



# Chromium Schiff base complex as a electrocatalytic probe for the determination of hydroquinone

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**Abstract:** — Salen type chromium Schiff base complex was synthesized by microwave irradiation. The complex was characterized by UV-visible, FT-IR spectroscopy and EPR spectroscopy. Electrochemical property of chromium complex was tested with the aid of cyclic voltammetry (CV). The synthesized chromium Schiff base complex was electrochemically polymerized and used for the detection of hydroquinone. Chromium metal ion has various oxidation states, (i.e., +3, +5 and +6) due to this nature it acts as a good oxidizing agent. The polymerized chromium Schiff base complex has better selectivity and sensitivity for hydroquinone determination. Hydroquinone (HQ) is an important organic compound that is widely used in many fields such as pharmaceutical, antioxidant, dye, photographic developers, lithography and cosmetic industries. It is toxic to human and difficult to degrade in the environment. So there must be an effective method for the determination of HQ. The polymerized Schiff base chromium complex modified GCE has better response when compared with the bare GCE. Therefore it can be a good electrochemical sensor for HQ determination.

**Key words:** Chromium, Schiff base, Hydroquinone, Glassy carbon electrode, Micro wave.

## I. INTRODUCTION

In recent years a great interest was shown to synthesize the Schiff bases and their metal complexes, due to their wide range of applications [1-3]. The Schiff base transition metal complexes have been found to be used in antimicrobial agents, anticancer agents, homogeneous and heterogeneous catalysts, in electrocatalytic processes, chemical sensors and pesticides [4-6]. In addition, the Schiff base metal complexes have been used as efficient electrode modifiers for electrochemical sensing processes. Chromium exists in both +3 and +6 oxidation states, the +3 state of chromium trivalent ion is biologically more important. The Cr<sup>+3</sup> state is less toxic

than Cr<sup>+6</sup> state. The +3 oxidation state of chromium metal ion forms stable complex due its d<sup>3</sup> electronic configuration [7]. In our work the chromium Schiff base complexes contain +3 oxidation state. Chromium metal is a high focused substance for its multifunctional nature in photochemistry, electrochemistry and electromagnetic property. Chromium metal ion is involving an important function in carbohydrate metabolism through redox interaction. The chromium +3 is essentially required for carbohydrate and lipid metabolism. Chromium binds with insulin as activate receptor and stimulator for the kinase activity [8]. The chromium Schiff base complex has been prepared by microwave irradiation method in green chemical route, with high yield. In microwave method the reaction occurs faster than thermal method.

Hydroquinone (HQ) is widely used in many fields such as pharmaceutical, antioxidant, dye, photography and cosmetic industries. HQ also been used as reducing agent, polymerization inhibitor, and other chemical intermediate [9]. HQ has toxic nature to human cells and low degradability in the ecological environment. Therefore, the US Environmental Protection Agency (EPA) and the European Union (EU) have considered the HQ as a serious environmental pollutant. Thus, it is very important to detect the HQ with high efficiency and cost effective analytical method. Numerous of methods are available for the determination of HQ, such as high performance liquid chromatography, spectrophotometry, chemiluminescence, flow injection analysis and electrochemical method etc., in all these electrochemical method has high attraction because of its high selectivity and sensitivity for the determination of HQ. HQ has good electrochemical redox nature, hence it gives good response in the electrochemical process. This method has low detection limit, low cost effective, easy preparation, high conductivity, and renewable surface [10]. In our present work we utilize the glassy carbon electrode (GCE) as a working electrode and it was modified by the chromium Schiff base complex. The modified GCE was fabricated for the determination of HQ

## II. EXPERIMENTAL

Chemicals and Instruments 5-methylsalicylaldehyde was prepared by following literature [11] method, N,N'-bis-(3-aminopropyl) ethylenediamine was purchased from Sigma Aldrich, Chromium(III) chloride hexahydrate was purchased from Alfa Aesar, Hydroquinone, ethanol and methanol were purchased from Qualigens,

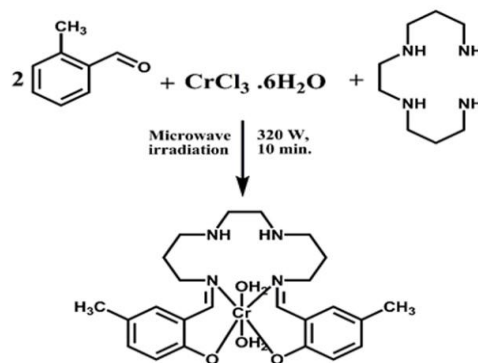
IR spectra were recorded on a PerkinElmer FT-IR 8300 series spectrophotometer on KBr disks from 4000 to 400  $\text{cm}^{-1}$ , Electronic spectral studies were carried out on a PerkinElmer lambda 35 UV-visible spectrophotometer, Electron paramagnetic resonance (EPR) studies were carried out in the Bruker X-Band CW EPR spectrometer, 9.4GHz and cyclic voltammograms were obtained on a CHI-1103A electrochemical analyzer using a three-electrode cell in which a bare and modified GCE were the working electrode.

### General synthesis of 5-methyl-salicylaldehyde

A mixture of glycerol (150 g, 1.63 mol) and boric acid (35 g, 0.57 mol) were heated for 30 min at 170 °C to expel water. Then a mixture of 4-methylphenol (25 g, 0.23 mol) and hexamethylenetetramine (25 g, 0.18 mol) was added. The mixture was stirred for 15 min. The thick brown liquid obtained was allowed to cool to 110 °C. A solution of concentrated sulphuric acid (30 mL) in water (70 mL) was added and the whole mixture was boiled in a current of steam. The product was collected by steam distillation. The solid obtained was recrystallized from 80% ethanol. Yield: 8.2 g (26%), M.P.: 55 °C. [11].

### Synthesis of Chromium Schiff base complex

An absolute methanolic solution of 0.262 g (1 mmol) of chromium(III) chloride was added drop wise to the stirred methanolic solution of 0.272 g (2 mmol) of 5-methyl-salicylaldehyde, the stirring was continued for 30 min. Then 0.18 ml (1 mmol) of N,N'-bis-(3-aminopropyl) ethylenediamine was taken in 10 ml of methanol, the methanol solution was added to the reaction mixture. In the reaction mixture 320W radiation was applied in microwave oven for 10 min. After the irradiation the reaction mixture was cooled to room temperature. A green colour solid product was obtained it was collected and recrystallized by using ethanol. The reaction scheme was shown in Scheme-1.



Scheme -1: Synthesis of Chromium Schiff base complex  
Electrochemical measurements

Glassy carbon electrode (GCE) was modified by electrochemical polymerization. Before the electrochemical polymerization the working electrode was polished by different size of alumina slurry (i.e., 0.1 and 0.05 micron) and sonicated for about 5 min in deionized water. The GCE was dried at room temperature and used for the electro- polymerization in a three electrode cell, Ag/AgCl as reference electrode platinum wire as counter electrode, the GCE as working electrode. 0.1 M chromium Schiff base complex solution was prepared by using acetonitrile solvent. The electro-polymerization was carried out in the potential range of 1.2 to -1.0 V, at 50  $\text{mVs}^{-1}$  scan rate. The chromium Schiff base complex was polymerized on the surface of GCE, and it was fabricated for the determination of HQ.

Detection of HQ was measured using saturated calomel electrode (SCE) as reference, and other electrodes are the same. The electrochemical response of the HQ was tested for both bare GCE and modified GCE in phosphate buffer at pH 7.0.

## III. RESULTS AND DISCUSSION

Chromium Schiff base complex was synthesized by microwave irradiation method and it was characterized by the following spectral techniques. The chromium Schiff base complex was green in colour. It is soluble in DMF, DMSO, Ethanol, Methanol and dichloromethane.

### Electronic Spectral analysis

UV-visible spectrum was carried in methanol solution in the range 200 to 800 nm. The UV-Visible spectrum of chromium Schiff base complex was shown in Fig.1.

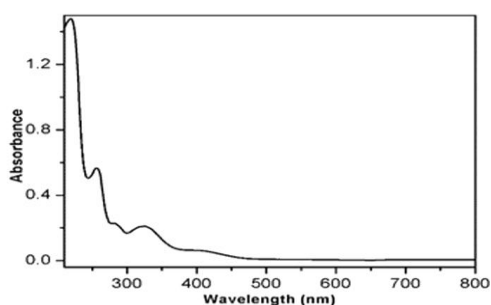


Fig. 1:- UV-Visible spectrum of chromium Schiff base complex

In this spectrum the chromium Schiff base complex shows five different peaks. The peaks in the range of 400 nm and 320 nm attributed to d-d transition of chromium central metal ion. A peak at 285 nm shows that  $n \rightarrow \pi^*$  transition in C=N chromophore. At 255 nm a peak was appeared due to the  $\pi \rightarrow \pi^*$  electronic transition in C=N. The peak at 210 nm is exhibit for the  $\pi \rightarrow \pi^*$  electronic transition in aromatic C=C. From the electronic spectrum, we understood that the complex has chromium as central metal ion in +3 oxidation state and octahedral geometry [12-14].

#### FT-IR spectral analysis

The FT-IR spectrum of the chromium Schiff base complex was analyzed in the range of  $400 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  with the aid of KBr pellets. In the IR spectrum a sharp peak at  $1626 \text{ cm}^{-1}$  exhibit due to the presence of C=N imine group the shift shows that the imine group bind with the central metal ion. The peak at  $525 \text{ cm}^{-1}$  shows the bond between phenolic oxygen and chromium ion. These are two important bands which explain the bond formation between the Schiff base and the chromium ion. A peak at  $2950 \text{ cm}^{-1}$  shows the presence of C-H bond. The peak at  $3410 \text{ cm}^{-1}$  shows the bond between water molecules and the metal ion [15-18]. A small peak at  $450 \text{ cm}^{-1}$  explains the bond formation of nitrogen with central chromium ion. All the peaks systematically explain the complex formation in Schiff base chromium complex. The FT-IR spectrum was shown in Fig. 2.

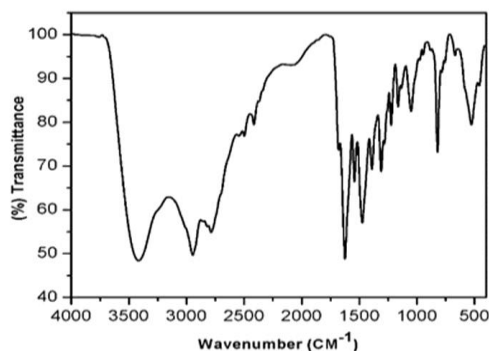


Fig. 2:- FT-IR spectrum of chromium Schiff base complex

#### EPR spectral analysis

X-band EPR spectra of Chromium Schiff base complex were recorded in the solution state at room temperature. It was shown in Fig. 3. The EPR spectrum of chromium Schiff base complex shows a single peak at 3000 G. Also the spectrum give g value 1.9784 with  $g_{\text{iso}}$  2.0, it explains that the chromium metal ion has three unpaired electrons in  $d^3$  electronic configuration. The complex has paramagnetic nature,  $\mu_{\text{eff}}$  is 3.71 BM. From the EPR and electronic spectral data the chromium Schiff base complex is said to be in octahedral geometry [19].

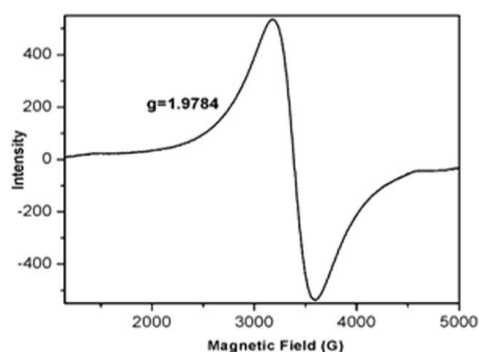


Fig. 3:- EPR spectrum of chromium Schiff base complex  
Electrochemical studies

A cyclic voltammogram was recorded at a scan rate of  $50 \text{ mVs}^{-1}$  with a freshly polished glassy carbon electrode in 0.1 M acetonitrile solution of chromium Schiff base complex, in the presence of 0.1 M TBAP (tetrabutylammoniumperchlorate) as a supporting electrolyte. The voltammogram was shown in Fig. 4., and it explains that the chromium Schiff base complex is electroactive in the potential range of 1.2 V to -1.0 V. The cyclic voltammogram of the chromium Schiff base complex exhibit an irreversible reduction peak (small hump) at the potential -0.80 V. This reduction peak appeared due to the irreversible one-electron reduction process of chromium (III)–chromium (II) [20]. The same condition was applied for electrochemical polymerization (i.e., modification of GCE). It was given in Fig.4A. In the electrochemical polymerization the chromium adsorbed at GCE surface. It was utilized further for the determination of HQ.

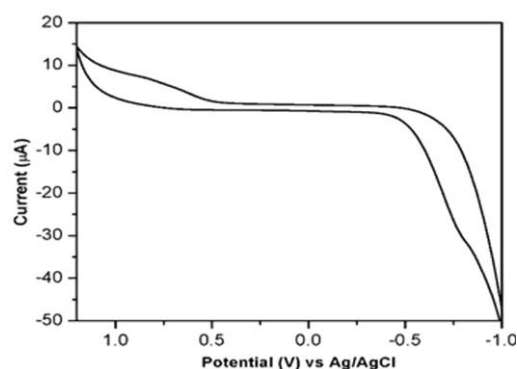


Fig. 4:- Cyclic voltammogram of chromium Schiff base complex at the scan rate of  $50 \text{ mVs}^{-1}$  in acetonitrile containing 0.1 M TBAP.

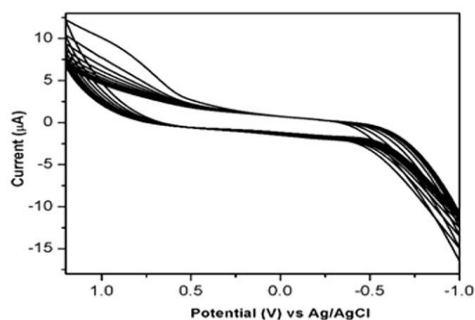


Fig. 4A:- Electrochemical polymerization of chromium Schiff base complex at the scan rate of  $50 \text{ mVs}^{-1}$  in acetonitrile containing  $0.1 \text{ M}$  TBAP

In the cyclic voltammogram some other peaks are appeared it because of the electroactivity of the ligand. Based on the potential variation we conclude that metal center activity.

#### Electrochemical detection of HQ

A set of cyclic voltammograms was shown in Fig. 5. The CV shows the electrochemical response of  $1 \text{ mmol}$  HQ in  $0.1 \text{ mol}$  PBS at pH 7.0 on GCE and chromium Schiff base complex modified GCE at  $50 \text{ mVs}^{-1}$ . The HQ gives a well separated redox peak at  $0.189 \text{ V}$  and  $-0.003 \text{ V}$ . The potential difference  $0.191 \text{ V}$  explains that the redox process on bare GCE is irreversible. The chromium Schiff base complex modified GCE gives a pair of redox peaks at  $0.176 \text{ V}$  and  $0.127 \text{ V}$  with the separation of  $0.049 \text{ V}$  potential indicate that the modified GCE gives highly reversible process of the HQ. The potential difference indicated that chromium Schiff base complex accelerate the electron transfer of hydroquinone on the electrode surface and improved the reversibility of redox process. When compare the peak currents of modified GCE and bare GCE, the modified GCE gives three fold higher peak currents than bare GCE. The much higher increases in redox peak currents of HQ totally attributed by the excellent electrocatalytic activity of chromium Schiff base complex at electrode surface [21]. It clearly indicate that the chromium Schiff base modified GCE can be a good electrochemical sensor for the HQ sensing. The electrochemical redox reaction of HQ is given in Scheme-2, it two electron transferred process.

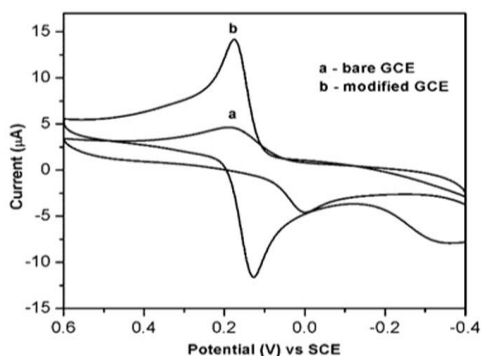
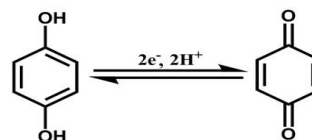


Fig. 5:- Cyclic voltammogram of  $0.1 \text{ mM}$  HQ at the scan rate of  $50 \text{ mVs}^{-1}$  containing  $0.1 \text{ M}$  PBS.



Scheme- 2: Electrochemical redox reaction of hydroquinone (HQ)

#### Effect of scan rate

The effect of scan rate was studied by cyclic voltammetry for the HQ at pH 7. The increase in scan rate increases the peak current for both reduction and oxidation process of HQ. Increasing scan rate will shift the anodic peak current in positive direction as well as negative direction for cathodic peak current. It indicate that increasing scan rate will leads to reversible electrochemical process turns to quasi- reversible process of HQ. The scan rate was increased from  $10$  to  $500 \text{ mVs}^{-1}$ , and the CVs of scan rate effect are given in Fig.6.

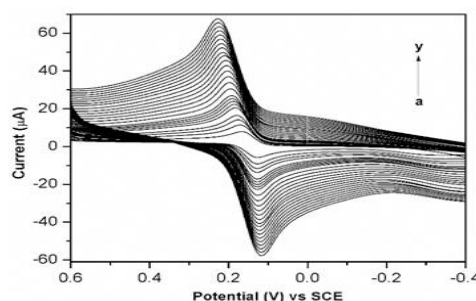


Fig. 6:- Effect of scan rate of  $0.1 \text{ mM}$  HQ in  $0.1 \text{ M}$  PBS for modified GCE (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80, (i) 90, (j) 100, (k) 125, (l) 150, (m) 175, (n) 200, (o) 225, (p) 250, (q) 275, (r) 300, (s) 325, (t) 350, (u) 375, (v) 400, (w) 425, (x) 450, (y) 500.

#### Determination of HQ

The hydroquinone was determined by Differential Pulse Voltammetry (DPV) method. This method is highly sensitive when compared with the CV. The detection limit was found by the utilization of DPV method. In this HQ electrochemical process we consider anodic peak current, with the addition of  $5 \mu\text{l}$  HQ. The oxidation peak current of HQ increased with the increase in concentration. It clearly indicates that the modified GCE is a good electrochemical sensor for the HQ. The DPV response of HQ for modified GCE in PBS shows in Fig. 7. [22].

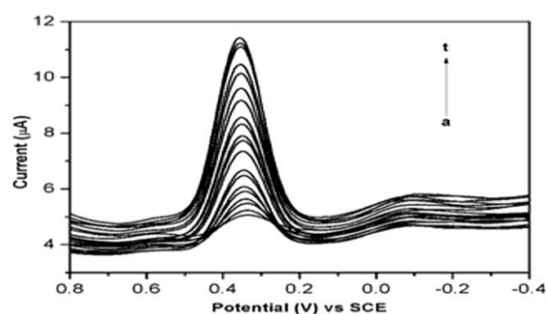


Fig. 7:- DPV response of HQ at pH 7 PBS for chromium Schiff base complex modified GCE

#### IV. CONCLUSION

The chromium Schiff base complex was prepared by microwave irradiation method. It was characterized by UV-Visible, FT-IR and EPR spectral techniques. The cyclic voltammetry technique was used for the detection of hydroquinone and electrochemical behavior of chromium Schiff base complex. In our present work a simple electrochemical polymerization was used for the modification of GCE surface. The modified GCE showed good electrocatalytic effect to the redox reaction of HQ and it gives highly reversible process. In the electrochemical reaction two electron and two protons were involved. Under the optimal conditions the prepared chromium Schiff complex modified GCE shows better electrocatalytic response than bare GCE, which indicated that chromium Schiff base complex modified electrodes had excellent potential applications in the electrochemical determination of hydroquinone.

#### V. ACKNOWLEDGEMENTS

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