

Synthesis, Characterization of Acyclic Schiff base and its Electrochemical Sensing property for Hydroquinone

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Abstract— A salen type Schiff base was synthesized by microwave irradiation method. It was derived from 5-methylsalicylaldehyde and triethylenetetraamine. The Schiff base was characterized by UV-Visible, Infrared (FT - IR) and NMR (Nuclear Magnetic Resonance) spectral techniques. The electrochemical redox property of Schiff base was examined by cyclic voltammetry and it was electrochemically polymerized. The polymerized Schiff base was used for the electrochemical sensing of phenolic compound like hydroquinone (HQ). The result could be attributed to the presence of high conductive polymerized Schiff base on the electrode surface. The polymerized Schiff base formed hydrogen bond with HQ. This hydrogen bond formation caused the better sensing ability to polymerized Schiff base. Hydroquinone (HQ) is widely used in many fields, however, because of its toxicity to humans and difficulty in degradation, HQ is also considered as a serious environmental pollutant. There is a necessity to improve the electrochemical sensor for the detection of HQ. The polymerized Schiff base modified GCE showed better electrocatalytic activity towards HQ detection than the other sensors.

Key Words: Schiff base, electrochemical polymerization, hydroquinone, hydrogen bond, electrocatalytic sensor.

I. INTRODUCTION

The Schiff bases are getting more important in research due to their wide range of applications. Schiff base ligands having major role in biological applications like antifungal, antibacterial, antimalarial, anti-proliferative, anti-inflammatory, antiviral, and antipyretic properties[1]. Schiff bases were used in the synthesis of metallo-organic hybrid complexes. It has high tendency to bind with the metal atom and form the complexes with different oxidation states [2]. The Schiff bases are containing different heterocyclic moieties and they are important class of compounds in organic chemistry. Schiff base can be used for the heavy metal sensing, and removal of pollutant in the environment. They are good spectrophotometric and fluorimetric agents [3]. In this work we applied the Schiff base as electrocatalytic sensor for environmental pollutants. The Schiff base ligands sense the analyte through hydrogen bond formation. Last few decades we had revolution in manufacturing industries, it leads to environmental pollution. There is a necessity to save the life of living organism, hence we have to develop some facilities to detect the pollutant and their nature. Based on this factor we tried to detect the hydroquinone as an environmental pollutant. The fields of medical, food, dye and photography chemicals hydroquinone widely used. Due to their toxicity and low degradability it is consider as pollutant [4]. There are several methods for the detection of hydroquinone, but the electrocatalytic method is one of the best for the detection of hydroquinone at very low concentration and high sensitivity [5]. This work is a new approach for sensing of analyte, electropolymerization was used for the modification of GCE.

II. EXPERIMENTAL

A. Reagents

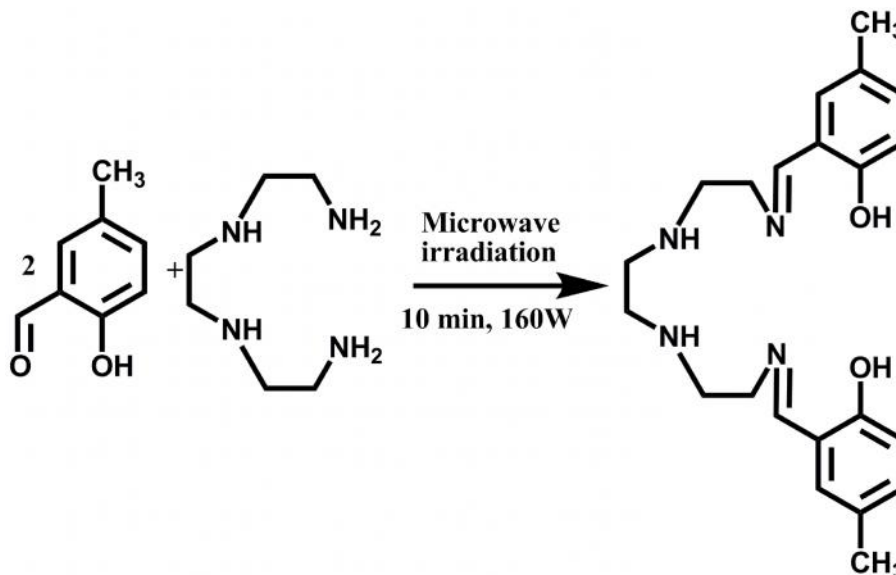
5-methylsalicylaldehyde was prepared by the following literature method, triethylene tetraamine was purchased from Alfa aesar, hydroquinone and solvents were purchased from Quilogens. TBAP, used as supporting electrolyte in electrochemical measurements, was purchased from Fluka and recrystallized from hot methanol.

B. General synthesis of 5-methylsalicylaldehyde

A mixture of glycerol (150 g, 1.63 mol) and boric acid (35 g, 0.76 mol) were heated for 30 min at 170 °C to expel the 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 steam. The product was collected by steam distillation. The solid obtained was recrystallized from 75mL of 80% ethanol. Yield: 8.2 g (26%) M.P.: 55 °C.

C. Preparation of Schiff base

1 mmol of triethylenetetramine (0.1473 g) in methanol, was added drop wise in the stirred methanolic solution of 2 mmol 5-methylsalicylaldehyde (0.272 g). Yellow colour solution was obtained; it was irradiated in microwave at 5 min, 320W. The reaction mixture was cooled at room temperature. Yellow precipitate was formed; it was filtered and washed with distilled water. The crude product was recrystallized by the hot 80% ethanol. The systematic synthesis procedure was given in scheme-1.



SCHEME-1: SYNTHESIS OF SCHIFF BASE

III. RESULT AND DISCUSSION

A. FT-IR analysis

The FT-IR spectrum of the Schiff base was shown a peak in the range of 3500 cm^{-1} due to the presence of phenolic hydroxyl group. A peak at 2934 cm^{-1} shows that internal hydrogen bond in the Schiff base ($\text{OH}\cdots\text{N}$). The formation of Schiff base was confirmed by a peak at 1639 cm^{-1} . The phenyl ring carbon ($\text{C}=\text{C}$) exhibit a peak at 1491 cm^{-1} . A peak in the range of 1578 cm^{-1} reveals the presence of amine group (N-H), it further confirmed by the peak at 1337 cm^{-1} due to existence of (C-N). The IR spectrum shows that Schiff base formed in the reaction, since the carbonyl peak was not appear at the same time it exhibit the imine functional group at 1639 cm^{-1} ($\text{C}=\text{N}$) [6,7]. The FT – IR spectrum was shown in Fig-1 (A).

B. Electronic Spectrum

UV-Visible spectrum of the ligand was recorded in the region of $200 - 800\text{ nm}$, using methanol solvent. A sharp absorbance band at 220 nm is reveals that existence of phenyl ring with substitution. The band at 256 nm shows that transition of electrons from nonbonding level to π anting bonding ($n \rightarrow \pi^*$). In the absorbance spectra another band exhibit at 323 nm mainly give the π bonding electron transfer to π antibonding state ($\pi \rightarrow \pi^*$). These three transitions are appeared in the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ [8]. The electronic spectrum was given in Fig-1 (B). Due to the presence of conjunction the transition bands are shifted in Bathochromic shift in Schiff base.

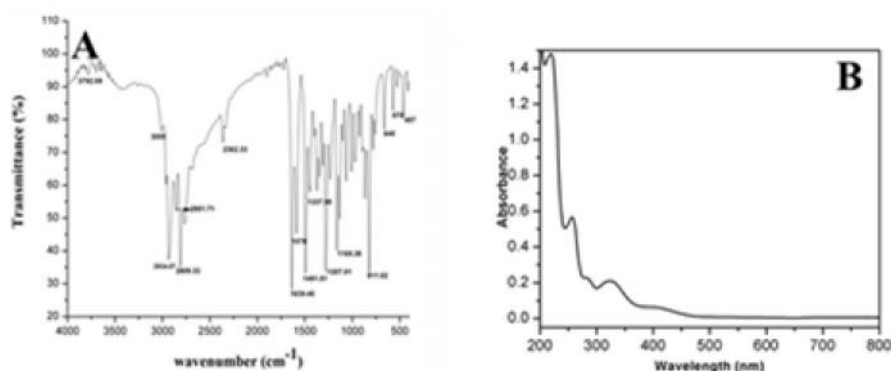


Fig. 1: (a) FT-IR spectrum and (b) Electronic spectrum of Schiff base.

C. NMR Spectrum

The H^1 and C^{13} NMR spectra were recorded in the $CDCl_3$, TMS as the internal standard. The NMR spectra of the Schiff base was given in Fig-2. H^1 NMR spectrum give the nature of protons which is present in the Schiff base. The shifts are appeared in down field region when compared with the reference. At 13.27 ppm a small peak was obtain due to presence of phenolic proton in Schiff base. The aromatic ring protons are appeared in the range of 6.85 – 7.27 ppm. In amine group protons are gives the peak at 8.3 ppm. Multiple peaks exhibit in the range of 2.28 -2.47 ppm due to the presence of alkyl protons. The C^{13} NMR give the various nature carbon atoms present in the Schiff base. In the C^{13} NMR spectra aromatic phenyl ring carbons were give the signals in the range of 116 – 132 ppm. The imine group carbon shows a peak at 164 ppm. The substituted methyl group in the phenyl ring exhibit a peak at 20 ppm. The ethylene group carbon present in amine shows peak at 47 and 57 ppm. The appearance of signals in various region due to the different electronic nature in the ligand [9].

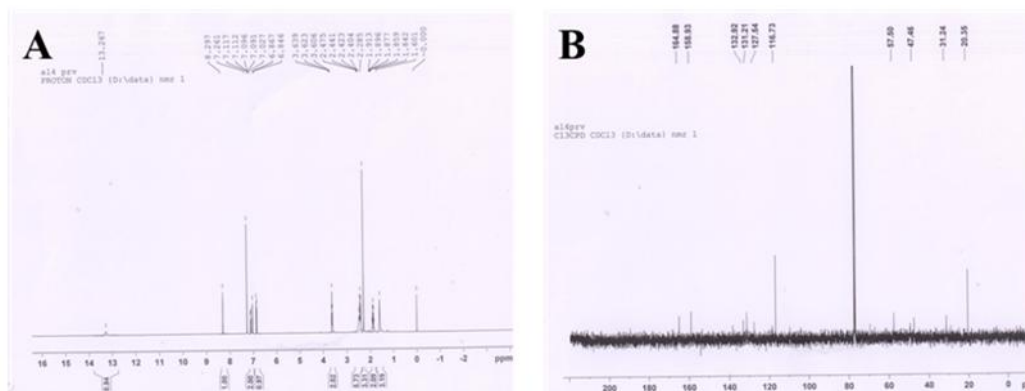


Fig. 2: (a) H^1 NMR and (b) C^{13} NMR spectrum of the Schiff base

D. Electrochemical polymerization of Schiff base

The redox behavior of the Schiff base was examined by the cyclic voltammetry, at 0.1 mmol of Schiff base solution in acetonitrile. 0.1 M of TBAP (Tetrabutylammonium perchlorate) was used as supporting electrolyte. We used Ag/AgCl as reference electrode and GCE was the working electrode. The cyclic voltammogram was shown in Fig – 3. To determine the hydroquinone working electrode was modified by electropolymerization. In this method the Schiff base was polymerized on the surface of GCE.

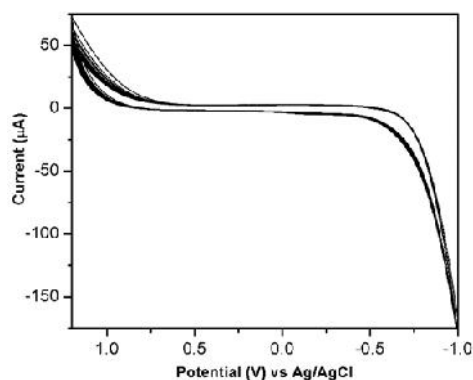


Fig. 3: Electrochemical polymerization of Schiff base

E. Electrocatalytic sensing of hydroquinone

Fig – 4 displays the electrocatalytic sensing ability of bare GCE and modified GCE. Electrocatalytic sensing ability of the polymerized Schiff base (P-SB) modified GCE was investigated by using cyclic voltammetry (CV) and Differential pulse voltammetry (DPV). The figure shows well define redox peak at 0.1814 mV and -0.0031 mV gives oxidation and reduction respectively for bare GCE, polymerized Schiff base modified GCE exhibit the oxidation and reduction peaks at 0.2603 mV and 0.113 mV respectively. In both the cases the sensing occur irreversible redox process and potential shifted positively. The modified GCE has good conduct with the analyte to form hydrogen bond, hence it gives two fold higher current response when compare with the bare GCE. From above results it is clear that the Schiff base modified GCE is a good electrocatalytic sensor for sense the hydroquinone [10].

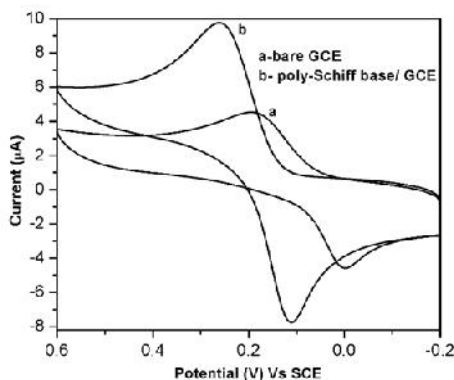


Fig-4: CV of bare and modified GCE in presence of 1 mM HQ at the scan rate of 50 mVs⁻¹

F. Determination of Hydroquinone

Fig – 5 shows the determination of hydroquinone in the modified GCE using DPV, it generally has high sensitivity and selectivity. The oxidation peak current increase linearly with addition of 5 µL HQ. Each addition of 1 mM HQ leads to increase the current, we obtained linear relationship between peak current and HQ concentration in the range of 5µL to 35 µL. The linear plot between concentration and current gives a straight line with the slope of 0.1514. It shows that the redox reaction in the electrocatalytic sensing of HQ is a diffusion controlled process [11]. The straight line equation is $I \mu A = 0.1514 CHQ + 4.9624$ with the regression coefficient of (R²) 0.996. The possible electrocatalytic reaction and the calibration plot were given in Fig- 6.

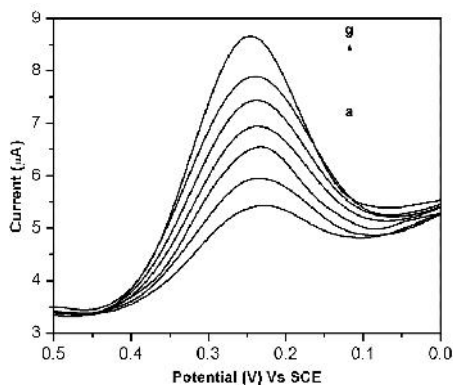


Fig. 5: DPV response of modified GCE in the presence of HQ at 5 µL to 35µL

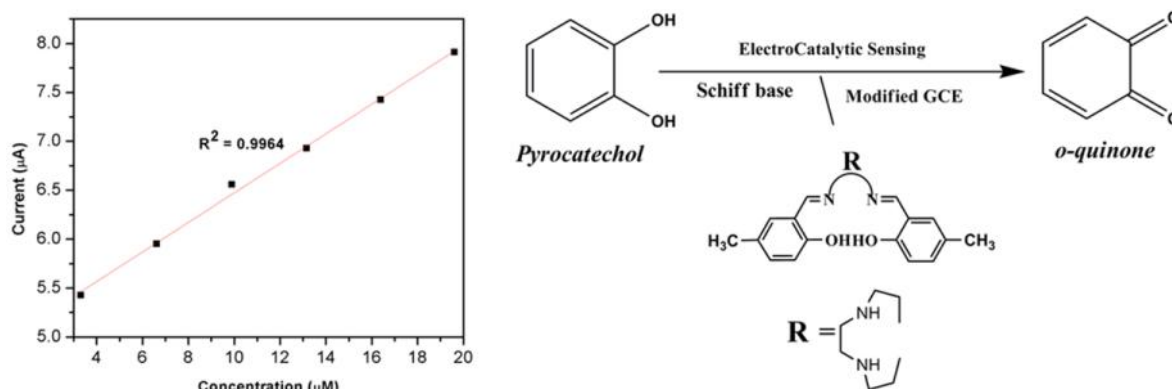


Fig. 6: Plot of scan rate vs current and graphical representation of electrocatalytic reaction

IV. CONCLUSION

In this work gives a new route for the Synthesis of Schiff base ligand and characterized by FT-IR, UV-Vis. and NMR spectral techniques. Schiff base was electrochemically polymerized and used for the electrocatalytic sensor. The results are demonstrated that Schiff base was successfully used for the detection of hydroquinone. It is more efficient electrode material towards the hydroquinone detection with better electrocatalytic activity and higher sensitivity

V. REFERENCES

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