

Electro-oxidation and Detection Limit of Catechol as a precursor for Pharmaceutical Applications at a Glassy Carbon Electrode

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Abstract: Herein, the electrochemical oxidation and detection limit of catechol at a glassy carbon electrode using cyclic voltammetry has been studied. Catechol can be electrochemically oxidized to *o*-benzoquinone via a quasi-reversible reaction process. Supporting electrolyte of 0.1 M K₂HPO₄ solution was used for each experiment. The effect of catechol concentrations, scanning rates and pH values has been investigated. According to the effect of pH on oxidation peak current, the best value was at 9. It was found that, both of the anodic and cathodic peaks are increased by increasing of catechol concentrations range from 0.39 to 6.67 mM. Limit of detection (LOD) was calculated to be 2.30×10^{-6} M.

Keywords: Catechol; Detection limit; Pharmaceutical applications, Glassy carbon electrode

1 Introduction

Catechol (1,2-dihydroxybenzene) and its derivatives is widely used in chemical and pharmaceutical industries. In point of fact, they are biologically effective materials as they act as antimicrobial agents and have strong influence against *Pseudomonas* [1]. Also, they have antioxidative behaviors where they are recognized as a firewall against reactive oxidizing species [2]. Additionally, catechol and catecholamines are from neurotransmitters that have great importance in the brain chemistry [3]. Thereby, scientists are continuously looking for alternative methods for determination of catechol and their derivatives. Recently, phenol compounds were determined by high-performance liquid chromatography, carbon paste electrode modified with copper phtalocyanine and histidine and carbon nanotubes modified electrode to study the electrochemical oxidation of catechol [4-6]. Meanwhile, quinones have various biological activities and they can be used for drugs production [7-11]. Their derivatives can be easily and quickly prepared by electrochemically oxidation of their corresponding phenol derivatives. The electro generated quinones are quite reactive and can strongly attack to different types of nucleophiles [12-17].

However, there are quite useful uses of the phenolic compounds and their derivatives (e.g. used in some special

Organic synthesis, pharmaceutical and biomedical applications), but these compounds can be easily introduced to the environment via a variety of natural and industrial sources. Indeed, degradation of these compounds is considered as environmental pollutants. Consequently, they are treated as highly toxic compounds to humans, and therefore they are suspected to be carcinogenic materials. From this point, continuous determination of phenol derivatives, e.g. catechol, suppose to be of a great necessary. For this purpose, the present study is focused on the electrochemical oxidation of catechol on the surface of a glassy carbon electrode in aqueous mediums. Limits of detection and quantification, response linearity range, sensitivity, repeatability and stability were evaluated.

2 Experimental

2.1 Chemical Reagents and Solutions

All the chemical reagents in our experiments were of analytical grade unless otherwise stated and they used as received without any further purification. All solutions were freshly prepared by dissolving the appropriate weight

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of reagents with double distilled water. K_2HPO_4 solution 0.1 M was used as supporting electrolyte.

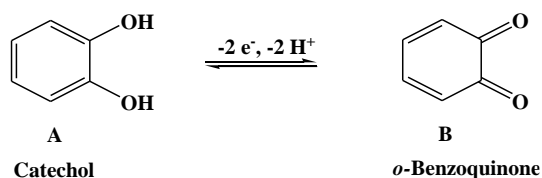
2.2 Electrochemical Equipments & Measurements

EG&G Princeton applied research potentiostat/galvanostat model 263 is used [18, 19]. The electrochemical cell consists of three electrodes. A glassy carbon electrode (GC) is used as working electrode (WE), Ag/AgCl saturated KCl electrode as reference electrode (RE) and Platinum wire served as counter electrode (CE). All experiments need to be conducted in duplicate; the estimations have demonstrated perfect reproducible. To adjust the pH values a few drops of HCl 0.1 M and 0.1 M NaOH solutions were added. Cyclic voltammetry is used to characterize the electrochemical behavior of catechol in aqueous mediums. A potential cycling between -1.0 to +1.0 V was applied to the WE vs. RE at room temperature and sweep rate of 100 mV s^{-1} . The effect of catechol concentrations (0.39 - 6.67 mM), scan rates ($50\text{-}500 \text{ mV s}^{-1}$) and pH values range from 2.01 to 12.88 have been investigated.

3 Results and Discussion

3.1 Electrochemical Behavior of Catechol

Figure 1 shows the electrochemical behavior of 4.0 mM catechol on the surface of a glassy carbon electrode in 0.1 M K_2HPO_4 as supporting electrolyte at room temperature, $\text{pH} \approx 9$ and scan rate of 100 mV s^{-1} . It can be seen from this graph that the CV curve is characterized by appearance of an anodic peak (P_A) at the positive-going scan at potential of -0.11 V and its correspondence cathodic one (P_C) on the reverse step at -0.28 V. This is due to the transformation of catechol to *o*-benzoquin one and *vice versa* (scheme 1) within a quasi-reversible two electron process [20]. Under experimental conditions, the peak current ratio ($\text{Ip}^C / \text{Ip}^A$) is close to unity which is considered as an indication for the stability of *o*-benzoquin one formed at the surface of glassy carbon electrode [21, 22].



Scheme 1

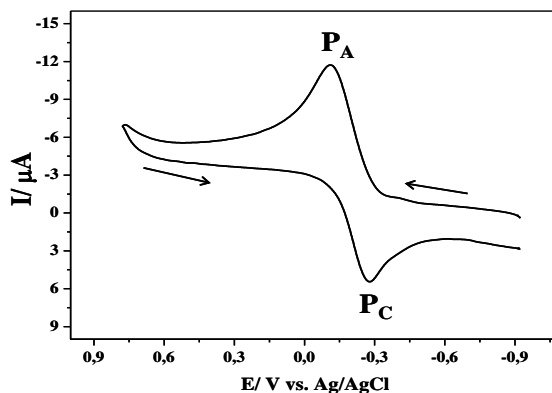


Fig. 1: Typical CV of 4.0 mM catechol at GC surface in 0.1 M K_2HPO_4 at RT. Experimental conditions: $\text{pH} = 9$ and scan rate 100 mV s^{-1} .

3.2 Effect of Solution PH

Figure 2 displays the influence of solution pH on the electrochemical behavior of catechol over GC in aqueous medium. The data were recorded in a solution contains 4 mM catechol and 0.1M K_2HPO_4 on GC and at different pH values (from 2.01 to 12.88). The results obtained from Fig. 2 suggested that, the redox process depends strongly on the solution pH values. Up on increasing of solution pH, the anodic peak current increased gradually till $\text{pH} = 9$. In other way, a maximum anodic oxidation peak was observed at $\text{pH} = 9$ which is indicating an excellent redox activity under moderate basic conditions. Consequently, pH value of 9 was chosen for all experiments. Further increase of the pH values has strongly negative effect on the oxidation peak current. Indeed, catechol nearly loses its electrochemical activity in a solution of strongly acidic or basic mediums.

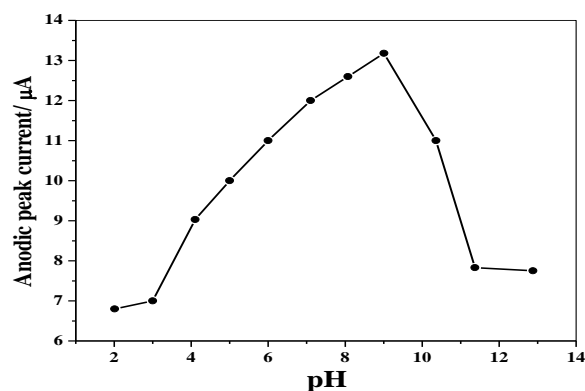


Fig. 2: Dependence of the oxidation peak current on solution pH values. Experimental conditions: 4.0 mM catechol, 0.1M K_2HPO_4 at RT and scan rate of 100 mV s^{-1} .

3.3 Effect of Catechol Concentration

Figure 3 demonstrates the effect of catechol concentrations on the trend of the redox peaks. Both the anodic and cathodic peaks current were increased by rising concentration of catechol. Also, the oxidation and reduction potential peaks shift towards more positive and slightly negative values, respectively. This indicates the inhibition of the electrode kinetics process via the creation of a tinny film of *o*-benzoquinone at the WE electrode surface.

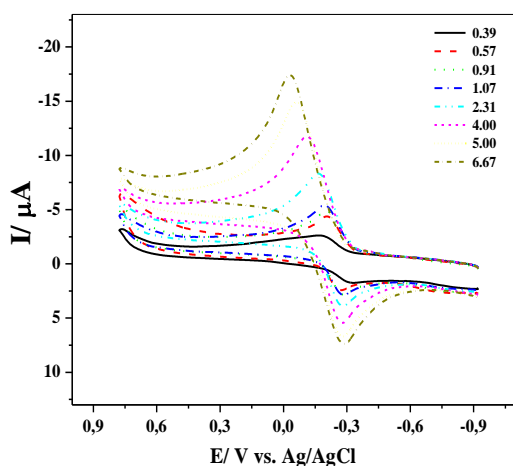


Fig. 3: Cyclic voltammograms of different concentrations of catechol in mM at GC surface in 0.1 M K₂HPO₄ at RT. Experimental conditions: pH= 9 and scan rate 100 mV s⁻¹.

For the electrochemical method characterization, the limit of detection (LOD), determination coefficient (R²), sensitivity and repeatability (RSD %) were calculated using seven data points according to Miller and Miller method [23].

The calibration curve of catechol at different concentrations is represented in Figure 4. As indicated by Fig. 4, the anodic peak currents response (peak height) and the analyte (catechol) concentrations are linearly dependent within the 0.57 - 6.67 mM concentration, following the linear regression Eqs. 1 and 2 [24]:

$$Y = mX + k \quad (1)$$

Where *m* is the slope of the regression line and *k* is the point at which the line crosses the Y-axis (Y intercept). In our case, Y-axis represents the anodic peak current (*I*, μA) and X-axis is the analyte concentrations (*C*, mM), then from Fig. 4 we got:

$$I (\mu A) = 2.18 C + 3.22 \quad (2)$$

Herein, the residual standard deviation of the linear regression or standard deviation of ordinate intercept (SD) for the anodic peak current vs. analyte concentrations stated on Fig. 4 is equal 1.52×10^{-6} . Consequently, the calculated

SD value was then used to determine the limits of detection (LOD) and quantification (LOQ) value as the following Eq.3 [25].

$$\text{LOD or LOQ} = F \times \text{SD}/m \quad (3)$$

Where *F* is a Factor of 3.3 and 10 for LOD and LOQ, respectively To conclude, according to Eq. 2 and Fig. 4 the value of R² is 0.99937 which shows the existence of positive correlation within the studied concentration range. The sensitivity which given by the slope of the straight line is equal 2.12 μA/mM. With applying Eq.3, the LOD and LOQ of determination of catechol over the surface of a glassy carbon was found to be 2.30×10^{-6} M and 6.97×10^{-6} M, respectively. These results are favorable result for sensitivity and quantitative analysis. Additionally, the GC electrode demonstrated long term stability. As a matter of fact, testing the reproducibility or repeatability (RSD) of the electrode after few weeks (for the same experiments and conditions) showed a slightly decrease of its activity as the change of the anodic peak current (*I*_p) was less than 1 %.

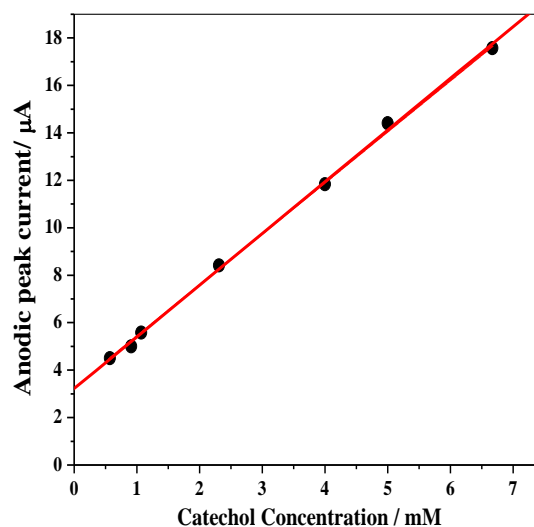


Fig. 4: Calibration curve of different catechol concentrations in 0.1 M K₂HPO₄ solution (pH= 9) at a GC surface and with scan rate of 100 mV s⁻¹.

3.4 Effect of Scan Rate

The effect of scan rate on the electrochemical oxidation of catechol at GC surface was also explored. Figure 5 shows the cyclic voltammograms of 4 mM catechol recorded at different sweep scan rates (50-500 mV s⁻¹) in supporting electrolyte of 0.1 M K₂HPO₄ (pH= 9). It can be seen that, both the oxidation and reduction peaks increased gradually with the increase of the sweep rates, i.e. the heights of redox peaks current were increased by increasing the value

of scan rate. Also, the oxidation and reduction potential peaks shifted to more positive and negative values, respectively. A straight line was obtained via plotting of the anodic peak current as a function of the square root of scan rates, demonstrating that the electrode reaction was diffusion controlled process (see Fig. 6).

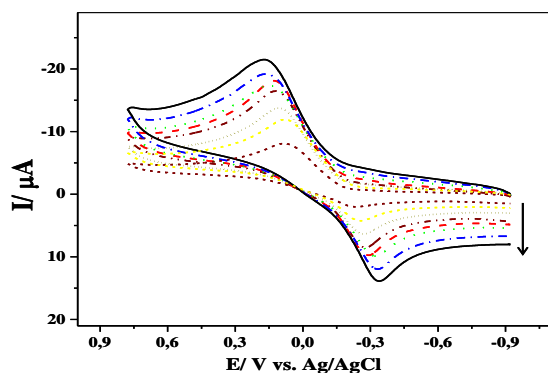


Fig. 5: Cyclic voltammograms of 4.0 mM catechol at GC (pH= 9) in 0.1 M K₂HPO₄ at different scan rates (v , from up to down) 50, 100, 150, 200, 250, 300, 400, and 500 mV s⁻¹.

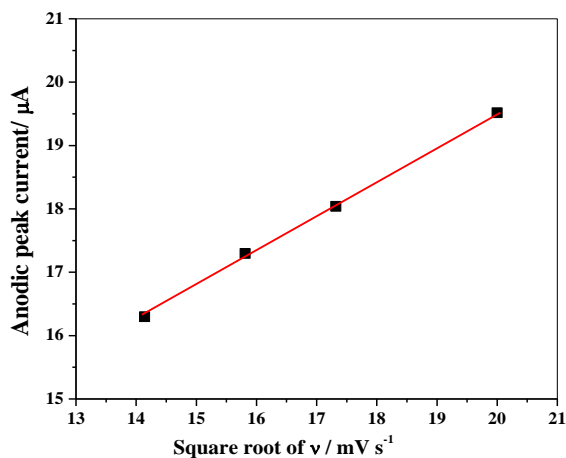


Fig. 6: Relationship between the oxidation current peak (I_p) and square root of scan rate. The data is taken from CVs curves presented in Fig. 5.

4 Conclusions

In this study, the electrochemical oxidation of catechol over the surface of a glassy carbon electrode has been investigated. It was demonstrated that the GC exhibits a higher electrocatalytic activity towards catechol oxidation. From the CVs and the analytical measurements, it was clear that the reaction of catechol was irreversible and the anodic

current achieved was under diffusion control. Also, the anodic peak current was strongly depends on pH values, scan rates and concentrations of the analyte. The limit of detection was estimated to be 2.30×10^{-6} M.

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