Full Paper

Sensitive and Selective Analysis of Nigrosine Dye at Polymer Modified Electrochemical Sensor

Chenthattil Raril and Jamballi G. Manjunatha[*]

Department of Chemistry, FMKMC College, Madikeri, Mangalore University Constituent College, Karnataka, India

*Corresponding Author, Tel.: +91-08272228334

E-Mail: manju1853@gmail.com

Abstract- Glycine was used to fabricate a modified electrode, as a highly sensitive voltammeric sensor and was used for the determination of Nigrosine (NG) in 0.2 M phosphate buffer solution (PBS) having pH 6.0. A fast and easy method for the fabrication of polyglycine modified carbon paste electrode (PGMCPE) by cyclic voltammetry was used. The resulted modified electrode shows superior electrocatalytic activity towards the oxidation of NG compare with (BCPE) in 0.2 M PBS at 6.0 pH. The electrode surfaces were characterized by Field emission scanning electron microscopy (FESEM). The effect of various experimental parametrers on the voltammetric response of NG were investigated. At optimum conditions, the sensor has a linear response in the concentration range of 3×10^{-5} to 5×10^{-5} M and 6×10^{-5} to 1×10^{-4} M with the limit of detection 8×10^{-8} M and limit of quantification 2.6×10^{-7} M. The modified electrode demonstrated having many advantages such as simple preparation, high sensitivity, and low detection of limit, excellent catalytic activity, and reproducibility.

Keywords- Nigrosine, Carbon paste electrode, Electropolymerization, Cyclic voltammetry

1. INTRODUCTION

Nigrosine (NG) is a widely used colorant for lacquers and varnishes and in marker-pen inks. It is a mixture of synthetic black dyes [1-4]. Small amount of nigrosine are used for negative staining of bacteria, as well as capsule containing fungus Cryptococcus neoformans [5]. The variety of physical chemistry properties of each class of dyes and introduction of

several other chemicals during the dyeing process, such as dispersing agent, salt and many other organic compounds, make the available analytical methods usually inefficient, costly and not adaptable on its determination in a wide range of dye concentration. Due to the increasingly rigorous environmental legislation, it is important to develop an effective, rapid and reliable method for evaluating unfixed dyes with sufficient detectability.

The development of voltammetric sensors [6-15] for the determination of electro active species has received significant attention throughout the previous couple of years. In recent year polymer modified electrodes [16-17] have obtained important attention among the researchers for sensor applications. For the preparation of polymer modified electrodes electropolymerization is the good method by adjusting electrochemical parameters, can control film thickness, stability, permeation, strong adherence to the electrode surface, charge transfer characteristics.

Electrochemical techniques [18] are a powerful and versatile analytical technique that offers high sensitivity, accuracy, and relatively low cost instrumentation and are more used by most of the scientists, chemists and chemical engineers to study the dynamics and reaction. Among the electrochemical method cyclic voltammetry (CV) [19] is used widely used method in many area of electro analytical chemistry for accuring qualitative information about electrochemical reactions. Power of CV is its ability to provide information on the thermodynamics redox processes, absorption processes and kinetics of heterogeneous electron transfer reactions with low cost, simple and fast way of analyzing the biologically active molecule. CV is often the first experiment performed in an electrochemical study which measures the resulting current (Anodic and Cathodic peak current) when a potential is applied at working electrode in both forward and reverse direction.

In this research we fabricate stable electrode by electropolymerizing glycine on the surface of carbon paste electrode for determining the NG. Along the determination of nigrosine we extended our work for simultaneous for determination of Tartazine (TR) along with NG by differential pulse voltammetric (DPV) method. No study has reported the determination of NG using Poly (Glycine) modified carbon paste electrode.

2. EXPERIMENTAL

2.1. Apparatus

All the voltammetric measurement was carried out in a 50 ml electrochemical cell at RT in a three electrode configuration. BCPE or PGMCPE was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as a reference electrode. All experiment carried out room temperature (25 °C). Cyclic voltammetric measurements were performed with a model EA-201 Electro Analyzer (Chemilink System, India) connected to a personal computer for control and data storage.

2.2. Reagents and solutions

Nigrosine purchased from Himedia Laboratories Pvt. Ltd. Mumbai, Silicone oil, Glycine, Monosodium phosphate, Disodium phosphate, Graphite (150 mesh) and Tartazine were obtained from Nice chemicals, Cochin, India. Phosphate buffer solution was prepared by mixing the suitable amount of 0.2 M monosodium phosphate and 0.2 M disodium phosphate. Freshly prepared solutions of nigrosine used in the experiment. Stock solution of nigrosine 25×10^{-4} M was prepared in 2 N H_2SO_4, stock solution of Glycine was prepared (25×10^{-3} M) in double distilled water and a stock solution of Tartazine 25×10^{-4} was prepared in double distilled water.

2.3. Fabrication of PGMCPE

First, the BCPE was prepared by hand mixing graphite powder 70% and silicone oil 30% in an agate mortar to get a homogeneous paste. Next the paste is packed in the end of a teflon tube (3 mm in diameter.) A copper wire is inserted into the carbon paste provided an electrical contact. Polymer film modified electrode was fabricated by electro polymerization of glycine by cyclic voltammetry in the potential range 500 to 1800 mV (Fig. 2) at a sweep rate of 100 mV/s in phosphate buffer (pH 5.7). The monomer concentration was 1 mM. After the 10 cycle the surface of the electrode was washed with distilled water. The modified electrode was immersed in PBS (pH 6) and the electrochemical studies were carried out.
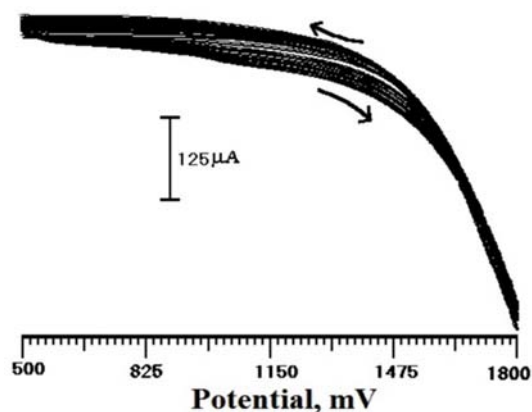

Fig. 2. Cyclic voltammogram for the electrochemical polymerization of 1×10^{-3} M glycine on a carbon paste electrode (CPE) in 0.2 M PBS (5.7 pH) at the scan rate 100 mV/s

3. RESULT AND DISCUSSION

3.1. Characterization of BCPE and PGMCPE

Fig. 3 explains the surface morphology of BCPE and PGMCPE using Field Emission Scanning Electron Microscope. Surface of BCPE (Fig. 3a) was irregularly shaped. However,

the PGMCPE (Fig. 3b) is more compact and uniform because of covering of thin film of poly (glycine) on the CPE. FESEM of PGMCPE clearly shows that poly (glycine) is uniformly attached on the electrode surface.
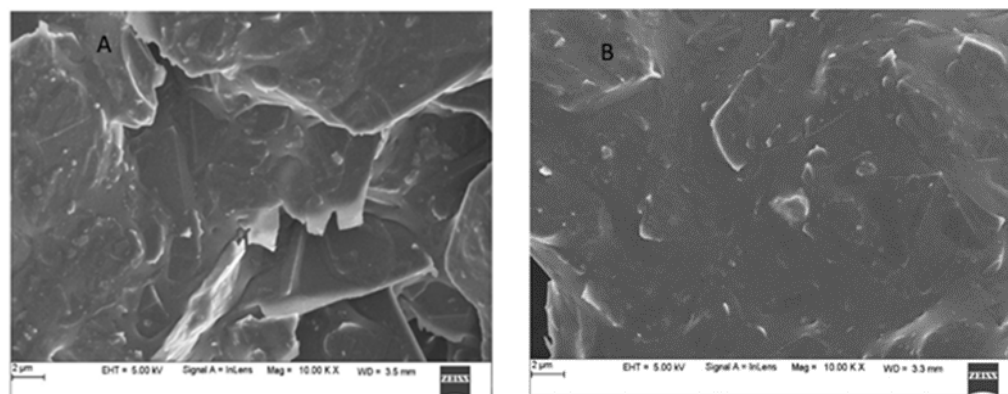

Fig. 3. FESEM image of BCPE (A) PGMCPE (B)

3.2. Optimization of experimental parameters

The better conductive film could be formed when potential scan window was from 500 to 1800 mV. It has been observed that oxidation current increases as the cycle were raised up to 10 cycles and decreases after 10 cycles (Data not shown), because of increase in the thickness of polymeric film resulted in the obstruction of the electron transfer on the electrode surface. There for 10 electropolymerization cycle were selected for this work.

3.3. Repeatability and stability of the modified electrode

Stability and reproducibility are the powerful features decide the fate of the sensors. Repeatability has studied for 10 consecutive determination of 1×10^{-4} M NG in 0.2 M PBS buffer solution (pH 6.0), relative standard deviation (RSD) was observed to 0.97%. Electrode shows a good stability and was measured by current response of PGMCPE by storing in open air for 24 h. The oxidation peak current of NG were reduced to less than 4%.

3.4. Electrochemical behavior of NG

Fig. 4 shows the CV of NG at PGMCPE with PBS at pH 6 within the potential window from -75 to 700 mV. There is no observable peak for PGMCPE (solid line). A well-defined peak appears at 322 mV (dashed line), upon addition of 1×10^{-4} mol/L of NG. Above results shows that the PGMCPE, which increase the electro catalytic activity of nigrosine oxidation. Above results shows that the PGMCPE, which increase the electroactive surface area of the

electrode, increase the electro catalytic activity for nigrosine oxidation and the electrode response was proportional to the oxidation of electroactive species produced.
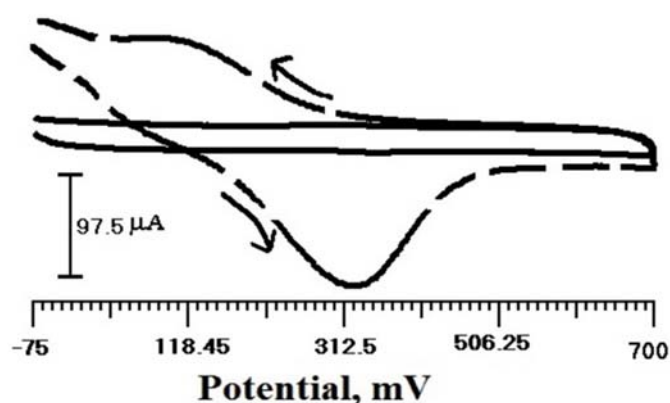

Fig. 4. Cyclic voltammogram of PGMCPE with NG (1×10^{-4} M) (dashed line) and without NG (solid line) in 0.2 MPBS, pH 6.0 without 1×10^{-4} M NG (dotted line) at pH 6, 0.2 M PBS

3.5. Electrochemical behavior of NG at PGMCPE

Fig. 5 shows the cyclic voltammogram of nigrosine in pH 6.0 PBS at BCPE (solid line) and PGMCPE (dashed line). The PGMCPE shows a better sensitivity in comparison to the BCPE. There is no peak was observed for BCPE, under the identical conditions, the PGMCPE gives a peak current to NG, a well-defined peak observed with the peak potential of 322 mV. Increase in peak current is also observed at PGMCPE this suggests an efficient oxidation reaction of NG at PGMCPE.
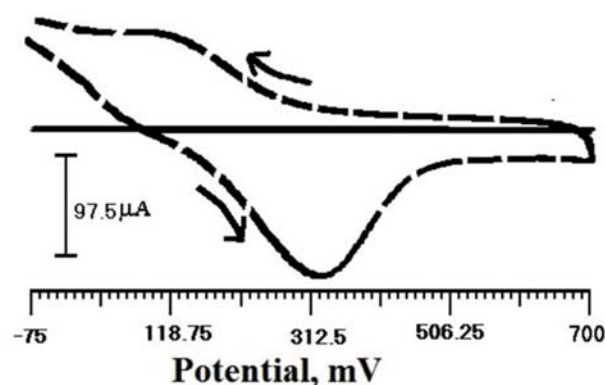

Fig. 5. Cyclic voltammogram of NG (1×10^{-4} M) in 0.2 M PBS buffer solution of pH 6.0 at BCPE (solid line) and PGMCPE (dashed line)

3.6. Effect of scan rate of NG

The effect of scan rate on the electrochemical response of 1×10^{-4} mol/L NG was investigated 100-200 mV/s at PGMCPE in 0.2 M PBS (pH 6.0) and the result were shown n Fig. 6a. It can be seen that the increase of the scan rate the oxidation peak potential is shifted to more positive potential, confirming that the electron transfer slowed down in the film because polymer film got thicker with the increase of scan rate. Also there is a linear relationship between oxidation peak current (I_{pa}) and scan rate over the range of 100-200 mV/s for NG which indicates electron transfer reaction of NG on PGMCPE was adsorption controlled process in the solution. A linear relationship between the peak current and scan rate was established and were got a straight line with a linear regression equation as I_{pa} (μA)=29.56 +1.23 v (mVs^{-1}) with a correlation coefficient R=0.99053 (Fig. 6b).
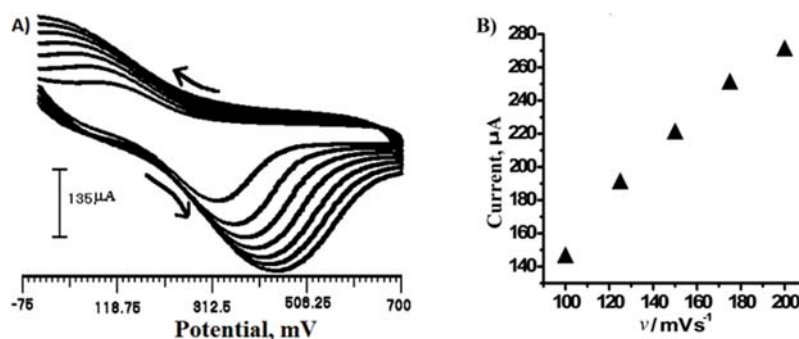

Fig. 6. (A) Cyclic voltammogram of NG (1×10^{-4} M) at PGMCPE in pH 6.0 at various scan rates. From 100, 125, 150, 175, 200 mV/s; (B) Plot of peak current of NG as a function of scan rate

3.7. Effect of pH of NG solution

The solution pH is another factor that affects the electrochemical reaction of NG. Fig. 7a shows the effect of pH on the current response of NG on PGMCPE. As seen, the oxidation peak potential of NG shifted towards negatively values with increase in pH from 6.0-8 in PBS (0.2 M), showing that proton takes part in their electrode reactions. The anodic peak potential of NG shifted from 322 mV to 232 mV with respect to the pH from 6.0 to 8.0. The potential diagram was constructed by plotting E_{pa} Vs pH of the solution (Fig. 7b). The linear regression equation for the anodic peak given by E_{pa}=587.4-44.2 pH with a correlation coefficient R=0.99695 and I_{pa}=441- 52.76 pH with a correlation coefficient R=0.99362 (Fig. 7c).
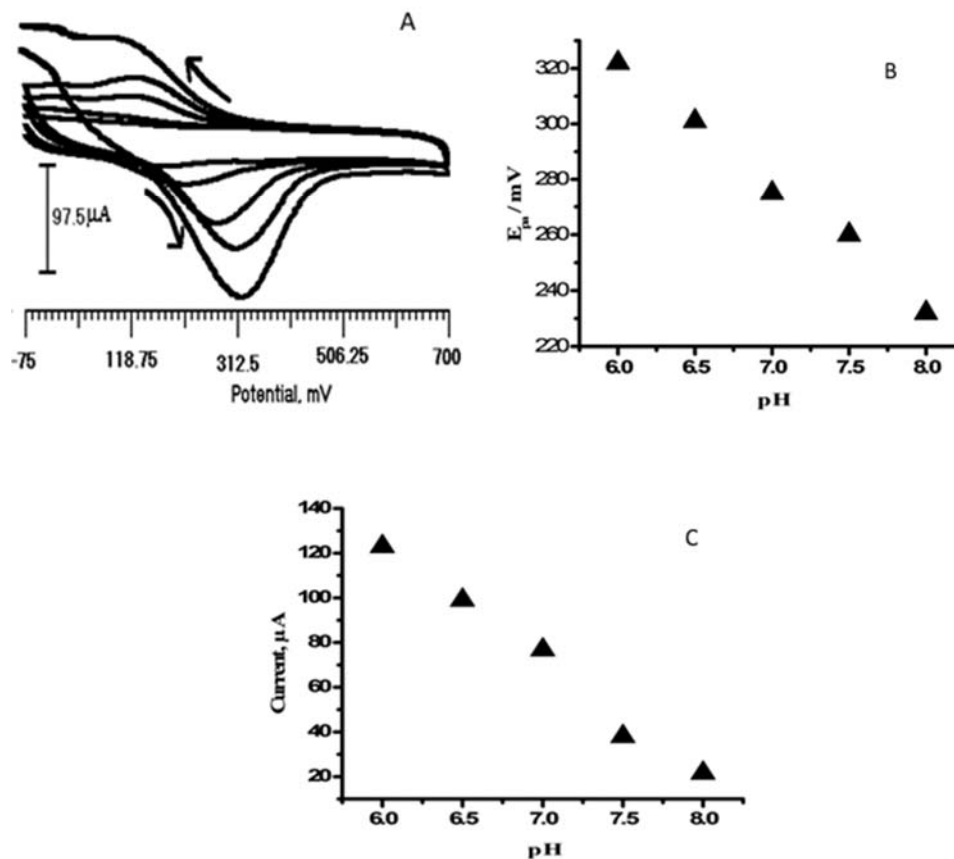
Fig. 7. (A) Cyclic voltammogram at PGMCPE in 0.2 M PBS in different pH values (a) 6.0 (b) 6.5 (b) 7.0 (d) 7.5 (e) 8.0 containing NG (1×10^{-4} M); (B) Plot of anodic peak potential (E_{pa}) Vs pH at PGMCPE; (c) anodic peak current (I_{pa}) Vs pH for NG

3.8. Calibration curve

Cyclic voltammetry used to investigate the current response of nigrosine using a standard addition method. Various concentration of nigrosine at PGMCPE in 0.2 M PBS at pH 6.0 is shown Fig.8. Anodic peak current of nigrosine directly proportional to nigrosine concentration range of 3×10^{-5} to 5×10^{-5} M and 6×10^{-5} to 1×10^{-4} M with the limit of detection (3S/M), 8×10^{-8} M and limit of quantification (10S/M), 2.6×10^{-7} M. The linear regression equation obtained is $I_{pa} = -1.67\times10^{-5}+1.18$ C with a correlation coefficient R=0.99735.
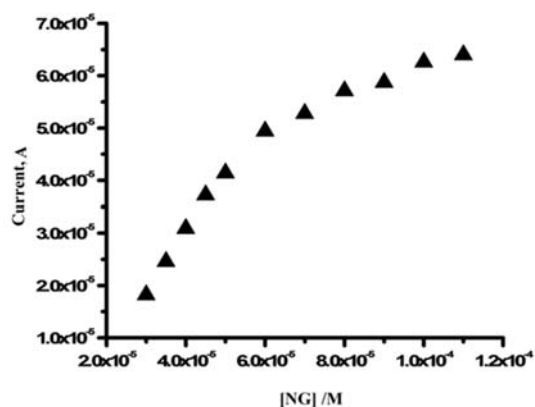
Fig. 8. Calibration plot for the determination of NG at the PGMCPE in pH 6.0 PBS with the scan rate 100 mV/s

3.9. Electrochemical behavior of NG by DPV

DPV was used for the determination of NG at PGMCPE because higher current sensitivity and better quality than CV. Fig. 9 depicts the DPV response from the electrochemical oxidation of 1×10^{-4} M NG at PGMCPE and BCPE. As can be seen, the anodic peak potential for the oxidation of nigrosine at PGMCPE is about 234 mV and there is no peak was observed for BCPE. From these results it is concluded that the best electrocatalytic effect for NG oxidation is observed at PGMCPE. In other words, the carbon paste electrode modified with poly (glycine) improves the characteristics of NG oxidation or PGMCPE could accelerate the rate of electron transfer of NG in pH 6.0, 0.2 M PBS.
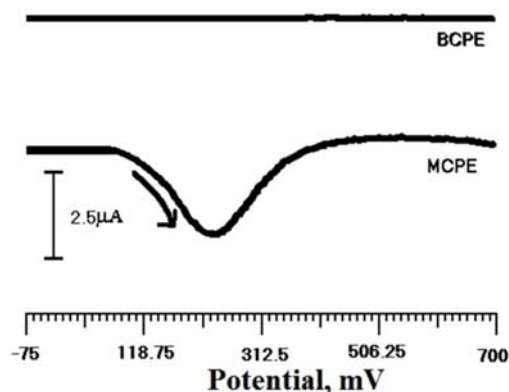

Fig.9. DPV of a solution containing NG (1×10^{-4} M) in 0.2 M PBS at the BCPE and PGMCPE

3.10. Simultaneous determination of NG and TR by DPV

For simultaneous determination of NG and TR at PGMCPE under optimized conditions, DPV was carried out in the potential range -75 to 1300 mV in 0.2 M PBS (pH 7.0). The DPV

showed the simultaneous determination of NG and TR with a well separated two peaks (Fig. 10) corresponding to their oxidation could be possible at PGMCPE. NG showed it's E_{pa} at 255 mV and TR was at 1046 mV. The peak to peak separation of NG-TR was found to be 791 mV, but BCPE there is no peak separation was observed for NG and TR showed and E_{pa} at 1002 mV. The data obtained show that the PGMCPE definitely improves the characteristics of oxidation of both NG and TR.
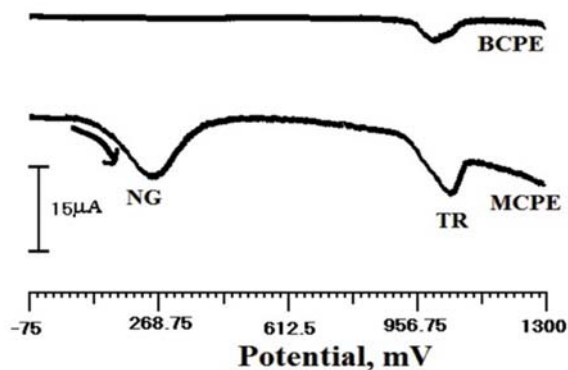

Fig. 10. DPV of a solution containing NG (1×10^{-4} M) and TR (2×10^{-4} M) in 0.2 M PBS pH 6.0 at the BCPE and PGMCPE.

Acknowledgments

4. CONCLUSION

The PGMCPE exhibit highly electro catalytic activity to the oxidation of NG in 0.2 M PBS at pH 6.0. The electrochemically manufactured PGMCPE exhibited a highly effective, electrocatalytic activity towards the determination of NG. The proposed method has showed excellent sensitivity, selectivity, and fast response, low detection limit with satisfactory stability, repeatability, reproducibility and good potential application towards the determination of nigrosine. NG was successfully determined with a limit of detection 8×10^{-8} M, and limit of quantification 2.6×10^{-7} M This low detection limit indicates that the proposed electro analytical method is attractive and also suitable for trace analysis. In addition, due to the simplicity of the preparation procedures, fast routine determination can be achieved by this method.

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