS/MCPE

3.4. Effect of scan rate

The effect of scan rates on the electrochemical response of TMP at SDS modified CPE was studied at different scan rates. Redox peak current increase linearly with the scan rate ($_{\gamma}$) in the range 25, 50, 75, 100, 125,150, 200, 225, and 250 mVs^{-1} and the cyclic voltammograms were shown in **Figure-5a** and **Figure-5b** shows linear relationship with a correlation coefficient of R= 0.99932 was obtained between the peak current and scan rate in the range of 25 - 250 mVs^{-1}. However linearity was also obtained for the plot of square root of scan rate versus anodic peak current with a correlation coefficient of 0.99933 shown in **Figure-5c** which revealed that a diffusion controlled process occurring at the SDS modified CPE. The relationship between the anodic peak potential and scan rate can be explained by plotting the anodic peak potentials versus Natural logarithm of scan rate **(Figure-5d)** by considering the relation: Epa= 0.4782 lnυ+1.3532; R= 0.98423 and the relationship between the anodic peak current and scan rate can be explained by plotting the Logarithm of anodic peak current versus Logarithm of scan rate **(Figure-5e)** by considering the relation: log$_{ipa}$= 1.2987 +0.0250 logυ; R= 0.99899

According to Laviron's theory [20] the slope is equal to RT/αn$_{\alpha}$F. For a totally irreversible electrode reaction the nα was calculated as 3.7585, which indicated that four electrons were involved in the oxidation process **(Scheme-I)** (21) of TMP at the SDS/modified CPE.



Scheme -I: Oxidation of TMP

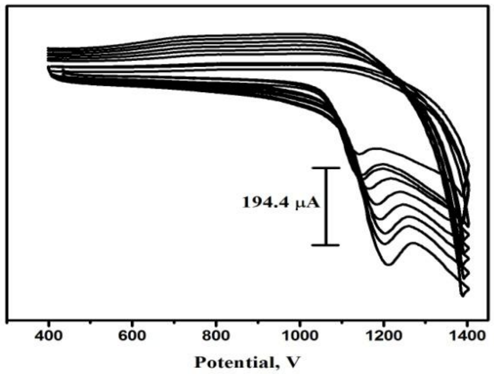


Figure-5a: Cyclic Voltammograms of TMP at SDS MCPE with different scan rates were (a) 25, (b) 50, (c) 75, (d) 100, (e)125 (f) 150(g)200 (h)225 and(i)250 mVs^{-1}

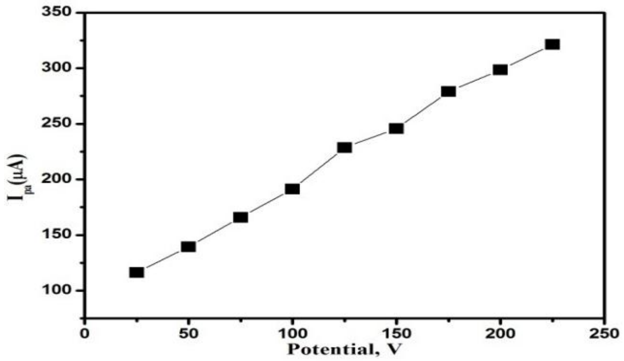


Figure-5b: Plot of Anodic peak current versus scan rates of TMP at SDS/MCPE

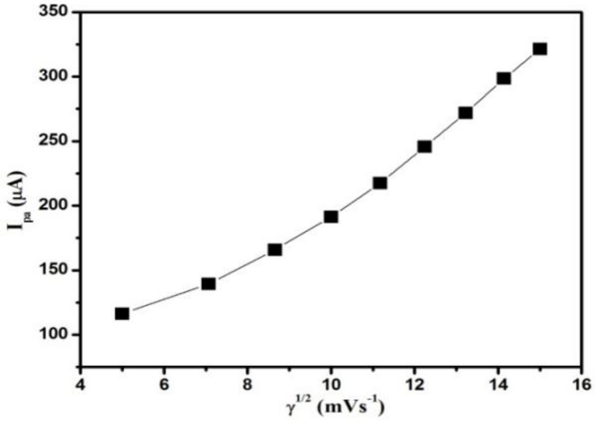


Figure-5c: Plot of Anodic peak current versus Square root of Scan rates of TMP at SDS/MCPE.

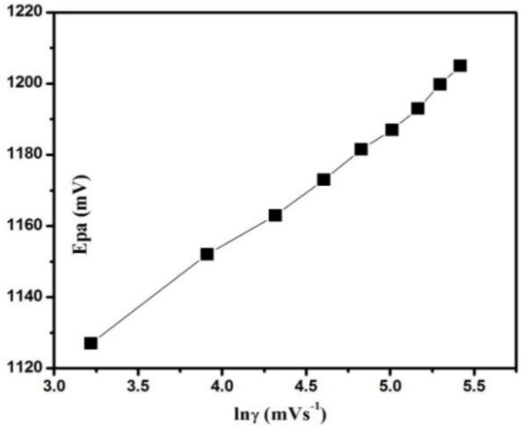


Figure-5d: The Plot of Anodic peak potential versus Natural logarithm of Scan rates of TMP at SDS/MCPE.

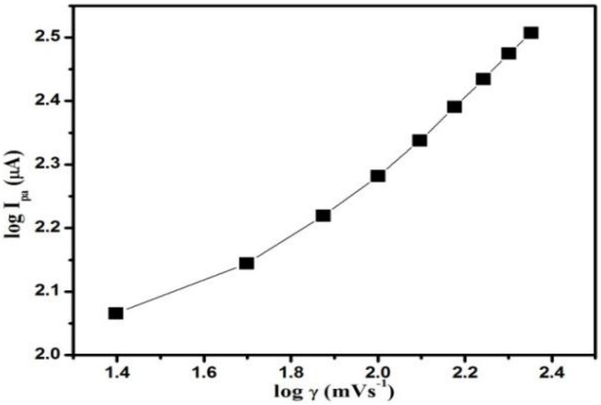


Figure-5e: Plot of logarithm of Anodic peak current versus logarithm of scan rates of TMP at SDS/MCPE

3.5. Effect of Trimethoprim (TMP) concentration and detection limit

The electrocatalytic oxidation of TMP was carried out by varying its concentration at SDS/MCPE. The effect of TMP concentration on the oxidation peak current was studied by cyclic voltammetry in PBS (pH 3.0) at the scan rate 50 mVs^{-1}. Under the optimum conditions, the oxidation peak current increases with increase in concentration of TMP. Figure-6a and Figure-6b shows the linear relationship between the oxidation peak current (Ipa) with TMP concentration in the range. The linear regression equation:

$$\mathrm{Ipa}\ (\mu A) = 17.4286+219.833c\ (R = 0.99764).$$

The limit of detection (LOD) and limit of quantification (LOQ) of TMP were found to be 0.1461μM and 0.48860 μM respectively.

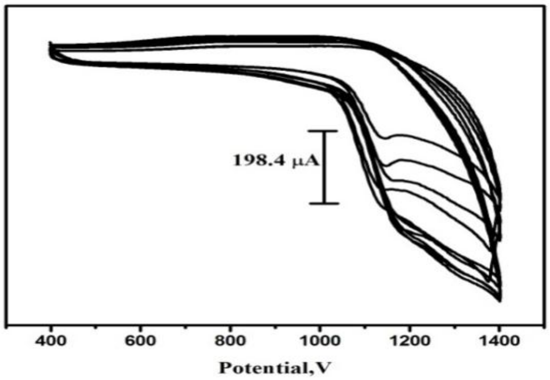


Figure-6a: Effect of variation of concentration of TMP on anodic peak current at SDS/ MCPE; υ=50 mVs^{-1}.

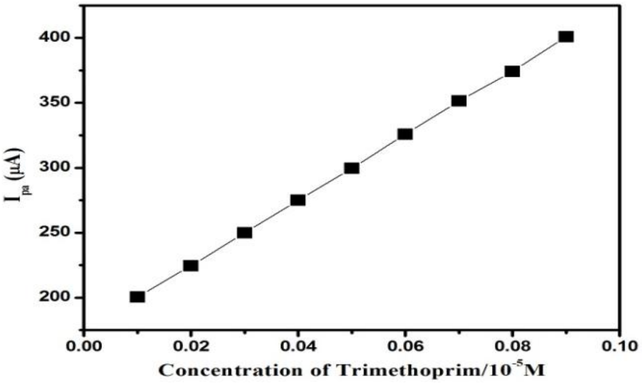


Figure-6b: Plot of Anodic peak current versus TMP concentration at SDS/MCPE.

3.6. Differential pulse Voltammetry (DPV) studies of Trimethoprim (TMP):

Differential pulse voltammetry (DPV) was used to investigate the possibility of SDS modified carbon paste electrode for determination of TMP. The current responses of TMP changed by changing the concentrations of TMP. As illustrated in **Figure-7** DPV responses of the modified electrode of TMP increased linearly with increase of their concentration.

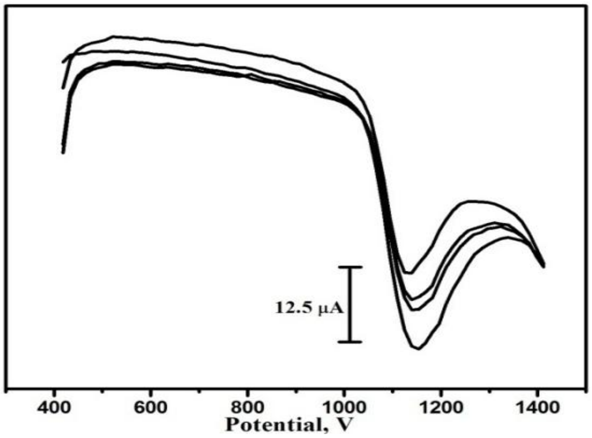


Figure-7: DPV of TMP at different concentrations (1X10^{-5} to 4X10^{-5} M)

4. Conclusions

In the present study, a SDS modified carbon paste electrode based on the immobilization of surfactant has been prepared for the electrochemical determination of Trimethoprim. Results showed that the oxidation peak current of Trimethoprim was improved at SDS modified carbon paste electrode. Scan rate studies showed that four electrons are involved in the electrocatalytic determination of TMP. The electrochemical response is diffusion controlled and irreversible in nature.

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