

# Synthesis, Characterization of Nickel Schiff Base Complex and its Electrocatalytic Sensing Nature for $\text{Hg}^{+2}$

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**ABSTRACT:** The Schiff base metal complexes have wide range of applications in the microbial studies, but there is a recent trend that these Schiff base metal complexes are employed as an electrocatalytic sensor. The electrochemical detection is one of the most selective and sensitive method. When compared with other detection methods this method has short time duration, cost effective, low detection limits and easy to handle. The Nickel Schiff base complex shows better electrochemical redox behaviour, it transfers the electron to heavy toxic metal ions for its redox process. This can be utilized for the sensing of heavy metal ions in electrochemical method. Heavy metal ions are harmful to the living organisms, and toxic to the human health. The heavy metal contamination in the environment causes severe pollution to the ecological systems. Hence, there is a necessity to develop a simple, sensitive and accurate method for the determination of heavy metal ions in the environment. In this work  $\text{Hg}^{+2}$  ion was determined by the nickel Schiff base complex modified GCE. The modified GCE was electrochemically characterized by cyclic voltammetry and linear sweep voltammetry. This result indicates that the nickel complex modified GCE showed a good linear response within the ranges of 16.7 – 166.4  $\mu\text{M}$  and the detection limits were 0.054 nM for  $\text{Hg}^{+2}$ .

**KEYWORDS:** Nickel Schiff base complex, mercuric ion ( $\text{Hg}^{+2}$ ), electrochemical sensor, electropolymerization.

## I. INTRODUCTION

The heavy metal ions like mercury, cadmium, lead, arsenic etc., are non-degradable and they are toxic to the soft tissues. These heavy metal ions are considered as the serious source to environment pollution in the world. Even a trace amount of the heavy metal ions can cause several diseases in the human [1]. However some heavy metal ions are necessary for the metabolism maintenance, they are cobalt, copper, iron, manganese and zinc. These heavy metal ions are essential in trace amount, at the same time if it present in excessive level in the living organism may be very toxic and cause serious health disorder. Heavy metal ions may damage the liver, kidney, bones, teeth, skin and central nervous system in human body [2-4].

The sources for heavy metals to the environment are from chemical, agriculture, painting, coating, extractive metallurgy, nuclear, tanning and mining industry. These rely on the heavy metal ions to the water source and terrestrial systems. Then it can be further transferred to the living organisms. Due to this factor there is a necessity, to develop a selective and sensitive method for the determination of trace heavy metals both in environment and living organisms.

There are several methods for the detection of heavy metal ions, UV – Vis, IR and Raman spectroscopy [5], HPLC [6], titration [7], and colorimetric analysis [8]. These methods require expensive instruments, more time to carry out the experiment and some complex operational procedures. Due to this factor, there is research going on to develop a low

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cost, rapid and friendly operational technique for the determination of trace heavy metal ions. Electrochemical methods [9], when compared to optical techniques overcome all the disadvantages. It is most cost effective, very fast detection, simple and friendly procedure, more selectivity and high sensitivity. The voltammetric and potentiometric techniques are commonly reported for heavy metals detection. In the electrochemical detection method nickel Schiff base complex was employed for the modification of electrode surface.

Schiff base ligands and their Metal complexes have wide range of applications in antibacterial and anticancer agents. These complex can be a very good homogeneous heterogeneous catalysts, it also play an important role in agriculture, pharmaceutical and industrial chemistry [10]. Schiff bases ligands is one of the most widely utilized classes of organic moiety for metal coordination chemistry [11]. Schiff base ligands are more capable to coordinate with metal ions through azomethine group and phenolic groups. It can easily formed stable metal complex due to strong metal binding ability therefore Schiff base ligands are mostly used for metal complex synthesis. The nickel(II) Schiff base complexes shows better catalytic activity among the all other transition metal complexes [12].

The nickel(II) complex was synthesized by microwave irradiation method. In this method the reaction occur very fast and high yield. The nickel(II) complex synthesized from the template synthesis of salicylaldehyde, 2-chloroaniline and nickel chloride. Nickel(II) shows better electrochemical redox behaviour this can be a better electrochemical sensor for the heavy metal ion sensing. Electropolymerization of Schiff base metal complexes shows good electro redox nature, it is an efficient method for the modification of electrode surface. The 0.1 M nickel Schiff base complex was taken as monomer in acetonitrile and 0.1 M tetrabutylammonium perchlorate (TBAP) was taken as supporting electrolyte for the electrode surface modification [13]. The modified electrode was utilized for the detection of heavy metal ions. This electrode shows a better result as an electrochemical sensor for mercury ( $\text{Hg}^{+2}$ ).

## II. EXPERIMENTAL

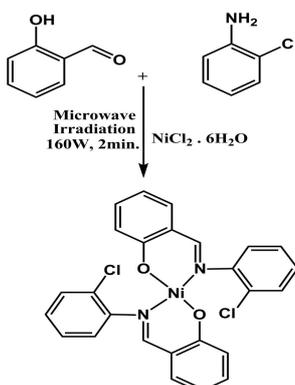
### 2.1 Reagents

Salicylaldehyde, o-chloroaniline, and nickel chloride was purchased from Alfa Aesar, mercury(II)chloride, and solvents were purchased from Qualigens. TBAP, used as supporting electrolyte in electrochemical measurements, was purchased from Fluka and recrystallized from hot methanol. Other solvents were purchased from Qualigens and used without further purification.

### 2.2 Synthesis of Nickel Schiff base complex with o-chloroaniline

The nickel Schiff base complex was prepared by using microwave irradiation method, an absolute methanolic solution of 1 mM nickel chloride was added with the stirred methanolic solution of 1 mM salicylaldehyde by drop wise, after the complete addition of metal salt the o-chloroaniline 1 mM solution in methanol was added with the reaction mixture, the stirring was continued about 30 min after the complete addition of o-chloroaniline.

The reaction mixture was allowed to microwave irradiation at 160 W for 2 min pale yellow colour solution was obtained. It was cooled to room temperature about 12 hrs. Pale yellow colour precipitation was obtained it was collected and recrystallized by hot ethanol solution [14]. The reaction was shown in the Schme-1.



Scheme-1: Synthesis of nickel Schiff base complex

Orange colour precipitate. Yield: 0.657 g, 88.9 %. m.p.: 202 °C. Molecular formula  $C_{26}H_{18}Cl_2N_2NiO_2$ ; Elemental Analysis Calcd (%): C = 60.05; H = 3.49; N = 5.39; Cl = 13.63; Ni = 11.29. Exp (%): C = 60.10; H = 3.55; N = 5.25; Cl = 13.55; Ni = 11.25. The molecular weight of the complex is  $520.03 \text{ gmol}^{-1}$ , Selected IR data (KBr) ( $\nu, \text{cm}^{-1}$ ): 3430  $\nu(\text{OH})$ , 2326  $\nu(\text{C-H})$ , 1633  $\nu(\text{C=N})$ , 1385  $\nu(\text{C-N})$ , 1119  $\nu(\text{C-N})$ , 1060  $\nu(\text{C-O})$ . UV-Vis spectrum in methanol: 478nm, 329nm, 278nm.  $\mu_{\text{eff}}(298 \text{ K})$ : 2.828 BM.

### III. RESULT AND DISCUSSION

#### 3.1 FT-IR Analysis

The FT-IR spectrum of Nickel(II) Schiff base complex was recorded in the KBr pellet at the range of  $4000\text{-}400 \text{ cm}^{-1}$ . In the spectrum a broad absorption band appeared at  $3400 \text{ cm}^{-1}$  due to the presence intramolecular hydrogen bond arising from the presence of hydroxyl groups in their molecular structures. Absorption band observed at  $1633 \text{ cm}^{-1}$  are attributed to  $\text{C=N}$  stretching vibrations in the complex, which indicates that the nitrogen atom of the azomethine group is coordinated to the metal ion [15]. In addition, the bands in the region of  $581 \text{ cm}^{-1}$  and  $490 \text{ cm}^{-1}$  confirm the nature of the metal-ligand bonding; these bands are assigned to  $\text{Ni(II)-N}$  and  $\text{Ni(II)-O}$  vibrations, respectively [16]. In the IR region from  $1100$  to  $1200 \text{ cm}^{-1}$  a band exhibit due to the presence of  $\text{C-O}$  bond. The typical FT-IR spectrum was shown in Fig.1.

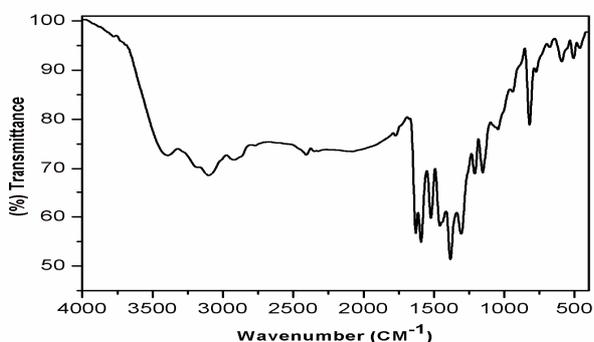


Fig. 1: FT-IR Spectrum of Nickel(II) Schiff base complex.

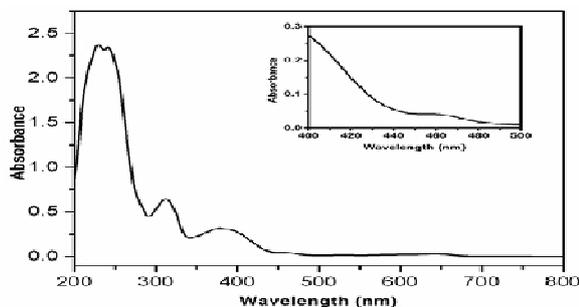


Fig. 2: Absorption Spectrum of Nickel(II) Schiff base complex.

#### 3.2 Electronic spectra

The electronic spectra of the Nickel Schiff base complexes were investigated in methanol solution at room temperature (298 k) in region of 200-800 nm. The Nickel Schiff base complex exhibits three absorption peaks. A peak

at 210 nm is due to the  $\pi \rightarrow \pi^*$  transition of C=C in benzene ring. The absorption spectra of the nickel complex show a band at 315 nm attributed to the  $n \rightarrow \pi^*$  transition of the azomethine group. The bands are observed in the regions at 390 and 485 nm due to d-d transition in nickel metal ion [17]. The absorption spectra of nickel complexes were shown in Fig. 2.

### 3.3 EPR analysis

The EPR spectrum of nickel Schiff base complex was recorded at room temperature in methanol solution. The spectrum for nickel complex shows a single line at a field close to that for a free electron. It explains that the electron present in the complex is delocalized over the whole ligand, it not fixed on nickel ion. The nickel Schiff base complex exhibits six coordination along with two solvent molecules. The solvent molecule binds with metal ion in axial position  $[\text{Ni}(\text{L})(\text{solvent})_2]$ , and with the metal center in a  $^3A_{2g}$  ground state. The EPR spectra exhibit rhombic symmetry and g tensor anisotropy, the g values are 2.238 with  $g_{\text{iso}}$  is 2 [18-20]. The EPR spectrum was shown in Fig. 3.

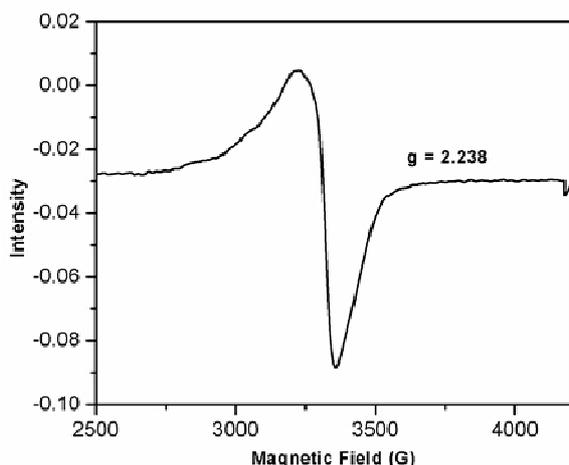


Fig. 3: EPR Spectrum of Nickel(II) Schiff base complex.

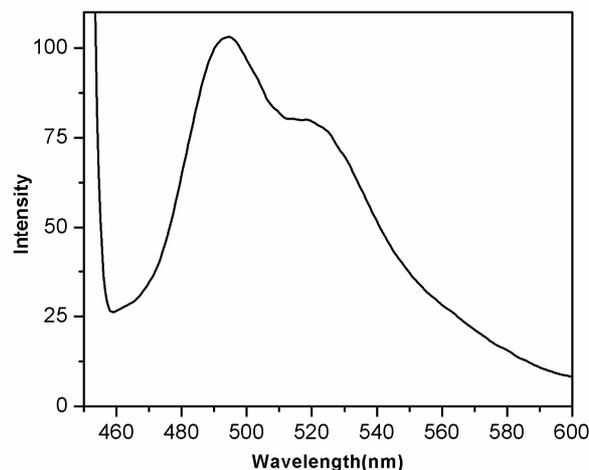


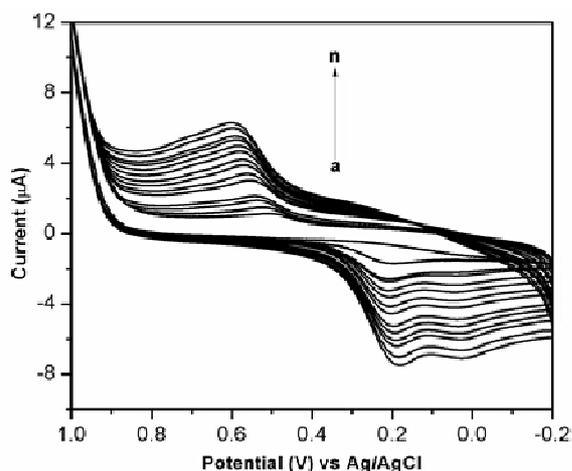
Fig. 4: Emission Spectrum of Nickel(II) Schiff base Complex.

### 3.4 Fluorescence spectral studies

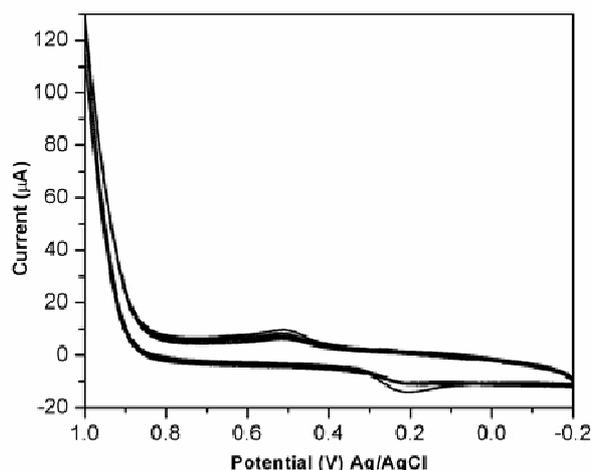
The fluorescence spectrum of the Schiff base nickel complex was investigated at room temperature (298 K) in methanol solution. This complex showed a broad emission bands indicating charge transfer nature of the transitions. The Nickel(II) Complex on excitation at 400 nm shows emissions at 520 nm. The nickel ion coordinate with two Schiff base ligands, emission appeared due to the intramolecular  $\pi \rightarrow \pi^*$  electron transition. In the emission spectrum Ni(II) complexes showed higher emission intensity than its corresponding Schiff base ligands due to coordination of metal with ligands [21, 22]. The fluorescence spectrum for the complex is shown in Fig. 4.

### 3.5 Electrochemical studies of Nickel complexes

The electrochemical property of Ni(II) Schiff base complexes have been studied in Acetonitrile in the presence of 0.1 M tetrabutylammonium perchlorate over the potential range from -0.6 to 1.0 V (vs. Ag/AgCl) using cyclic voltammetry (CV) technique, with different scan rates from  $50 \text{ mVs}^{-1}$  to  $400 \text{ mVs}^{-1}$ . The Ni(II) complex exhibits one irreversible redox peak, which are assigned to consecutive Ni(II)/Ni(III) and Ni(III)/Ni(II) redox processes [23]. The redox potential of nickel complexes are  $E_{\text{pa}} = 0.519 \text{ V}$ ,  $E_{\text{pc}} = 0.205 \text{ V}$ . The potential difference between the anodic and cathodic process is ( $\Delta E_{\text{p}}$ ) is 314 mV it shows that it completely irreversible process. The cyclic voltammogram was shown in Fig. 5. This same condition was employed for the electropolymerization of nickel Schiff base complex at 5 cycles for the modification of glassy carbon electrode (GCE) to sense the heavy metal ions. The electropolymerization is also shown in Fig. 6. This modified electrode was utilized for the sensing of  $\text{Hg}^{+2}$ .



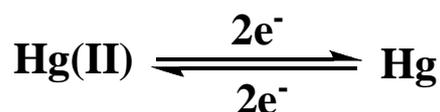
**Fig. 5:** Cyclic voltammogram of nickel Schiff complex in 0.1 M TEAP, between -0.6 and 1.0 V at different scan rates: (a) 50, (b) 75, (c) 100, (d) 125, (e) 150, (f) 175, (g) 200, (h) 225, (i) 250, (j) 275, (k) 300, (l) 325, (m) 350, (n) 375, (o) 400 mVs<sup>-1</sup>.



**Fig. 6:** Cyclic voltammogram of nickel Schiff complex in 0.1 mol L<sup>-1</sup> TEAP, between -0.2 and 1.0 V at scan rate of 50 mVs<sup>-1</sup>.

### 3.6 Electrochemical detection of Mercury ions

As mentioned above, the high conductive electropolymerized nickel Schiff base complex modified glassy carbon electrode (p-NiSBC/GCE) was used for the electrochemical determination of mercury metal ions. To enhance the sensing performance, p-NiSBC/GCE was in-situ formed on the surface of functionalized electrode. Ni, is an important biological metal ion, which is present in the many co-enzymes. The modified electrode shows well-defined, single and sharp redox peaks for mercury ion. When the results are compared between bare electrode and the modified electrode, this modified electrode shows better result than bare GCE it was shown in **Fig. 7**. This Figure shows a repetitive cyclic voltammogram of mercury(II) solution in the potential range -0.5 to 0.4 V versus SCE, and two peaks were observed. However, the cathodic peak, at about 0.08 V is assigned to the reduction of mercury(II) accumulated in the p-NiSBC/GCE. The anodic wave peak at 0.199 V is a well defined sharp peak, this is due to oxidation of the mercury metal. In the electrochemical sensing process the electrode redox reaction is irreversible. Peak current in the both process was higher than that of GCE. Since the anodic peak is sharp and is having larger current response it is utilized for the determination of mercury [24, 25]. The electrochemical redox reaction on the modified electrode surface was shown in the scheme-2.



**Scheme-2:** Electrochemical redox reaction of mercury.

### 3.7 Effect of Scan Rate

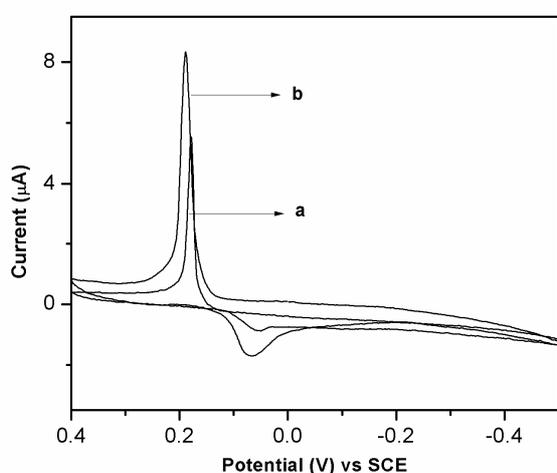
**Fig. 8** illustrate the influence of the potential scan rate V on the cyclic voltammograms of p-NiSBC/GCE modified electrode in 5 nM mercury ion solution (at 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375 and 400 mVs<sup>-1</sup>) in 0.1 M phosphate buffer pH 7. It shows that the increasing scan rate will leads to increase in the current also the oxidation and reduction potential was shifted. The oxidation potential moved positively and the reduction potential moved negatively. From the results there be a linear relation between the scan rate vs its

corresponding current. It was explain in the logarithmic plot of scan rate and current which is shown in **Fig.9**. The linear equations are given in below with their regression coefficient,

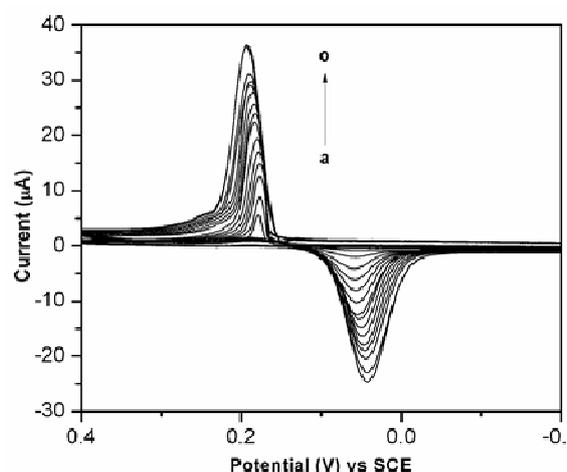
$$i_{pa}(\mu A) = 0.5579 \log(v) \text{ mVs}^{-1} + 0.0183, (R^2 = 0.9967),$$

$$i_{pc}(\mu A) = -0.6041 \log(v) \text{ mVs}^{-1} + 0.1511, (R^2 = 0.9979),$$

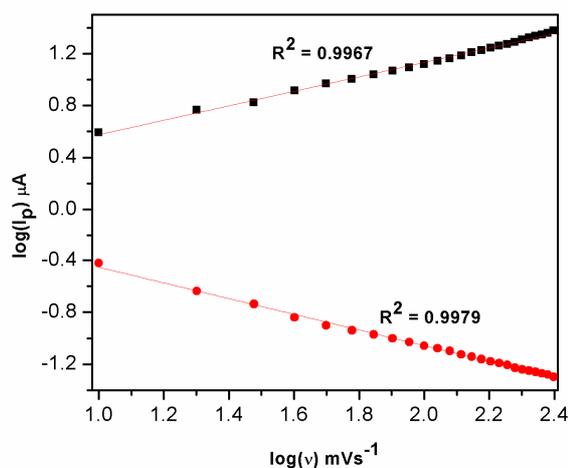
From this linear relation slope we conclude that the electrochemical sensing process of mercury ion is adsorption controlled process.



**Fig. 7:** Cyclic voltammogram responses of nickel Schiff complex modified GCE in 5 nM  $\text{Hg}^{+2}$  solution presence of PBS buffer (pH = 7) at scan rate of  $50 \text{ mVs}^{-1}$ .



**Fig. 8:** Cyclic voltammogram responses of nickel Schiff complex modified GCE in 5 nM  $\text{Hg}^{+2}$  solution presence of PBS buffer (pH = 7) at different scan rates a) 50, (b) 75, (c) 100, (d) 125, .....(o)  $400 \text{ mVs}^{-1}$ .

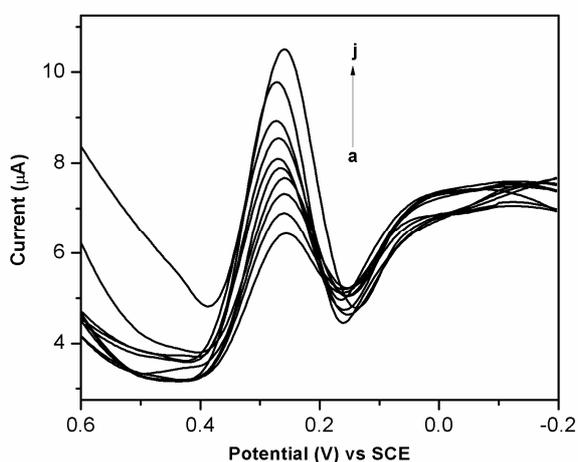


**Fig. 9:** Logarithmic Plot of scan rate vs current

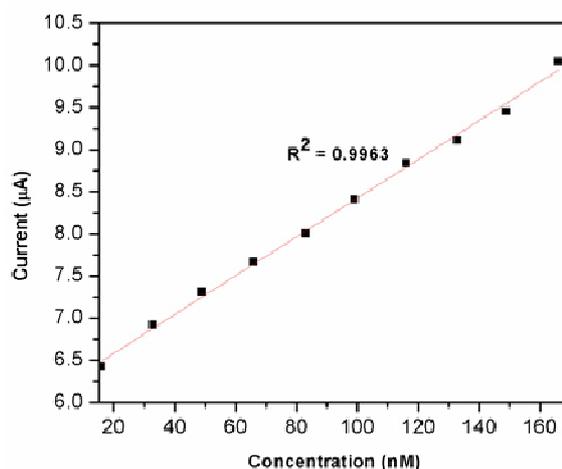
### 3.8 Determination of mercury ion

The differential pulse voltammetry (DPV) usually gives higher analytical sensitivity, but most of the detection of heavy metal ions were performed using square wave voltammetry, but in this present work we utilized one of best sensitive

method DPV for mercury ion sensing. To obtain better resolution and sensitivity, DPV method allows for an enhanced analytical signal by eliminating the non-Faradaic current and permitting a better resolution compared to other techniques. The DPV responses of the mercury ion, with increases in the concentration will leads to increase in current response at the modified electrode. This result indicates that the nickel Schiff base complex modified GCE showed a electrochemical sensing response for the determination of mercury ion. A good linear response within the ranges of 16.7 – 166.4  $\mu\text{M}$  was exhibit in the derivative plot between the concentration of mercury ion and it corresponding current response. The detection limits was also calculate using (3S/N) relationship, the limit of detection for mercury ion sensing is 0.054 nM. **Fig. 10** and **Fig. 11** shows the DPV response of the p-NiSBC/GCE electrode for different concentration of mercury ion, and their derivative plot of concentration vs current. Due to the better response the detection of mercury ions using the nickel Schiff base complex modified GCE is feasible [26].



**Fig. 10:** DPV responses of nickel Schiff complex modified GCE in different concentration of  $\text{Hg}^{+2}$  solution presence of PBS buffer (pH = 7).  
(a) 1 nm to (j) 10 nm.



**Fig. 11:** DPV derivative plot of different concentration vs current

#### IV. CONCLUSION

In this present work we synthesized nickel Schiff base complex using microwave irradiation method. The synthesized complex was characterized by the following spectral techniques, FT-IR, UV-Vis, Photoluminescence and EPR. The electrochemical redox property also tested using cyclic voltammetry. The nickel Schiff base complex was electrochemically polymerized on the GCE surface and the modified electrode was successfully used for the detection of mercury metal ion. The modified electrode shows a better result than bare GCE.

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