

Electropolymerization of Glycine at Carbon Paste Electrode and its Application for the Determination of Methyl Orange

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Abstract

A recently constructed polyglycine modified carbon paste electrode (PGMCPE) was employed to evaluate the electrochemical behavior of methyl orange (MO). The developed electrode was characterized by FESEM to understand the morphology of the modified electrode and bare carbon paste electrode (BCPE). The modified electrode exhibits an excellent electrochemical activity towards the oxidation of MO. Through the cyclic voltammetry (CV) measurement it was found that MO oxidized at the potential of 651 mV. The peak current obtained for the electrode which was modified with glycine was 4.2 times higher than that exhibited for BCPE. The influence of the experimental parameter on electrochemical oxidation of MO like pH, scan rate, and concentration was studied. Simultaneous analysis (with indigo carmine) was also studied by Differential pulse voltammetry (DPV) technique. Under optimized condition, the linear calibration curve obtained for MO is in the concentration range 1.5×10^{-5} to 1.8×10^{-4} M, leading to the detection limit of 7.4×10^{-6} M.

Keywords: Carbon paste electrode; Glycine; Methyl orange; Indigo Carmine; Cyclic voltammetry.

Introduction

Azo dyes have found broad application in science, medicine, and technology. Many industries use dyes to color their products. The presence of dyes in the water system reduces the penetration of light and will affect the photosynthesis of aquatic vegetations. Methyl orange (MO) is an acidic, aromatic, synthetic dye and widely used as a coloring agent in textiles, leather, gasoline, food industries and pharmaceuticals [1-4]. The presence of such compounds leads to the serious environmental problem for aquatic and human life. So it is become essential to develop a method for the

determination of MO.

There are various methods devised for the determination of azo dyes including liquid chromatography [5] and capillary electrophoresis [6] etc. These methods are time - consuming and require several processing steps. Among these conventional methods available, the electroanalytical technique having several advantages like a simple instrument, speediness and allow sensitive detection of the electroactive compound. Cyclic voltammetry (CV) [7-9] is an electroanalytical technique widely used in the many fields of chemistry which measures the current response against the applied potential. The development

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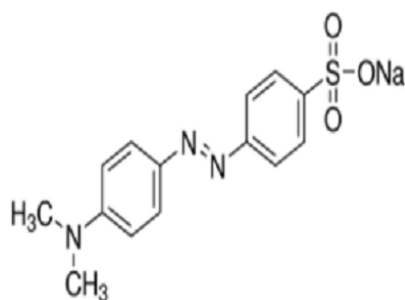


Figure 1. Molecular structure MO

of electrochemical sensors for azo dyes becomes an increasing interest in the last few decades.

Among the researchers for electrochemical sensor application, polymer modified electrode prepared by electropolymerization [10-16] have obtained significant attention. Glycine was widely used in electroanalytical studies as a modifier in electrochemical sensors due to their charge transport properties. Past few decades there has been a considerable effort devoted to developing the voltammetric method for the detection of MO due to the electroactive nature. The molecular structure of MO was shown in the Figure 1 [17]. Among the different electrodes carbon paste electrode is widely used in electrochemical studies because of their easy preparation, reproducible surface, low residual current, low cost, porous surface, and carbon paste electrode exhibit compatibility to biological systems higher than that of commonly used electrode material [18-26].

In this present work, polyglycine modified carbon paste electrode (PGMCPE) was developed by electropolymerization technique. Different parameters like pH, scan rate, and concentration on electrochemical oxidation of MO were studied. We stretch out the work for simultaneous determination of IC along with MO by Differential Pulse Voltammetry (DPV) technique. From our best knowledge, there is no research work was done on the determination of MO using PGMCPPE.

Materials and Methods

Chemicals and Reagents

MO was purchased from British drug houses Ltd., Silicone oil, glycine, graphite were purchased from nice chemical Pvt. Ltd (Cochin, India), Monosodium dihydrogen phosphate and di-sodium hydrogen phosphate were obtained from Himedia Laboratories Pvt. Ltd. 0.2 M phosphate buffer solution (PBS) was prepared by mixing an appropriate quantity of 0.2 M disodium hydrogen phosphate and sodium dihydrogen phosphate. MO (25×10^{-4} M), Glycine (25×10^{-3} M) and Indigo Carmine (25×10^{-4} M) stock solution were prepared in

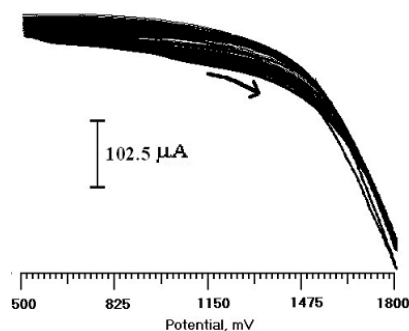


Figure 2. Cyclic voltammogram for the electrochemical polymerization of 1×10^{-3} M glycine at BCPE in 0.2 M PBS (pH 5.7) at the scan rate 100 mV/s.

distilled water.

Working electrode preparation

Bare carbon paste electrode (BCPE) was prepared by mixing graphite powder and silicone oil in the ratio of 70:30 (w/w %) in an agate mortar and pestle until to get a homogeneous paste. Prepared BCPE was packed into the end of the teflon tube having diameter 3 mm. The copper wire connected to the end of the tube which will provide the electrical contact. PGMCPPE was fabricated by electropolymerization of glycine by CV in the potential range from 500 to 1800 mV (Fig. 2) at the scan rate of 100 mV/s in 0.2 M PBS (pH 5.7) for 10 cycles. After electropolymerization, the electrode was washed with distilled water in order to remove the unreacted monomer, and the electrochemical studies were carried out by using this modified electrode.

Experimental Equipment

Three electrodes cell (50 ml) was used to do the electrochemical experiments. BCPE and PGMCPPE were used as a working electrode (WE), Pt wire used as a counter electrode (CE) and saturated calomel electrode (SCE) as a reference electrode (RE). CV and DPV were conducted with an EA-201 Electroanalyser (Chemilink System, India) and connected to a personal computer for control and data storage. All the experiment was carried out at room temperature ($25 \pm 1^\circ$ C).

Results and Discussion

Morphology characterization of BCPE and PGMCPPE

The morphologies of prepared BCPE and PGMCPPE were studied by using Field Emission Scanning Electron Microscopy (FESEM) and are shown in Figure 3. The surface of BCPE appears to be rough and irregularly shaped (Fig. 3a) and PGMCPPE (Fig. 3b) appears to be smooth with uniform, indicates that the surface of the

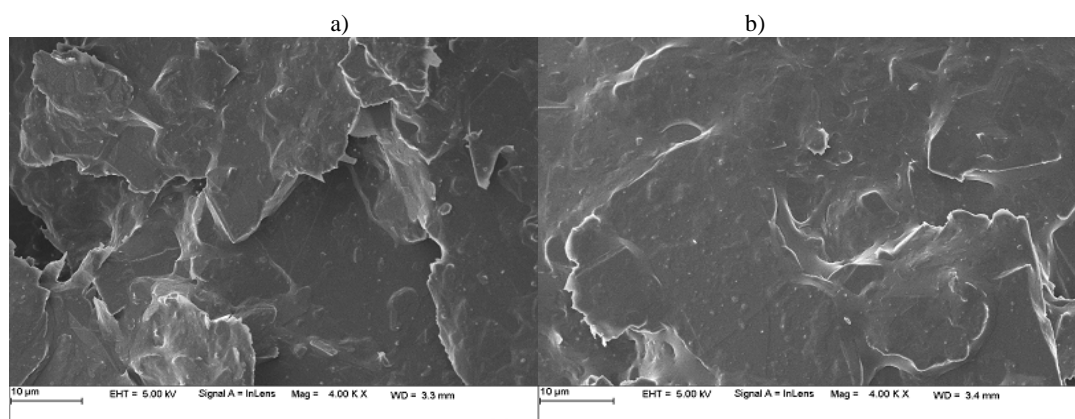


Figure 3. FESEM image of (a) BCPE (b) PGMCPPE.

BCPE is successfully covering with the polyglycine thin film.

Electrochemical studies of MO at PGMCPPE

Figure 4 shows the cyclic voltammogram of MO (2×10^{-4} M) in 0.2 M PBS, pH 7.0 at BCPE (solid line) and PGMCPPE (dashed line). On BCPE, the electrochemical response was weak with a small oxidation peak ($E_{pa} = 681$ mV, $I_{pa} = 2.7$ μ A) was observed for MO. On the carbon paste electrode coated with polyglycine film shows the oxidation peak ($E_{pa} = 651$ mV, $I_{pa} = 11.5$ μ A) which is higher than that observed at BCPE. The peak current of MO at PGMCPPE increased by about 4.2 times compared to those at BCPE. Also, there was no peak appeared in the reverse scan; indicates that the present electrochemical process is irreversible. This all result shows that the modified electrode improves the sensitivity by increasing the peak current.

Figure 5 shows the cyclic voltammogram of the MO (2×10^{-4} M) in 0.2 M PBS, pH 7.0 at PGMCPPE in the presence (dashed line) and absence (solid line) at the scan rate of 100 mV/s. During scanning towards

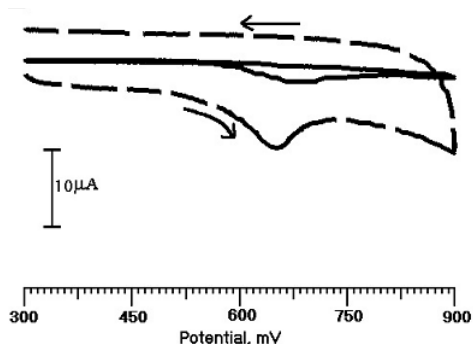


Figure 4. Cyclic voltammogram of MO (2×10^{-4} M) in 0.2 M PBS of pH 7.0 at BCPE (solid line) and PGMCPPE (dashed line).

positive direction an oxidation peak was observed at potential 651 mV (Vs SCE) with a peak current of (I_{pa}) 11.75 μ A, the process at this potential can be attributed to being the direct electrochemical oxidation of MO at PGMCPPE and which is absent in the blank solution (only background current was observed). This shows that the electrochemical properties of MO improved at PGMCPPE.

Effect of pH and scan rate on PGMCPPE

pH is a key parameter that can affect the mass transport to the electrode surface. Fig. 6a CVs of MO (2×10^{-4} M) at PGMCPPE at different pH values (6.0-8.0) in 0.2 M PBS at the scan rate of 100 mV/s. It was observed that electrode response (peak current) was high at buffer solution having pH 7.0 [E_{pa} (651 mV) and I_{pa} (11.5 μ A)]. However, the oxidation peak current began to decrease further increasing pH. The high electrostatic attraction was observe negatively charged dye and positively charged polymer film at pH 7.0. Therefore pH 7.0 was chosen for the whole other analytical experiments. A linear relationship was obtained between anodic peak current and pH (Fig. 6b)

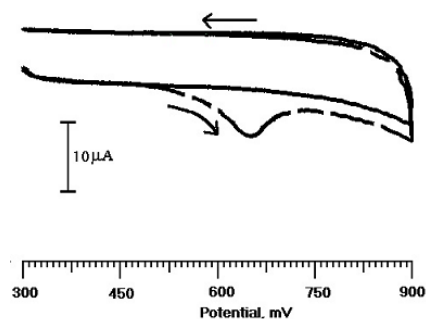


Figure 5. Cyclic voltammogram of MO at PGMCPPE with 2×10^{-4} M MO (dashed line) and without MO (solid line) in 0.2 M PBS, pH 7.0 at the scan rate 100 mV/s.

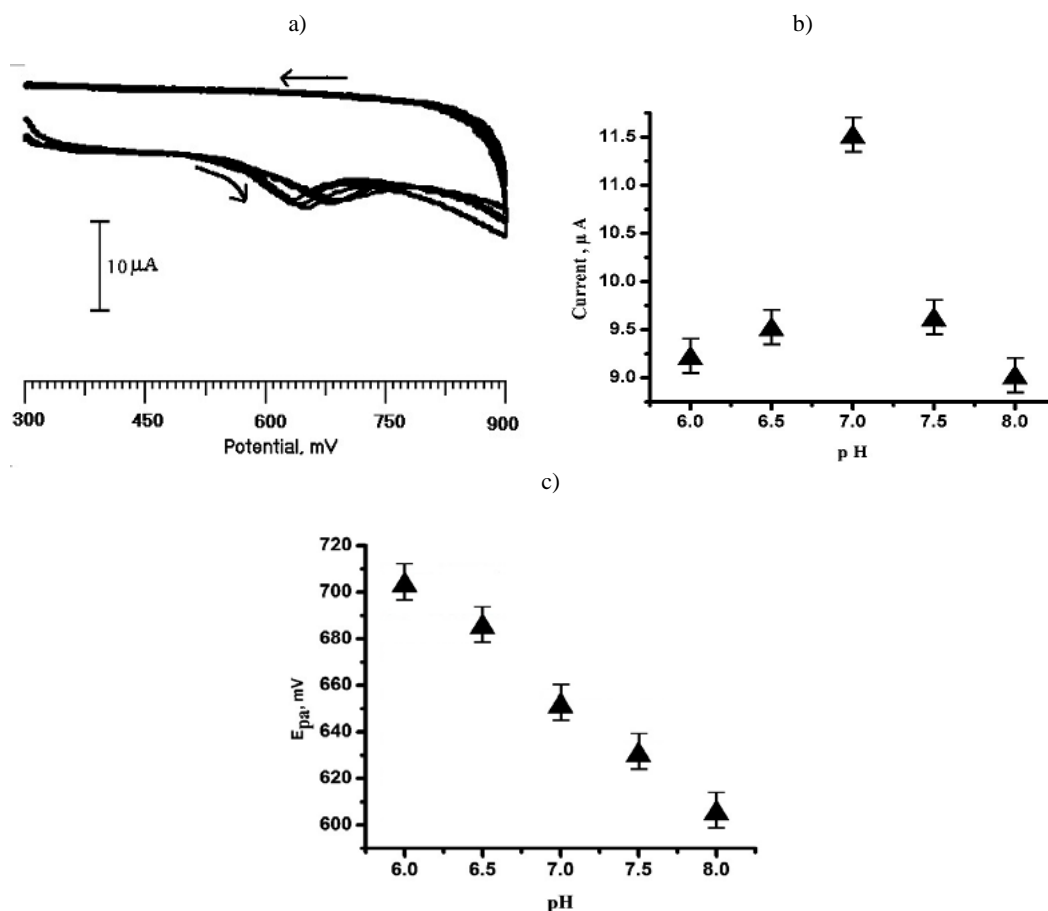


Figure 6. (a) Cyclic voltammogram MO at PGMCPPE in 0.2 M PBS in different pH values 6.0-8.0 containing MO (2×10^{-4} M) (b) anodic peak current (I_{pa}) Vs pH at PGMCPPE (c) Plot of anodic peak potential (E_{pa}) Vs pH at PGMCPPE.

with a linear regression equation $E_{pa} = 1006.2 - 50.2 \text{ pH}$ with a correlation coefficient of 0.99061, The slope 50.2 is near to the theoretical value 58.5 mV/pH. Revealing

that the number of protons taking park in the oxidation of MO is equal to the number of electrons.

Figure 7a shows the cyclic voltammogram of MO at

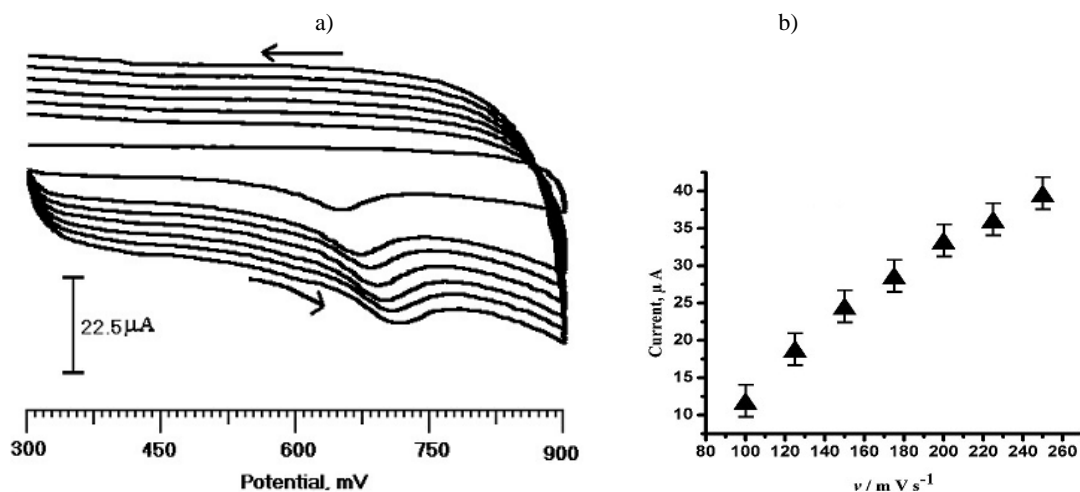


Figure 7. (a) Cyclic voltammogram of MO (2×10^{-4} M) at PGMCPPE in pH 7.0 at various scan rates, 100, 125, 150, 175, 200, 225, 250 mV/s. (b) anodic peak current (I_{pa}) Vs scan rate (v).

different scan rates from 100 to 300 mV/s. With the increase of the scan rate, the peak current increased (to the more negative side). It is observed that there is a linear relationship between peak current (I_{pa}) and scan rate (ν) with a linear regression equation, $I_{pa} = -4.47 + 0.18 \nu$ (mV/s) (Fig. 7b) with a correlation coefficient of 0.99, which confirms that the electrode process is adsorption controlled.

Calibration Curve

Under the optimized condition, the relationship between oxidation peak current and concentration of MO was studied by CV. It is observed that anodic peak current (I_{pa}) is proportional to the concentration of MO in the range from 1.5×10^{-5} to 1.8×10^{-4} M. Figure 8 indicates the cyclic voltammogram of different concentration of MO with peak current and shows a linear relationship with a linear regression equation, I_{pa} (A) = $5.42 \times 10^{-6} + 0.012 C$ (M) with a correlation coefficient (R) 0.9941. Detection limit (D_L) of the investigated analyte can be calculated as $D_L = 3S/N$ [27] where S is the standard deviation of the blank and N is the slope of the linear regression equation. In this work, D_L was estimated to 7.4×10^{-6} M.

Stability and Repeatability

Stability of the modified electrode was evaluated by continuously scanning for 45 cycles in 0.2 M PBS, pH 7.0 (Data not shown). The percentage of degradation of modified electrode was calculated and (% Degradation = I_{pn} / I_{p1} , I_{pn} and I_{p1} are the n^{th} and first anodic peak current respectively) [28] which is less than 1%, shows that the modified electrode is stable. Repeatability of the fabricated electrode was investigated base on the 5 replicated measurements with the same electrode and observed relative standard deviation of 3.2% shows the good repeatability of the modified electrode.

Voltammetric Behavior of MO by DPV

DPV which gives good current sensitivity and better quality than CV technique because due it will minimize the migration current. Figure 9 shows the DPV of MO (2×10^{-4} M) in 0.2 M PBS (pH 7.0) at BCPE and PGMCPCE. For PGMCPCE an anodic peak current was observed at 609 mV ($I_{pa} = 13.39$) and for BCPE weak and low intense current response was observed at potential 631 mV ($I_{pa} = 2.35$). Which indicates that the PGMCPCE accelerates the electron transfer of MO in 0.2 M PBS (pH 7.0).

Simultaneous determination of MO and IC by DPV

Figure 10 shows the DPV of IC (2×10^{-4} M) and MO (2×10^{-4} M) in 0.2 M PBS (pH 7.0) at BCPE and PGMCPCE in the potential range from 200 to 800 mV. A well separated two peaks was observed at PGMCPCE for MO ($E_{pa} = 596$, $I_{pa} = 7.7 \mu\text{A}$) and for IC ($E_{pa} = 302$, $I_{pa} = 14.01 \mu\text{A}$) and an weak response was observe at BCPE (For MO, $E_{pa} = 633$ mV, $I_{pa} = 2.42 \mu\text{A}$ and for IC, $E_{pa} = 451$ mV, $I_{pa} = 0.57 \mu\text{A}$). These data show that the PGMCPCE improves the oxidation of both MO and IC.

Simultaneous determination of MO and IC with changing the concentration of one species and keeping other species constant has also carried out at the PGMCPCE by DPV technique. Fig.11a shows the DPV of MO ($2 - 2.5 \times 10^{-4}$ M) and IC (2×10^{-4} M). It can see that peak current of MO was proportional to the concentration increases from 2 to 2.5×10^{-4} M. The corresponding linear regression equation can be expressed as $I_{pa} = 4.59 + 1.54 C$ (Fig.11b) with a correlation coefficient of 0.99506 and there is no much variation of the peak current of IC. This result indicates that the MO and IC were present independently in their mixture of samples.

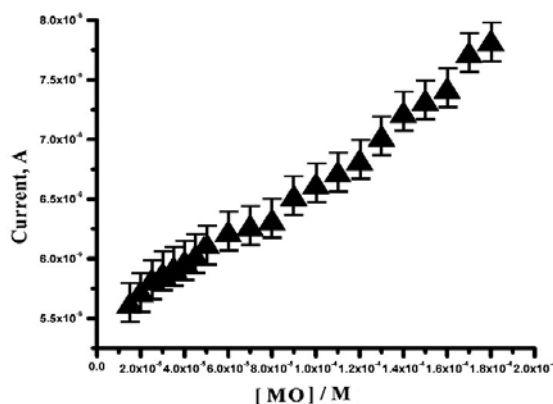


Figure 8. Calibration plot for the determination of MO at PGMCPCE in 0.2 M PBS, pH 7.0 with the scan rate of 100 mV/s.

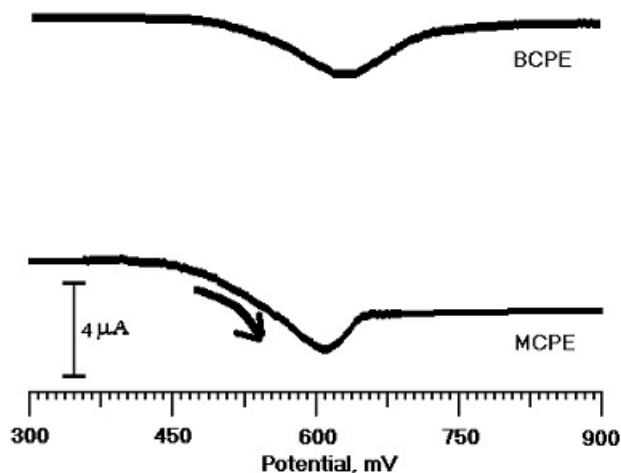


Figure 9. DPVs of the solution containing MO (2×10^{-4} M) in 0.2 M PBS, pH 7.0 at BCPE and PGMCPPE.

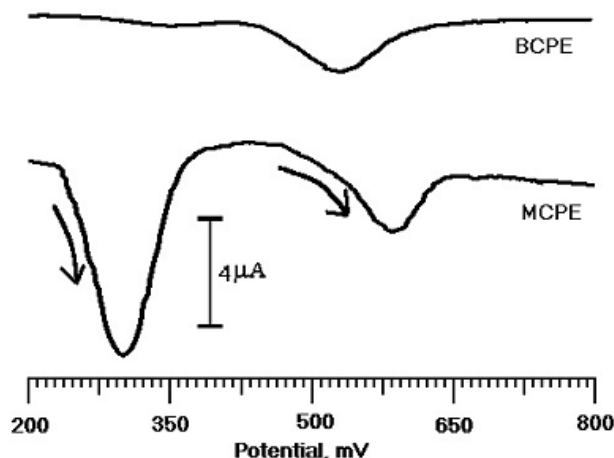


Figure 10. DPVs of a solution containing MO (2×10^{-4} M) and IC (2×10^{-4} M) in 0.2 M PBS, pH 7.0 at the BCPE and PGMCPPE

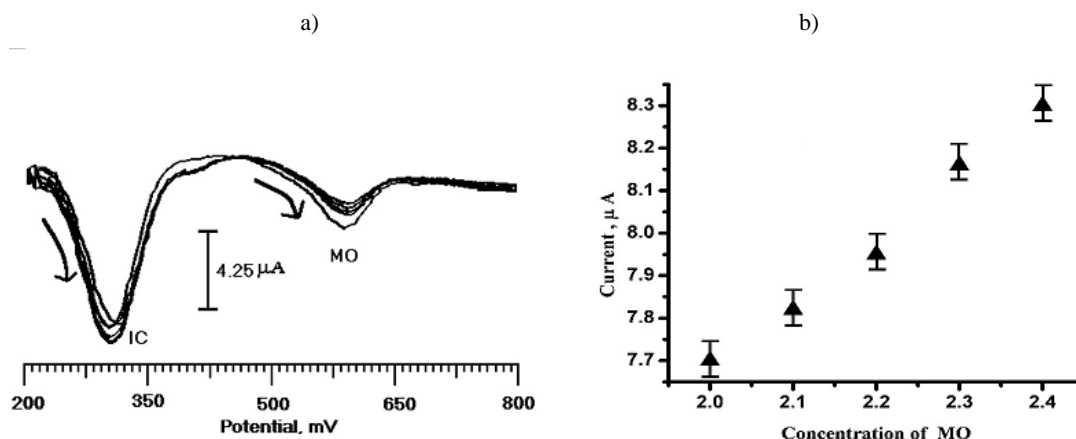


Figure 11. (a) DPVs for MO at PGMCPPE in the presence of 2×10^{-4} M IC and different concentration of MO (2×10^{-4} M to 2.4×10^{-4} M) in 0.2 M PBS (pH 7.0), (b) Plot of anodic peak current of MO (I_{pa}) Vs concentration in pH 7.0 PBS at the scan rate of 50 mV/s

Conclusion

In this work, a polymer modified electrode prepared

by electropolymerization was shown to be an attractive and effective electrochemical sensor electrode for the

MO determination. Surface morphology was studied by FESEM. When polymer film deposited as a thin film on the surface of the carbon paste electrode a significant enhancement of peak current (Oxidation peak current) was observed which is 4.2 times higher than that of BCPE. After optimization, detection limit 7.4×10^{-6} M and limit of quantification 24×10^{-6} M was achieved. Prepared electrochemical sensor electrode shows a low detection limit with satisfactory stability, repeatability.

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