



## The Electrochemical Redox Behavior of Pyrocatechol Violet and its Quantitative Measurement at Graphene Modified Glassy Carbon Electrode: A Voltammetric Study

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### ABSTRACT

The electrochemical oxidation and reduction behavior of pyrocatechol violet (PCV) at graphene modified glassy carbon electrode were investigated by employing cyclic voltammetry (CV) and differential pulse voltammetry techniques. PCV exhibited an oxidation peak at  $\approx 0.16$  V and a reversible reduction peak at 0.14 V. The effect of pH on the PCV was observed using the phosphate buffer solution, and pH-5.0 was chosen as optimum pH for all the remaining experiments. The effect of scan rate on the PCV was observed and it was determined as diffusion controlled process. We have also studied, the effect of PCV concentration on the peak current response, from the linear plot of the calibration curve, we have evaluated the limit of detection and limit of quantification as  $3.248 \times 10^{-8}$  M and  $10.22 \times 10^{-8}$  M. Finally, the surface nature of the electrode was characterized using the electrochemical impedance spectroscopy.

**Key words:** Pyrocatechol violet, Cyclic voltammetry, Differential pulse voltammetry, Electrochemical impedance spectroscopy, Glassy carbon electrode.

### 1. INTRODUCTION

Pyrocatechol violet (PCV) (3,3',4'-trioxifuchsin-2''-sulfonic acid or pyrocatecholsulfophthalein) (Scheme 1) is a sulfone dye which was made from condensing pyrocatechol with O-sulfobenzoic acid anhydride [1,2]. PCV also has indicator properties and forms complexes with metal ions. It is photometric reagent and indicator for heavy metals and rare earth metals. This was used as pH indicator with a transition interval from 0 to 8 pH (red to violet). In general, the dyes are chemically bonded to the substance and converts into a part of the material on which it was applied [3]. In our daily life, the usage of dyes were increased rapidly because of its wide range of applications. The dyes are toxic in nature and make contamination with effluents eluted from the industries. The water contamination with dyes causes severe health diseases hence the sensitive and selective determination, separation, and quantification of dyes are of great importance [2,4,5].

CV was the technique which was widely used in many fields of chemistry. This technique is based on measuring current response against applied potential. Using this technique, we can predict

the redox mechanism of an analyte. Differential pulse voltammetry (DPV) is a sensitive technique in comparison with CV because it minimizes the migration currents. Glassy carbon electrodes (GCE) has been used by many numbers of electrochemists, however, the conventional electrodes such as GCE, carbon paste electrode, and platinum (Pt) electrodes have very poor sensitivity and selectivity. To overcome this challenge, the modification of electrode surfaces with conductive materials such as nanoparticles [6-8], polymers [9-11], enzymes [12-14] clays [15,16], and amino acids [17] have received more importance. In this study, we have used GCE modified with graphene as a working electrode.

At present, very few reports were established about the quantitative determination of PCV, among the all analytical techniques; the electroanalytical techniques such as CV and DPV were widely used for the quantification of various analytes. These techniques were mainly based on the surface modification of the working electrodes with different conductive materials. In this study, due to the conductive and catalytic properties of graphene, the GCE was modified with graphene and used as working electrode [18,19].

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In this work, we have studied the redox behavior of PCV at graphene/GCE working electrode and proposed a redox mechanism (Scheme 2). We have studied the redox nature of PCV in different pH values, scan rate, and concentration. Electrochemical impedance spectroscopy (EIS) was employed for the determination of surface nature of the working electrode.

## 2. MATERIALS AND METHODS

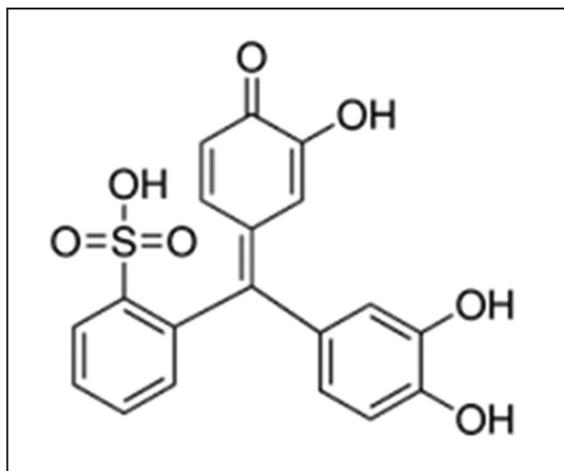
### 2.1. Experimental

#### 2.1.1. Apparatus

CHI-660D (CH-instruments) electrochemical workstation was used for CV, DPV, and EIS experiments. The experiments were performed with a conventional three-electrode electrochemical cell. In the three electrode system, graphene modified GCE was used as a working electrode, Pt - wire and silver-silver chloride electrodes were used as counter and reference electrode, respectively. The homogeneous solution of graphene suspension was prepared using Toshiba ultrasonication bath made in India. A model LI 120 (ELICO) pH meter was used for the preparation of various pH buffer solutions.

#### 2.1.2. Chemicals

Graphene was from acros organics, PCV was from Sigma-Aldrich and dissolved in double distilled



Scheme 1: Molecular structure of pyrocatechol violet.

water to prepare 0.1 mM/L standard stock solution.  $\text{NaH}_2\text{PO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$  were from Fisher scientific, India, and Merck India. 0.1 M phosphate buffer solution was prepared from  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$ . All other chemicals used were of analytical grade quality and used as received.

#### 2.1.3. Modification of GCE

Before the modification of GCE, it was first polished with an alumina slurry having sizes 1, 0.3, and 0.05 microns, respectively. After getting mirror like shine 5  $\mu\text{L}$  of graphene solution which was dissolved in ethanol (1:2 W/v) was immobilized on the surface of the GCE and allowed to dry, the designed electrode was used as working electrode and denoted as graphene/GCE.

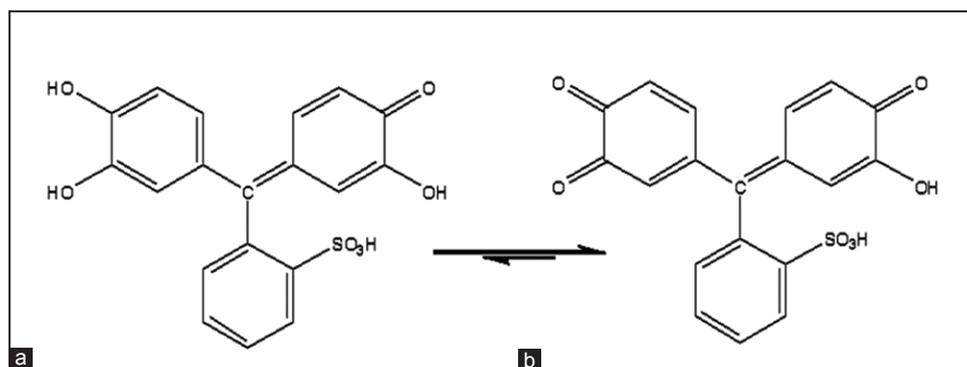
## 3. RESULTS AND DISCUSSIONS

### 3.1. Electrochemistry of PCV

The electrochemical redox behavior of 1 mM PCV in PBS having pH-5.0 at graphene/GCE was studied by employing CV technique. The CV response of  $1 \times 10^{-4}$  M solution of PCV was studied in a forward scan, i.e.,  $-0.2$  V to  $0.8$  V an oxidation peak was observed at a potential of  $0.16$  V, which corresponds to the oxidation of catechol group present in the PCV which forms a carbonyl compound. An oxidation peak was observed at potential  $0.48$  V, which corresponds to the oxidation of phenolic group of PCV. In a reverse scan, i.e., from  $0.8$  to  $-0.2$  V, we have observed two reduction peaks corresponding to the reduction of carbonyl compound into catechol group. Scheme 2 shows the electrochemical redox mechanism of PCV at graphene/GCE [3]. Figure 1 shows the voltammograms of PCV at bare GCE and graphene/GCE and it depicts that there was a small oxidation currents at bare GCE; after the modification of GCE surface with graphene, the peak currents were greatly enhanced and the enhancement in the currents was due to the conductive nature of the graphene [19].

### 3.2. EIS of GCE and Graphene/GCE at $K_3[\text{Fe}(\text{CN})_6]$

EIS is one of the most useful techniques for the study of the surface nature of different materials. The EIS plot

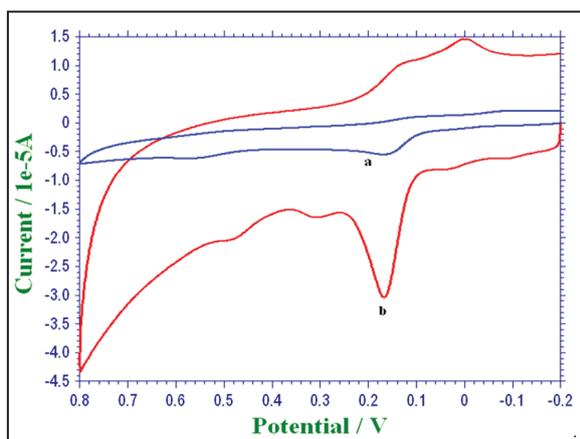


Scheme 2: (a and b) Proposed electrochemical redox mechanism for pyrocatechol violet at graphene/glassy carbon electrodes.

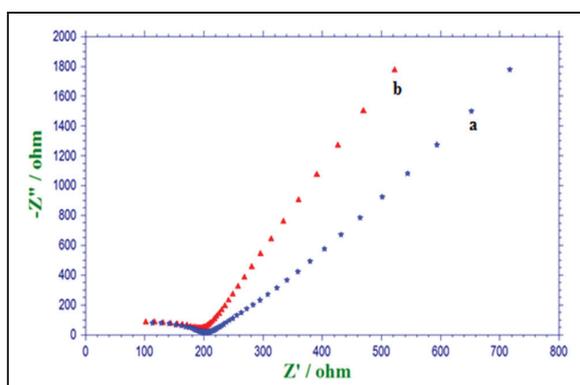
typically consists of two portions in which semicircular part represents the charge transfer resistance at the electrode surface and linear portion of EIS indicates the diffusion process of the analyte. The EIS linear part having more slope value indicates that the analyte has more diffusion tendency toward the electrode surface and the current response in voltammetry is mainly due to the diffusion of analyte [20]. From Figure 2, it represents the nyquist plots for bare GCE (a) and graphene/GCE (b), from this the graphene/GCE has more slope value in comparison with bare GCE indicating that the modified electrode has more diffusion tendency toward the analyte [21,22].

### 3.3. Effect of pH

The effect of different pH's on the electrochemical responses of the  $1 \times 10^{-4}$  M PCV was studied with phosphate buffer solutions. The pH of the supporting electrolyte was varied with the ranges from pH-5.0 to 8.5, and the DPV responses were recorded between the potential window of  $-0.2$  to  $0.6$  V. Figure 3A,



**Figure 1:** (a) The cyclic voltammograms of  $1 \times 10^{-4}$  M pyrocatechol violet in pH-5.0 phosphate buffer solution with scan rate of  $100 \text{ mVs}^{-1}$  at bare glassy carbon electrodes, and (b) graphene/glassy carbon electrodes.



**Figure 2:** (a) The nyquist plot of electrochemical impedance spectroscopy representing bare glassy carbon electrodes and (b) graphene/glassy carbon electrodes.

shows the pH of the supporting electrolyte influencing on the peak currents and peak potentials of the PCV, indicating the involvement of protons in the electrochemical redox reaction system of PCV. From Figure 3A, the DPV responses for pH-5.0 was having more peak currents than other pH values, therefore pH 5.0 was selected as optimum pH for all the further experiments. At higher pH values, an additional peak was seen at potential of  $\approx 0.4$  V which corresponds to the oxidation of phenolic group present in the PCV. From Figure 3B, a linearity was achieved for the pH versus potential plot, and the linear regression equation was found to be as  $E_p \text{ (V)} = 0.544 \text{ (V)} - 0.077 \text{ V/pH}$  with a correlation coefficient of 0.995. The slope value of the linear regression equation was  $0.077 \text{ V/pH}$  which was close to the theoretical value of  $0.060 \text{ V/pH}$  confirming the involvement of an equal number of protons and electrons in the electrochemical redox mechanism of PCV [23,24].

### 3.4. Effect of Scan Rate

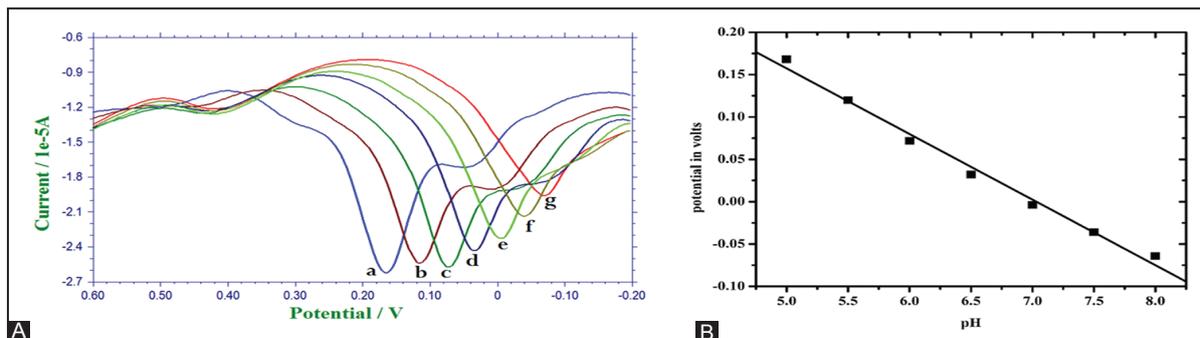
To evaluate the kinetic parameters for the electrochemical oxidation and reduction of PCV, we have studied the scan rate effect by changing scan rate from  $10 \text{ mV s}^{-1}$  to  $100 \text{ mV s}^{-1}$ . Figure 4A exhibits the linear sweep voltammograms (LSV's) of  $1 \times 10^{-4}$  M PCV in PBS solution having pH-5.0 at different scan rates. From Figure 4A, we have observed that the LSV responses of  $1 \times 10^{-4}$  M in PBS pH-5.0 were gradually increasing with increase in the scan rate. From Figure 4B, a typical linearity was observed for the peak current responses of PCV and square root of scan rate and the linear regression equation was obtained as  $i_p \text{ (}\mu\text{A)} = 3.779 \text{ (}\mu\text{A)} + 0.139 \text{ v}^{1/2} \text{ (mV/s)}^{1/2}$  with the correlation coefficient  $R^2 = 0.986$ . The linearity between the peak currents and square root of scan rate indicates the electrochemical redox behavior of PCV was controlled by diffusion process. Figure 4B is the linear plot for peak currents and square root of scan rate [25-28].

### 3.5. Effect of Concentration

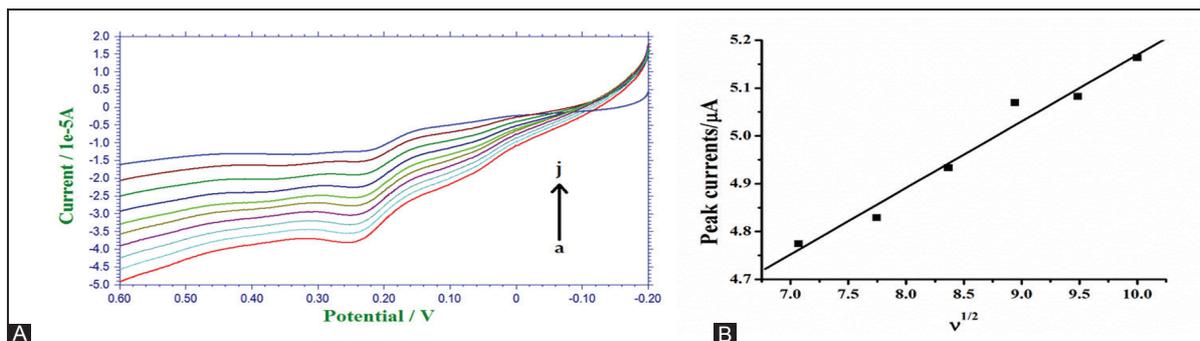
DPV was the most widely used sensitive analytical technique for the quantification of various analytes. To quantify the PCV in buffer solution, we have performed the DPV measurements for different concentrations of PCV. Figure 5 exhibits the peak currents of DPV's for different concentrations of PCV. A gradual increase of peak currents against the concentration of PCV was observed. A good linearity was achieved for the peak currents versus concentration of PCV. Based on the following equations and linear calibration plot, we have found the limit of detection (LOD) and limit of quantification (LOQ) as  $3.248 \times 10^{-8} \text{ M}$  and  $10.22 \times 10^{-8} \text{ M}$ , respectively. Where  $S_b$  was the standard deviation and "m" was the slope of calibration curve [29].

$$\text{LOD} = 3S_b/m$$

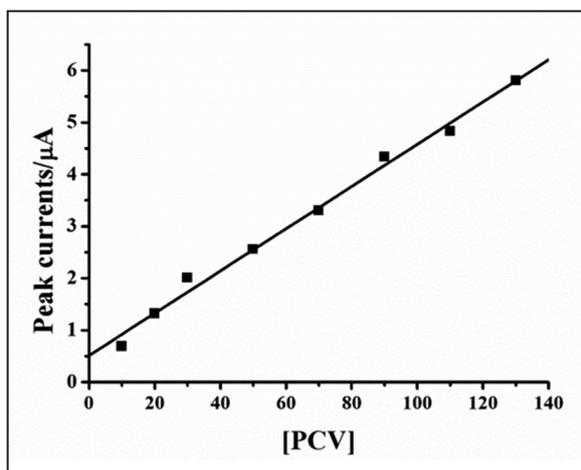
$$\text{LOQ} = 10S_b/m$$



**Figure 3:** (A) The DPV's of  $1 \times 10^{-4}$  M pyrocatechol violet in PBS at pH-5.0 (a), pH-5.5 (b), pH-6.0 (c), pH-6.5 (d), pH-7.0 (e), pH-7.5 (f), and pH-8.0 (g) at graphene/glassy carbon electrodes, (B) A plot drawn between pH of the supporting electrolyte and corresponding peak potentials in volts.



**Figure 4:** (A) The linear sweep voltammograms of  $1 \times 10^{-4}$  M pyrocatechol violet in phosphate buffer solution of pH-7.0 with scan rates  $10 \text{ mVs}^{-1}$  (a),  $20 \text{ mVs}^{-1}$  (b),  $30 \text{ mVs}^{-1}$  (c),  $40 \text{ mVs}^{-1}$  (d),  $50 \text{ mVs}^{-1}$  (e),  $60 \text{ mVs}^{-1}$  (f),  $70 \text{ mVs}^{-1}$  (g),  $80 \text{ mVs}^{-1}$  (h),  $90 \text{ mVs}^{-1}$  (i), and  $100 \text{ mVs}^{-1}$  (j), at graphene/glassy carbon electrodes, (B) A plot between square root of scan rate and peak currents of pyrocatechol violet.



**Figure 5:** The plot between the peak currents against different concentrations of pyrocatechol violet.

#### 4. REPEATABILITY, REPRODUCIBILITY, AND STABILITY

The practical utilization of graphene/GCE was examined with  $1 \times 10^{-4}$  M PCV using CV. We have recorded several CV's and all the CV's exhibited almost the same current response with a low relative standard deviation values, conforming the good

repeatability of the modified electrode. We have scanned the CV responses for few newly prepared graphene/GCE's and the peak current results produced were almost the same indicating good reproducibility of the fabricated electrodes. We have also observed the stability of the graphene/GCE by storing the electrode for nearly 1 month, and the results were in satisfactory range [23].

#### 5. CONCLUSIONS

In this work, we have studied the electrochemical redox behavior of PCV at graphene/GCE. It was found that the redox mechanism of PCV was dependent on the pH of the solution. The scan rate effect was studied, and the results show that the redox process was controlled by diffusion process. The LOD and LOQ values were achieved from the effect of concentration. Finally, the surface nature, repeatability, reproducibility, and stability of graphene/GCE were examined, and the results were in satisfactory range.

#### 6. ACKNOWLEDGMENTS

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**\*Bibliographical Sketch**



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