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Detection of Methyl Parathion at an Electrochemically Reduced Graphene Oxide (ERGO) Modified Electrode

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An electrochemical sensor for the detection of methyl parathion (MP) was developed based on electrochemically reduced graphene oxide (ERGO) modified GCE (ERGO/GCE). ERGO was characterized by Raman and IR spectroscopy, scanning electron microscopy and atomic force microscopy. The electrochemical reduction of MP was investigated using cyclic voltammetry technique in phosphate buffer (pH 7). Using square wave voltammetry, a linear calibration curve for the detection of MP was obtained in the concentration range from 3.0×10^{-8} M - 2×10^{-9} with a detection limit of 8.87×10^{-10} M. The selectivity of the ERGO/GCE was tested in the presence of a few metal ion and organic interfering species. Real sample analysis using potato samples had been carried out.

Keywords: Methyl parathion ,electrochemically reduced graphene oxide , real sample analysis.

1. INTRODUCTION

Methyl parathion (*o*,*o*-dimethyl-*o*-(4-nitrophenyl) phosphorothioate, MP) is an organophosphorous compound widely used as a pesticide in agriculture [1]. It is used for pest control in a large variety of crops including cereals, fruits, coffee, potato and sugarcane [2, 3]. It has been reported that MP irreversibly inhibits acetylcholinesterase and leads to excessive cholinergic neurotransmission resulting in autonomic dysfunction and the lethal dosage of MP as declared by WHO is 3 mg/kg [4]. Due to its high toxicity, bio-accumulation effect and long-term damage to environment and living species even in such low concentration, the quantitative detection of MP becomes very essential [5].

Various methods such as high performance liquid chromatography, gas chromatography combined with mass spectroscopy, capillary electrophoresis and colorimetry have been developed to measure MP in environment and in food samples [6-9]. These methods are time consuming, expensive and require trained personnel. Alternatively, electrochemical methods are very attractive for on-site monitoring, offering high sensitivity, good stability and cost-effectiveness [10]. The inherent electroactivity of MP makes the electrochemical method particularly suitable for its detection and determination.

The electrochemistry of MP was well studied in early 80s [11]. MP showed sluggish electrode kinetics often resulting in electrode fouling which affected the performance of the electrode during electrochemical measurements [12]. This problem has been overcome by the use of the chemically modified electrodes. There have been several studies on the use of nanostructured chemically modified electrodes in the development of electrochemical sensors for MP. Vicente *et al*. [13] first reported the detection of MP using a C_{16} modified carbon paste electrode with a detection limit of 2×10^{-8} M. Then MP was detected based on a hexadecane-coated glassy carbon electrode [14]. Various modified surfaces such as nafion-coated glassy carbon electrode [15], bismuth modified electrode [16], hanging mercury drop electrode [17] carbon fiber microelectrode modified with tetrasulfonated nickel phthalocyanine with and without nafion films [18], graphite-modified basal plane pyrolytic graphite electrode [19], silicate-cetyltrimethylammonium bromide nanocomposite film [20], nanosilver/nafion composite electrode [21] and *p*-sulfonatocalix[6]arene-modified silver nanoparticles [22] were developed for the detection of MP. MP was detected at various clay based composites [23-26]. Carbon paste and multiwalled based composites were developed for the electrochemical detection of MP [27-33]. Parham and Rahbar [34] investigated nano ZrO_2 modified carbon paste electrode for the detection of MP.

Recently graphene-based composites are being used in the electrochemical detection of pesticides. ZrO_2 nanoparticles decorated graphene nanosheets was found to dramatically facilitate the enrichment of MP with a detection limit of 2.27×10^{-12} M [35]. Graphene–chitosan (GR–CS) composite was prepared for the electrochemical detection of MP giving a detection limit of 3.03×10^{-12} M. The combined effect of large surface to volume and high conductivity of graphene and biocompatibity and adsorption ability of chitosan enhanced the sensing ability of MP [36]. Cathodic stripping voltammetry was employed in the detection of MP using Ni/Al layered double hydroxide decorated graphene nanosheet hydride (LDHs-GNs) [37]. Electrochemically reduced □□cyclodextrin dispersed graphene acted as a sorbent for the preconcentration and electrochemical sensing of MP. The material possessed ultra-large surface area [38]. Au nanoparticles decorated graphene nanosheets modified GCE was used as solid phase extraction. The stripping analysis was highly linear over the MP concentration ranges of 3.43×10^{-12} M - 3.43×10^{-10} M and 6.86×10^{-10} M - 3.43×10^{-9} M with a detection limit of 2.05×10^{-12} M [39]. A novel poly (malachite green)/graphene nanosheets–nafion composite film-modified GCE was developed for the detection of MP. The sensor was applied for the determination of MP in real samples, with recoveries from 97.20 to 104.53 % [40].

In this work, we describe the results obtained on a performance evaluation study of an electrochemically reduced graphene oxide modified glassy carbon electrode (ERGO/GCE) applied to the detection of MP.

2. MATERIALS AND METHODS

2.1. Reagents

Methyl parathion was purchased from Sigma Aldrich (USA). The other chemicals used in this investigation were of analytical grade (99%). All the solutions were prepared using double distilled water. Phosphate buffer solution (PBS) of pH 5 and 7 were prepared by mixing appropriate volumes of 0.1 M $KHPO_4$ and 0.1 M HCl and 0.1 M $KHPO_4$ and 0.1 M K_2HPO_4 respectively [41]. Pure N_2 gas was passed through the electrolyte solution before electrochemical measurement.

2.2. Apparatus

Electrochemical measurements like cyclic voltammetry (CV), square wave voltammetry (SWV) were performed by using CH instruments 700C. A conventional three-electrode cell was used with glassy carbon electrode (GCE) (surface area = 0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. All the potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the fabricated films was studied by HRSEM (XL30-SFEG) and AFM (Shimadzu 9500). The IR data were obtained using a FT-IR spectrophotometer (Shimadzu 8400S). Raman spectrum was obtained using a laser Raman confocal microprobe (LabRam HR 800).

2.3 Preparation of Graphene oxide (GO)

GO was prepared by Staudenmaier method [42-44]. About 5 g graphite was first mixed with sulphuric acid (87.5 mL) and nitric acid (45 mL) and stirred vigorously for 30 min. The mixture was then cooled to about 5˚ C by immersion in an ice bath. To the ice-cold mixture potassium chlorate (55 g) was added slowly within 30 min and then added to complete the oxidation of graphite. The mixture was then washed repeatedly with distilled water and then filtered. The graphite oxide solid was treated with 5 % HCl three times followed by repeated washing with distilled water until the pH of the filtrate was neutral. The graphite oxide thus obtained was dried and the yield was found to be about 56%. About 2 mg of the graphite oxide was dispersed in 1 mL of water and sonicated for 2 h to get a uniform aqueous dispersion of GO.

2.4 Preparation of ERGO modified GCE

The graphene modified GCE was prepared by following an electrochemical procedure reported in literature [45]. About 2 mg of GO was dispersed in 1 mL of water. 5 μL of the dispersion was coated on a GCE (0.07cm^2) and dried for 2 h. The electrochemical reduction of GO was carried out from a nitrogen-purged aqueous electrolyte solution containing 0.1 M phosphate buffer (PBS) (pH 5) by cycling the potential between 0 and -1.5 V *versus* Ag/AgCl at 0.05 V s^{-1} to form electrochemically reduced graphene oxide (ERGO).

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammogram of ERGO modified GCE

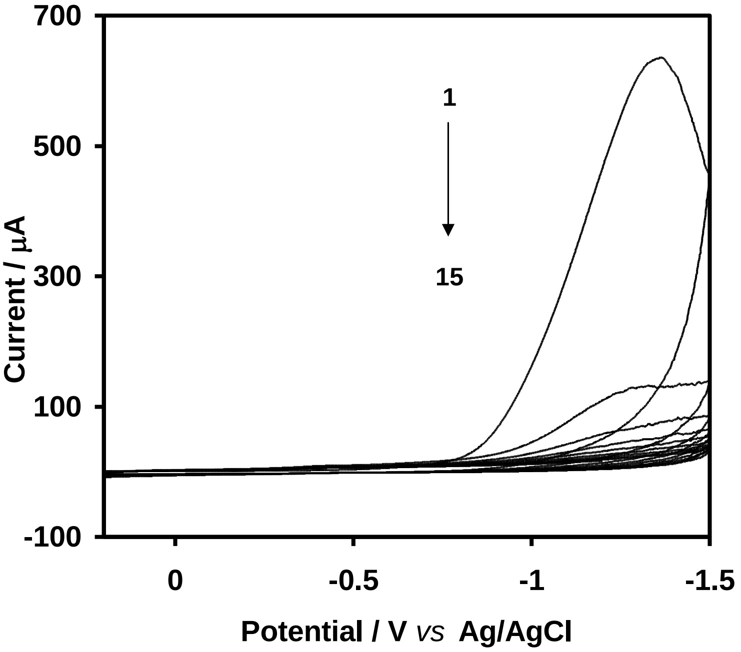


Figure 1. Consecutive cyclic voltammograms recorded at GO/GCE in 0.1 M PBS (pH 5) at 0.05 V s^{-1}. The numbers indicate the cycle number.

Fig. 1 shows the electrochemical reduction of GO from a nitrogen-purged 0.1 M PBS (pH 5) by cycling the potential between 0 and -1.5 V *vs* Ag/AgCl at 0.05 V s^{-1}. The cyclic voltammogram in the first cycle shows a large cathodic peak at about -1.35 V whose current magnitude reduces drastically on cycling further. After 15 cycles, the cathodic peak disappears completely. The drastic decrease in the cathodic peak current can be attributed to the irreversible reduction of surface oxygen functionalities present in GO [45].

3.2 Characterization of ERGO

Raman spectroscopy is used to confirm the formation of graphene by electrochemical reduction of GO. Fig. 2 shows typical Raman spectrum of ERGO which displays three prominent bands namely D-band (1329 cm^{-1}), G-band (1599 cm^{-1}) and 2D band (2655 cm^{-1}). In addition, a small band at 2927 cm^{-1} corresponding to D+G mode is also observed. These results compare very well with those reported in literature for the pristine graphene [46] and also for the ERGO [45]. FTIR spectroscopy is used to identify the residual functional groups present in ERGO. Fig. 3 shows the FT-IR spectrum of ERGO with a broad peak at about 3400 cm^{-1} which can be assigned to the O-H stretching mode of intercalated water molecules. Another strong band at 1652 cm^{-1} can be assigned to the C=C in graphene [45]. The IR data also demonstrate the good purity of ERGO. Fig. 4 shows the HRSEM image of ERGO. The image shows the presence of relatively large sheet-like structures characteristic of planar graphene sheets [47]. Atomic Force Microscopy (AFM) is used to measure the layer thickness of ERGO. Fig. 5 shows the 2D and 3D AFM images along with the height profile of ERGO/GCE. The AFM shows the presence of flat sheets with an average thickness of 3.72 nm suggesting that a graphene sheet is composed of 9 layers.

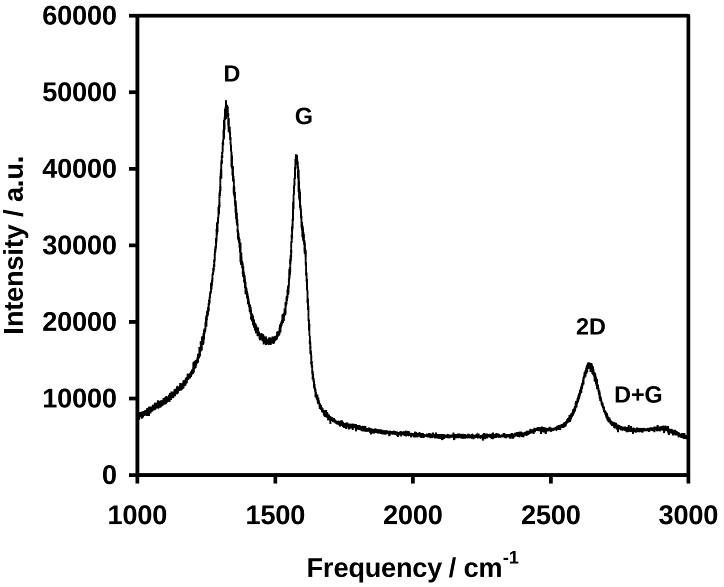


Figure 2. Raman spectrum of ERGO

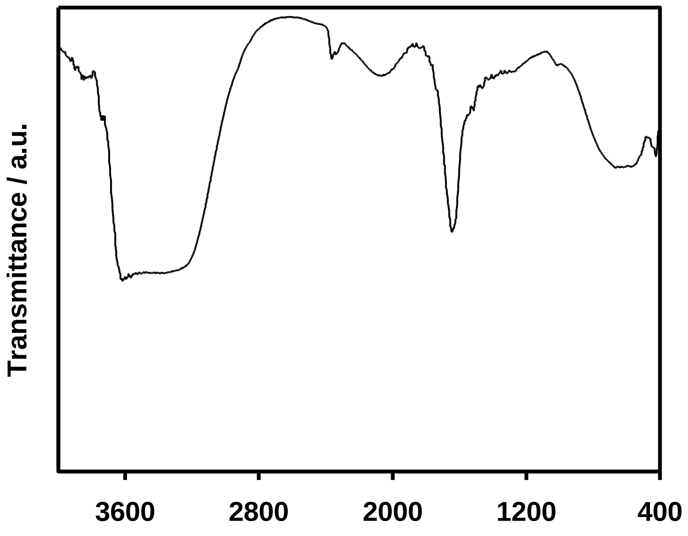


Figure 3. FT-IR spectrum of ERGO

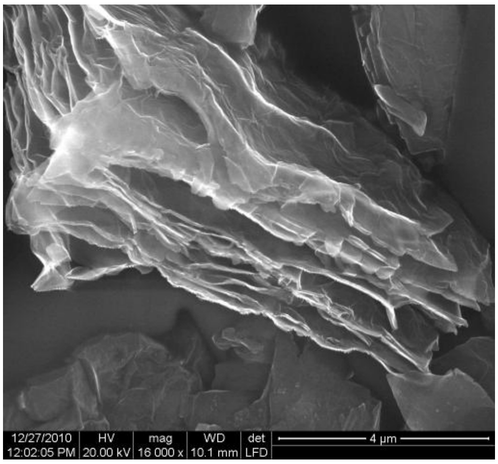


Figure 4. HRSEM image of ERGO

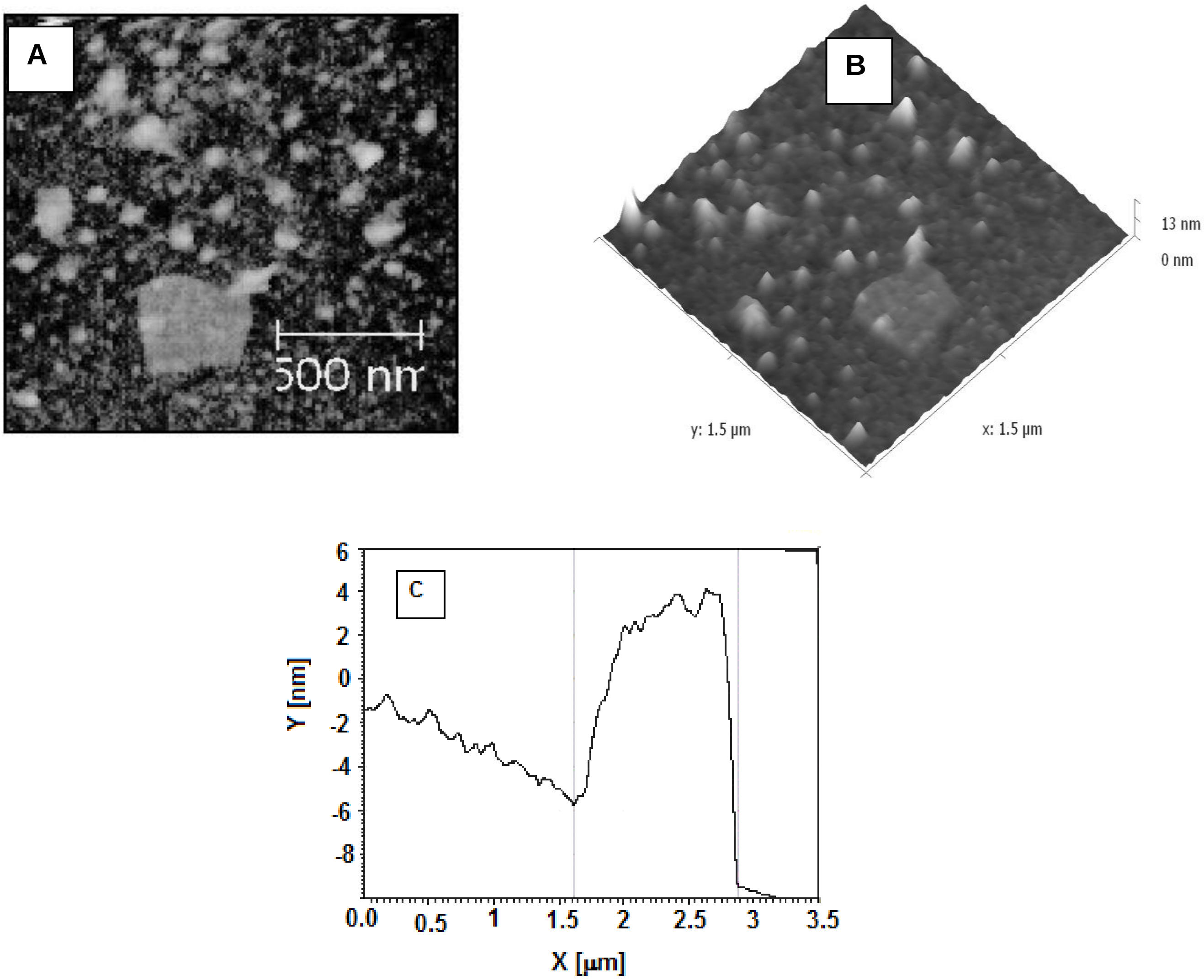


Figure 5. AFM image of ERGO (A) 2-D (B) 3-D (C) Height profile

3.3 Electrochemical Behaviour of MP - Cyclic Voltammetry and Effect of Scan Rate

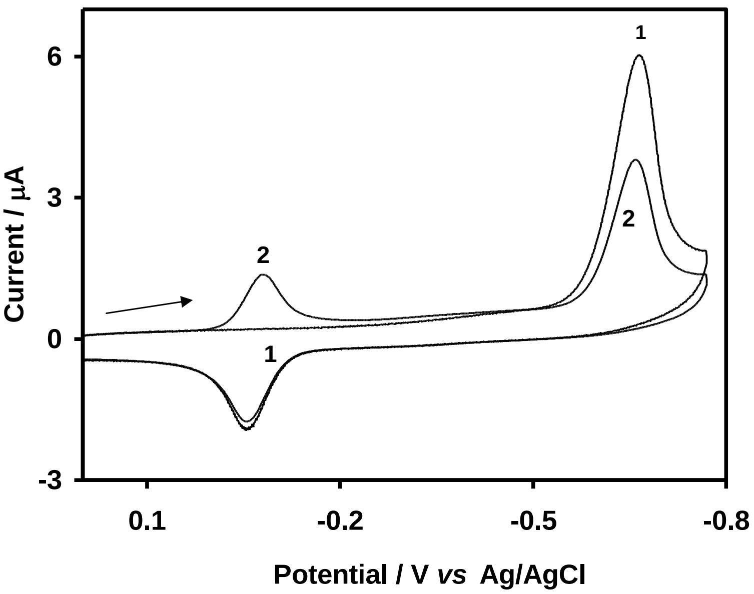
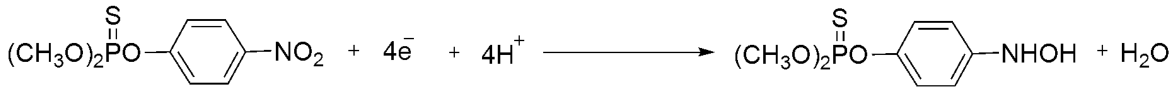
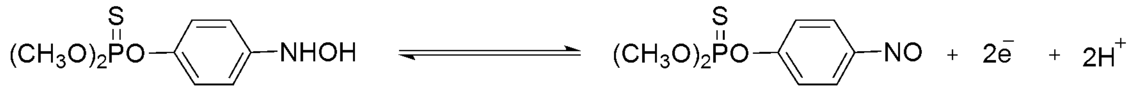


Figure 6. Cyclic voltammograms at GCE in 0.1 M PBS (pH 7) containing 3×10^{-5} M MP (1) First cycle (2) Second cycle. Scan rate = 0.1 V s^{-1}

Fig. 6 shows the cyclic voltammogram at bare GCE obtained in the potential range between 0.15 V and -0.7 V in deaerated 0.1 M PBS (pH 7) containing 3×10^{-5} M MP at a sweep rate of 0.1 V s^{-1}. Two cycles have been presented. In the first cycle, during the forward scan, a large reduction peak at -0.67 V is observed. In the reverse scan, a small anodic peak at -0.05 V is formed which gives rise to a corresponding cathodic peak at -0.09 V. The irreversible reduction peak at -0.67 V corresponds to the 4e$^-$ reduction of the nitro group in MP to 2-phenylhydroxylamine (Eq.1) and the pair of reversible peaks is attributed to the 2e$^-$ nitrosobenzene-phenylhydroxylamine redox process (Eq. 2) [20,36,45]. The cyclic voltammetric observations are consistent with previous reports on the organophosphorous pesticides and nitroaromatic compounds [20,48].



---- (1)



---- (2)

The cyclic voltammetric reduction of MP under identical conditions at ERGO/GCE (Fig. 7) yields similar observation and results obtained with bare GCE. The significant observation is that the 4e$^-$ nitro group reduction peak current at the ERGO/GCE is about five times greater than at GCE and the peak potential is shifted favourably to nearly 0.06 V compared to bare GCE.

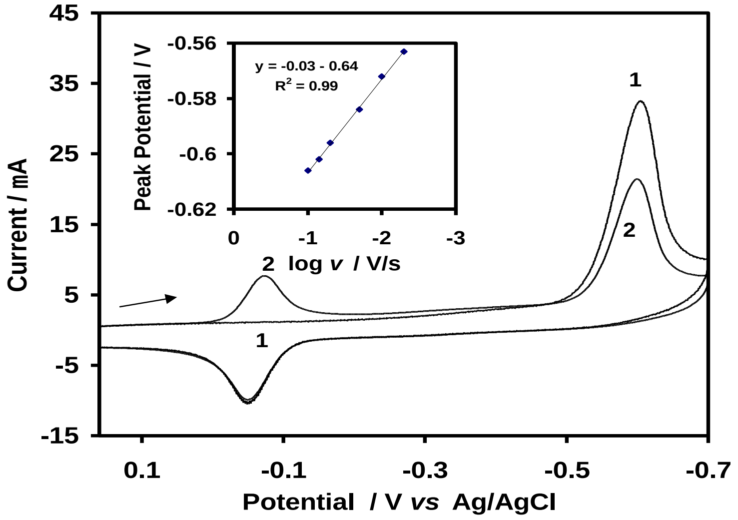


Figure 7. Cyclic voltammograms at ERGO/GCE in 0.1 M PBS (pH 7) containing 3 × 10^{-5} M MP. (1) First cycle (2) Second cycle. Scan rate = 0.1 V s^{-1}. Insert. Plot of MP reduction peak potential against log v

3.4 Calculation of Number of Electrons from Laviron Equation

The irreversible nature of the reduction of MP on ERGO/GCE can be ascertained by the absence of an oxidation peak on reversing the scan and also by the shift of cathodic peak potential with respect to the scan rate in the cyclic voltammograms. The Laviron equation (Eq. 3) for a totally irreversible and adsorption controlled electrode can be written as [49]

$$y = 2.303\ RT / \square n_a F \times \log (RTk_f^o / \square n_a \square F\ v) \qquad \ldots\ldots (3)$$

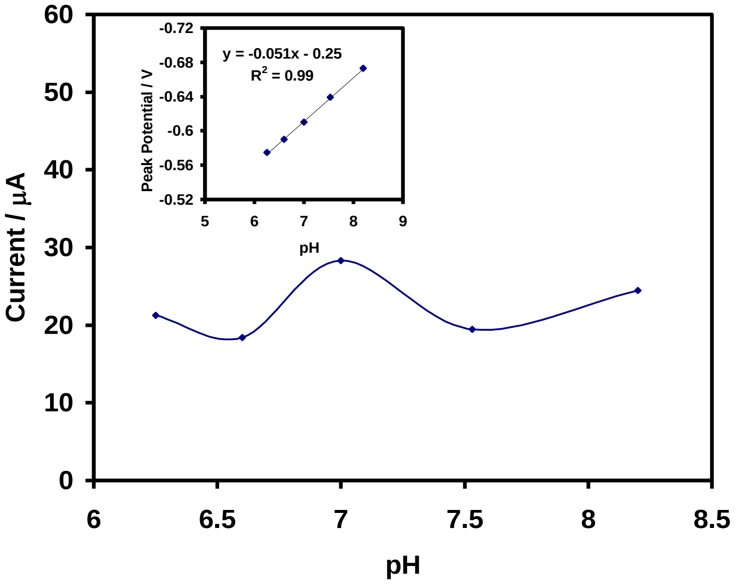
where α is the transfer coefficient, n_a is the number of electrons transferred in the charge-transfer step and k_f^o is the standard heterogeneous rate constant, □v is the sweep rate (V s^{-1}), R is the gas constant (J K^{-1} mol^{-1}), F is the Faraday constant and E_{pc} is the cathodic peak potential. The number of electrons transferred can be calculated by equating the slope of the plot between E_{pc} vs log v□□to 2.303 RT / □n_a F and assuming the value of transfer coefficient□□□ as 0.5. From the linear plot of E_{pc} vs log v shown in inset of Fig. 7, a slope of 0.034 leads to a "n_a" value of 3.6. Therefore, it is confirmed that the nitro group in MP undergoes a $4e^-$ reduction to phenylhydroxylamine.

3.5 Effect of pH of PBS

The electrochemical response of MP at ERGO/GCE is examined in 0. 1 M PBS of pH values *viz*. 6.2, 6.6, 7, 7.5 and 8.2. The best electrochemical response in terms of current sensitivity of the irreversible cathodic peak is obtained in 0.1 M PBS at pH 7 (Fig.8). According to Nernst equation (Eq. 4) [50]

$$E = E^{0'} + (0.059\ m/n)\ \mathrm{pH} \qquad \text{----- (4)}$$

where m and n are the transference number of protons and electrons, respectively.



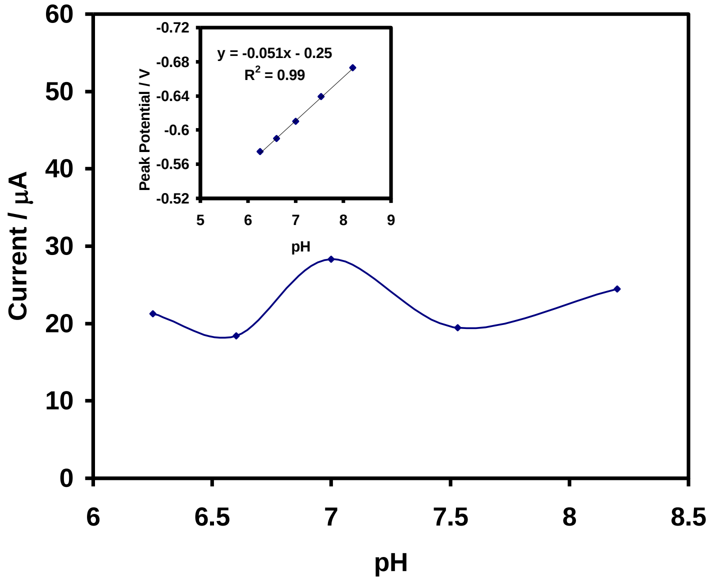


Figure 8. Plot of MP reduction peak current against pH. Inset. Plot of MP reduction peak potential against pH ; Concentration of MP - 3×10^{-5} M

Thus a slope of 0.051 V is expected in an electrochemical reaction for a transfer of equal number of electrons and protons. A plot of E_{pc} versus pH (Inset of Fig. 8) gives a straight line with a slope value of 0.051. Since the observed slope value is close to the theoretical value of 0.059 V, it can be inferred that the reduction of nitro group in MP involves equal number of protons and electrons.

3.6 Square Wave Voltammetric (SWV) Characteristics and Calibration Plot

The SWV experiments have been performed in the potential range from -0.5 to -0.8 V using the following optimal parameters: pulse amplitude 0.025V, scan increment 0.005 V and frequency 15 Hz. Fig. 9 shows typical SWV voltammograms of ERGO/GCE in 0.1 M PBS (pH 7) in the MP concentration range 3.0 x 10^{-8} M - 2 x10^{-9} M. The sensor calibration curve is obtained by plotting the SWV peak current against the respective concentration (Inset of Fig 9).

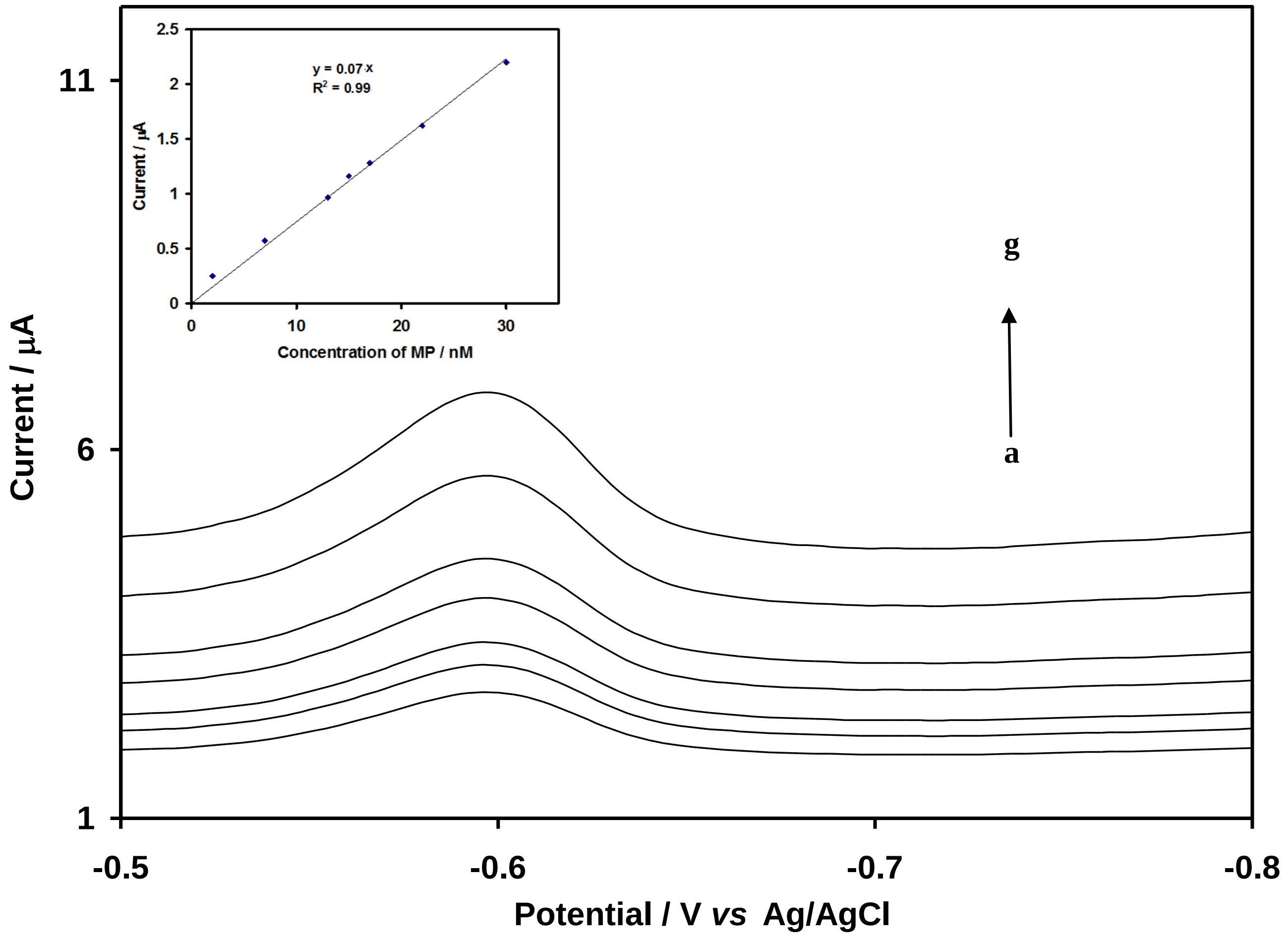


Figure 9. Square wave voltammograms at ERGO/GCE in 0.1M PBS pH = 7 at various concentration of MP. (a) 30 × 10^{-9} M (b) 22 × 10^{-9} M (c) 17 × 10^{-9} M (d) 15 ×10^{-9} M (e) 13 × 10^{-9} M (f) 7 × 10^{-9}M (g) 2 ×10^{-9} M. Inset. Sensor calibration plot for MP.

A linear correlation is obtained which can be represented by Eq. 5

$$y = 0.074\,x \qquad (R^2=0.99) \qquad \ldots\ldots\ (5)$$

Based on the mean value (0.27 μA) of the SWV current values obtained for 4 repeat measurements at the lowest concentration used (2 x 10^{-9} M), the relative standard deviation is calculated to be 8.14 %. The detection limit (Eq..5) is then estimated to be 8.87 x 10^{-10} M for a signal to noise ratio of 12.2. Table 5.1 shows a compilation of the MP sensor data reported for graphene-based modified electrodes along with the results obtained in the present study. The detection limit of electrochemically reduced graphene oxide is comparable to that of □□cyclodextrin-graphene [38] and poly(malachite green)/graphene-nafion [40] but the value is found to be higher than that reported for various graphene based composites [35-37,39].

Table 1 Comparison of reported MP sensor parameters with one obtained with at ERGO/GCE

S.No.	Electrode	Medium	Method	Linear range / M	Detection limit / M	Ref.
1	Graphene-chitosan	Acetate buffer, pH 5.2	SWV	1.3×10^{-11} - 1.37×10^{-9}	2.74×10^{-12}	[36]
2	Poly(malachite green)/graphene-nafion	PBS , pH 5	C	2×10^{-8} – 1.5×10^{-6}	2.00×10^{-10}	[40]
3	ZrO_2/graphene	KCl , pH 5.2	SWV	6.86×10^{-12} - 3.08×10^{-9}	2.00×10^{-12}	[35]
4	Ni/Al layeted double hydroxide/graphene	PBS, pH 5.7	SWV	3.43×10^{-10} – 3.43×10^{-9}	2.05×10^{-12}	[37]
5	Graphene / Gold nanoparticles	PBS, pH 5.7	SWV	6.85×10^{-10} - 3.43×10^{-9}	2.05×10^{-12}	[39]
6	□□cyclcodextrin/graphene	PBS, pH 7	DPV	3.43×10^{-9} - 1.71×10^{-6}	1.71×10^{-10}	[38]
7	ERGO	PBS , pH 7	SWV	3.0×10^{-10} – 2×10^{-9}	8.87×10^{-10}	Present work

SWV: Square wave voltammetry; C: Chronoamperometry DPV: Differential pulse voltammetry; PBS: Phosphate buffer solution

3.7 Interference studies

The selectivity of the ERGO/GCE was tested in the presence of various interferents such as glucose, potassium, sodium, magnesium, calcium and vitamin C that are likely to influence the SWV signal of MP especially in a vegetable sample like potato. A 200-fold excess of each of the interferents was added to the PBS (pH 7) containing solution 1×10^{-5} M MP. The resulting solutions were then analyzed by SWV. The percentage variation in the SWV current value can be calculated using Eq. 6.

$$\text{Percent variation in } I_{pc}(\text{MP}) = [I_{pc}(\text{interfering ions}) - I_{pc}(\text{MP})] / I_{pc}(\text{MP}) \qquad \text{-----} (6)$$

where I_{pc}(interfering ion) is the cathodic peak current of interfering species and I_{pc}(MP) is the cathodic peak current of MP.

Table 2. Effect of interferents on the detection of MP at ERGO/GCE

Interference Analyte	% variation in the cathodic peak current (I_{pc} (MP) = 100%)
Glucose	65
Potassium	42
Sodium	48
Magnesium	62
Calcium	71
Vitamin C	58

Table 2 shows the results obtained from the experiments on interference effects. It is inferred that 40-72 % increase in the SWV current is observed depending on the interfering species.

3.8 Real Sample Analysis

The application of ERGO/GCE has been evaluated by real sample analysis using potato samples. Vegetable sample (potato) was obtained from the local market and cleaned using double distilled water. Two samples of 5 g each were kept in distilled water spiked with 2.0 x 10^{-8} M and 2.8 x 10^{-8} M concentration of MP. After a standing time of 24 h, the two samples were extracted with 30 mL of ether. The supernatants were then filtered through a 0.45 μm membrane and then evaporated to dryness [34]. About 2 mL of ethanol was added to the dry residue and diluted to 100 mL with 0.1M PSB (pH 7). SWVs were then recorded at ERGO/GCE and the signals were compared with those obtained for the standard MP solutions of 2.0 x 10^{-8} M and 2.8 x 10^{-8} M in PBS (pH 7) The SWV profiles and the peak potentials compare very well with those obtained for the MP standard solutions. The amount of MP found in the potato samples is estimated by measuring the SWV current and substituting in the calibration equation (Eq. 5.5). The % recovery is then calculated from these data (Table 3). It is inferred that nearly 80 % recovery is possible.

Table 3. Recovery data of MP present in potato at ERGO/GCE

Sample	Added (1x 10^{-8} M)	Found (1x 10^{-8} M)	Recovery %
Sample 1	2.0	1.7	85.0
Sample 2	2.8	2.2	78.5

4. CONCLUSION

The performance of an ERGO/GCE in the electrochemical detection of MP is evaluated in PBS at an optimum pH of 7. The effects of interferences and real samples analysis have been investigated. The application of square wave voltammetry leads to a detection limit of 8.8 x 10^{-10} M which is lower than that reported at a carbon paste electrode [27], nanoporous acetylene black–

chitosan film [30], ionic liquid (i.e. 1-butyl-3-methylimidazolium hexafluophosphate)–single walled carbon nanotube paste [31], MWCNT -polyacrylamide nanocomposite film [32].

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