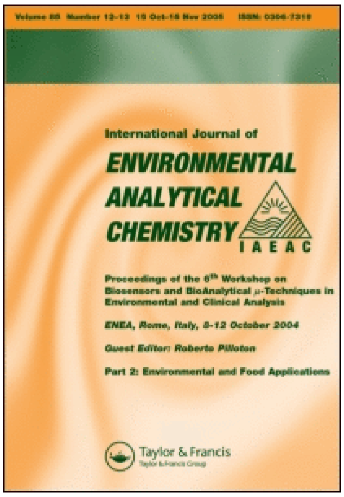

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Paramasivam Manisankar[a]; Palaniappan Abirama Sundari[a]; Raman Sasikumar[a]
[a] Department of Industrial Chemistry, Alagappa University, Karaikudi 630003, Tamil Nadu, India

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Square-wave stripping voltammetric determination of some organic pollutants using modified electrodes

Paramasivam Manisankar*, Palaniappan Abirama Sundari and Raman Sasikumar

Department of Industrial Chemistry, Alagappa University, Karaikudi 630003, Tamil Nadu, India

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A glassy carbon electrode (GCE) modified with multi-walled carbon nanotubes (MWCNT) and polymer/MWCNT composite was used to study the voltammetric behaviour of three common insecticides namely cypermethrin (CYP), deltamethrin (DEL) and fenvalerate (FEN). The modified electrode surface was characterised by scanning electron microscopy (SEM). The voltammograms of the above mentioned pollutants were studied in the pH range 1–13. Influence of scan rate (ν) was also studied. One well-defined reduction peak was observed for all the said insecticides at pH 13. A systematic study of the experimental parameters such as accumulation potential, accumulation time, initial scan potential, amplitude and frequency that affect the square-wave stripping voltammetric response was carried out and maximum peak current conditions were optimised. Under optimum conditions, stripping voltammetric procedure was developed for the determination of above-mentioned insecticides in conventional and real samples. Calibration plots were derived and the lower limit of determination was found. Sensing of polypyrrole/MWCNT/GCE well among the three electrode systems and the limit of detection (LOD) was found to be 1.17, 3.8 and 1.62 $\mu g\,L^{-1}$ for CYP, DEL and FEN, respectively. The percentage of relative standard deviation was also found.

Keywords: voltammetry; Carbon nanotubes (CNTs); modified electrode; square-wave stripping; real sample analysis; polymer composite

1. Introduction

Modified electrodes play a vital role in electroanalysis. Recently, conducting polymer [1], multi-walled carbon nanotubes (MWCNTs) [2,3] and polymer/MWCNT composite [4,5], modified electrodes have been developed and used as efficient sensors for the quantitative analysis of different analytes. Carbon nanotubes (CNTs) are attractive material because of their novel structure [6] since their discovery by Iijima [7]. They can be visualised as a sheet of graphite, which are rolled up into a cylinder and closed by two caps, with either a single-walled or multi-walled structure [8]. They are attractive materials for the development of electrochemical sensors because of their capability to provide strong electrocatalytic activity and minimise surface fouling of the sensors [3]. Carbon nanotubes display excellent chemical stability, good mechanical strength and electrical conductivity [6]. Their unique properties have led to significant applications in many fields such as electronics,

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*Corresponding author. Email: pms11@rediffmail.com

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medicine aerospace industry, etc., which has also prompted the need of analytical methodologies to characterise and control the quality of these nanomaterials. Furthermore, the use of CNTs as analytical tools, and the construction of nanodevices and nanosensors based on CNTs are other exciting areas of development for modern analytical science. Polyaniline (PANI) is an important conjugated conducting polymer, which shows good environmental stability, high electrical conductivity and unique redox properties [9,10]. More recently synthesis and properties of PANI/CNT composites have been reported by a number of authors [11–15]. Among the conducting polymers known to date, polypyrrole (PPY) have attracted special interest because of its high conductivity, ease and high flexibility in preparation, stability and good mechanical properties. Potential technological applications of PPY are in electronic and electrochromic devices [16,17], sensors [18,19], chromatographic stationary phases [20] and membrane separation [21]. Zhang *et al.* [22] synthesised PPY/MWCNT composite on gold electrode by *in situ* electropolymerisation method. Wang and Musameh [23] prepared glucose biosensor by incorporating MWCNT within electropolymerised PPY film. G. Han *et al.* [24], electrochemically synthesised PPY/MWCNT nanocomposite in 0.1 M aqueous solution of dodecylbenzene sulphonic acid. P3MT/MWCNT hybrid composite electrode has also been prepared, which gives rise to a remarkable improvement in the oxidation of NADH with respect to polymer-modified electrodes and CNTs-modified electrodes. Also, it enhances electrochemical behaviour of biologically important cytochrome c and FAD [25]. Nowadays, many research works have been focussed on CNT as modified electrode for the electrochemical determination of organophosphate pesticides [26], phenolic estrogenic compounds [27], ethamsylate [28] and rhein [29]. In addition, CNT paste electrodes (CNPE) are also prepared and employed as modifier for the effective determination of homo-cysteine [30].

The wide use of pesticides in agriculture to preserve crops from pests, as well as their high intrinsic toxicity, associated, in many instances, with a remarkable persistence in the environment, represents a potential danger for the health of ecosystems. Control of their concentration, in different matrices mainly in waters and soil is a key component of any strategy of environmental management and control. A wide number of analytical methods, based on the most commonly employed physico-chemical techniques such as UV, IR, high performance liquid chromatography (HPLC), gas chromatography (GC) and mass spectrometry (MS) [31–35] are available to detect and determine pesticides quantitatively in different matrices. But none of the above said techniques is effectively used to monitor the levels of pesticides in risk areas continuously. Hence, analytical methods are widely used which represents the most effective answer to the increasing worldwide demand of reliable and rapid determinations of the widest variety of analytes in complex matrices. In particular, stripping analysis is an extremely sensitive electrochemical technique for measuring trace level organics [36]. Recently, Souza and Machado [37] described the application of gold and carbon fibre microelectrodes for the electrochemical behaviour of organophosphate insecticides and bipyridilium herbicides, and the development of sensitive methodology for their analytical determinations in natural water samples. All the insecticides used in this work are pollutants, and used extensively in agricultural lands urging the researchers to develop and validate a suitable method for their effective detection and determination. The present article reports the use of MWCNT/glassy carbon electrode (GCE), PANI/MWCNT/GCE and PPY/MWCNT/GCE modified systems for the electrochemical determination of some insecticides such as cypermethrin (CYP), deltamethrin (DEL) and fenvalerate (FEN). Stripping voltammetric procedure was developed for the determination of above-mentioned pollutants at lower concentrations and in spiked soil samples.

2. Experimental

2.1 *Materials and methods*

Multi-walled CNTs (I.D. × length 2–15 nm × 1–10 μm) produced by arc method was purchased from Sigma Aldrich. AR sodium dodecyl sulphate (SDS) from Merck. Pyrrole (AR-Merck), Aniline (AR-Merck) and Lithium perchlorate (Sigma Aldrich) were used for electropolymerisation. Technical grade of all the insecticides were obtained from Bureau of Indian Standards. 0.1 M stock solution was made up in ethanol for all the three insecticides. For studies in aqueous media, 0.1 M H_2SO_4 (for pH 1), Britton Robinson Buffers (for pH 4, 7, 9.2), 0.1 M NaOH (for pH 13) in 50% aqueous alcohol were used.

CHI 760C electrochemical workstation (CH Instruments, USA) was employed mainly for carrying out electroanalytical studies. The modified GCE was used as a working electrode. The area of GCE is 0.0707 cm^2. Platinum wire and Ag/AgCl were employed as an auxiliary and reference electrode, respectively. Purging and blanketing of nitrogen were done for analyte solution placed in the electrochemical cell of 10 mL capacity for 20 min under stirring. To get reproducible results, great care was taken in the electrode pretreatment. GCE was pretreated in two ways as reported by us earlier [38,39]. Structures and physical properties of insecticides employed in this study are given in Table 1.

2.2 *Preparation of MWCNT modified GCE*

One milligram of MWCNT was dispersed in 1 mL of 0.1 M SDS using an ultrasonicator for 1 h to give black suspensions. GCE was modified by placing 5 μL of the MWCNT/surfactant suspensions, and then evaporating it in an oven at 50°C as reported by us earlier [40,41].

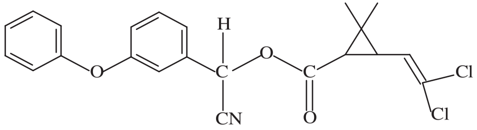
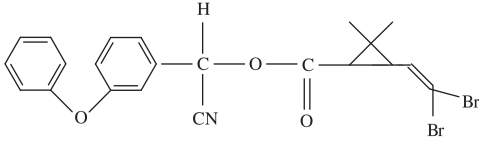
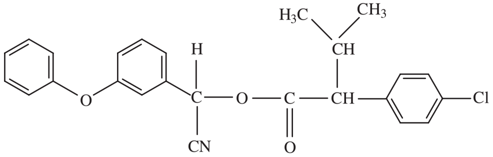
2.3 *Preparation of PANI/MWCNT/GCE and PPY/MWCNT/GCE*

Multi-walled carbon nanotube film-coated GCE was prepared as before. Polyaniline was deposited by electro-oxidation of 0.1 M aniline, in presence of 1 M sulphuric acid as a supporting electrolyte by applying a potential between −0.2 and 0.8 V and scan rate of 0.1 $V s^{-1}$. PPY film was deposited by the electro-oxidation of 0.1 M pyrrole in acetonitrile containing 0.1 M lithium perchlorate as a supporting electrolyte by applying a potential between 0 and 1 V and scan rate of 0.1 $V s^{-1}$.

2.4 *Cyclic voltammetry*

Preconditioned GCE, Pt wire and Ag/AgCl electrodes were inserted into the electrochemical cell and suitable aliquot of the stock solution was mixed with appropriate electrolyte solution to get 10 mL final volume of the required concentration. The solution was stirred and nitrogen was purged for 30 min. Then cyclic voltammograms were

Table 1. Structure and physical properties of the selected insecticides.

Compound	Structure	Class and physical nature
Cypermethrin [(RS)-α–cyano-3-phenoxybenzyl (1RS)-*cis*, trans-3-(2, 2-dichloro-vinyl)-2, 2-dimethylcyclopropanecarboxylate		Insecticide yellow brown viscous semi-solid, 2m.p. 60–80°C
Deltamethrin [cyano-(3-phenoxyphenyl)-methyl] 3-(2, 2-dibromoethenyl) -2,2-dimethyl-cyclopropane-1-Carboxylate]		Insecticide, crystalline, odourless, white powder m.p. 98–101°C
Fenvalerate [α-cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate]		Insecticide, clear viscous yellow liquid, vapour pressure 2.8 × 10^{-7} mm/Hg

recorded at various scan rates (0.025–0.5 V s^{-1}) and at various intervals of time. The criterion chosen for reproducibility was ±2 mV in the peak potential and ±2% variation in the peak current of a well-defined cyclic voltammogram. In analysing the experiment, care was taken to subtract the background current in each scan rate.

2.5 *Square-wave stripping voltammetry*

Measurements were made using square-wave stripping voltammetry (SWSV) for confirmation of cyclic voltammetry (CV) studies by following the similar procedure to that of CV studies. Square-wave stripping voltammetric studies were employed for the analytical study. Dilute solutions were preferred for stripping process.

Accumulation of the substrate was done in the first step and they were stripped in the second step. Various experimental parameters were optimised. The concentration limits were determined.

2.6 *Procedure for the preparation of soil samples*

The soil sample for analysis was collected from a Cauvery delta paddy field at Thiruthuraipoondi, Tamil Nadu State, India (10N31 79E39). Approximately 50 g of the sieved soil was spiked with 25 mL of 1 mM L^{-1} CYP solution by shaking in a closed bottle for about 30 min. CYP was extracted using dichloromethane. The extract was filtered and evaporated to dryness by gentle heating on a water bath. The residue was transferred into a 250 mL calibrated flask, dissolved in ethanol and made up to the mark. A 10 mL portion of this solution was transferred into a 50 mL calibrated flask and 0.1 mM L^{-1} NaOH containing 50% aqueous ethanol was used to dilute the contents of the flask to the required volume. The standard addition method was used. 0.05 mL aliquot of 1 mM L^{-1} CYP stock standard solution was added to the solution prepared as above. Square-wave stripping voltammetric studies under optimum experimental conditions were carried out to determine CYP in the soil sample. Similar soil samples analysis was done for DEL and FEN.

3. Results and discussion

3.1 *CV behaviour of the insecticides*

Cyclic voltammograms of the above said insecticides were recorded using three modified systems in the pH range 1–13 at a scan rate (ν) of 0.05 V s^{-1}. Cyclic voltammograms exhibited a reduction peak for all the three insecticides. Compared to other pHs, higher peak current, lower reduction potential and good peak shape were observed for the insecticides at pH 13 and hence this pH was chosen for detailed electroanalytical studies. The background current was recorded for all pHs and subtracted properly in calculating the peak currents.

Figure 1A(a–d) represented cyclic voltammograms of 0.7 mM L^{-1} CYP on bare GCE, MWCNT/GCE, PANI/MWCNT/GCE and PPY/MWCNT/GCE at pH 13 and scan rate of 0.05 V s^{-1}. It exhibited a well-defined reduction peak each at 1.44 V (10.02 μA), 1.42 V (40.59 μA), 1.41 V (60.41 μA) and 1.43 V (66.26 μA) on bare GCE and three modified systems, respectively. Absence of corresponding anodic peak in the reverse scan indicates

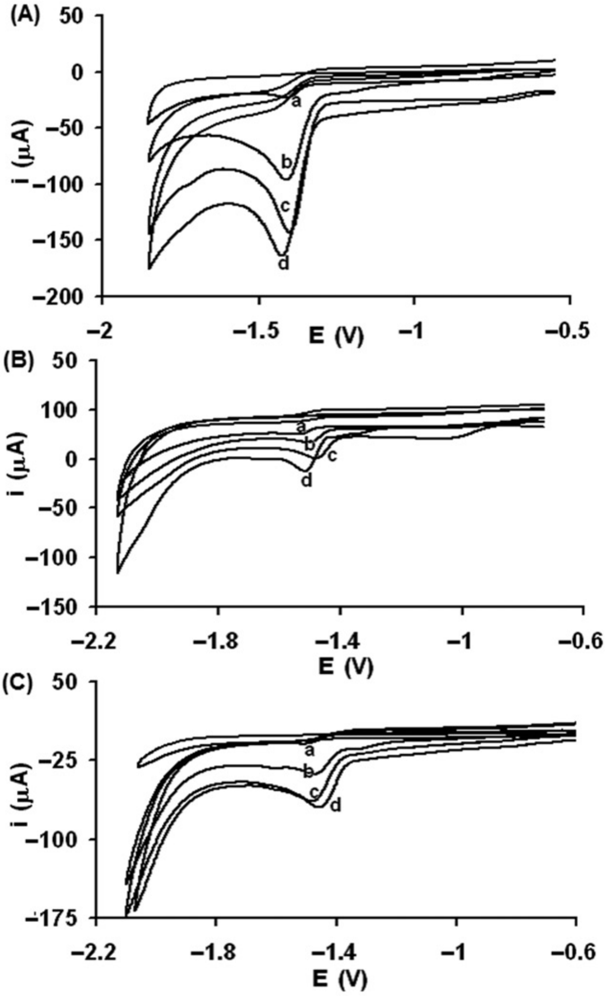


Figure 1. (A) Cyclic voltammogram of CYP; (B) Cyclic voltammogram of DEL; (C) Cyclic voltammogram of FEN at pH 13, scan rate = 0.05 V s^{-1} for concentration 0.7 mM L^{-1}, (a) bare GCE (b) MWCNT/GCE; (c) PANI/MWCNT/GCE; and (d) PPY/MWCNT/GCE.

irreversible electron transfer process. Scan rate was varied between 0.025 and 0.5 V s^{-1}. The relation between scan rate and peak current resulted in straight line at lower scan rates (up to 0.150 V s^{-1}) and at higher scan rates linearity with square root of scan rate is observed (Figures 4A and 4B). Log values of peak current ($\log i_p$) were plotted against log scan rate ($\log \nu$). Straight line with a slope from 0.47 to 0.56 was obtained at all the modified systems (Figure 4C). The –Ep versus $\log \nu$ plot also resulted in a straight line and a fractional αn value (0.66, 0.67, 0.71, 0.65 at bare GCE and three modified systems, respectively) indicating irreversible electron process. Hence, the overall reaction was irreversible and reduction of adsorbed reactant was found at all the modified systems.

The typical cyclic voltammogram of DEL is presented in Figure 1B(a–d). It exhibited a well-defined reduction peak each at 1.54 V (4.589 μA), 1.50 V (14.34 μA), 1.48 V

(24.12 μA) and 1.52 V (36.91 μA) on bare GCE and three modified systems, respectively. There was no anodic response observed in the reverse scan suggesting irreversibility. Peak current dependence on scan rate was studied by varying the scan rate from 0.025 to $0.5\,\mathrm{V\,s^{-1}}$. Peak current increases linearly with ν up to $\nu < 0.150\,\mathrm{V\,s^{-1}}$, while at higher scan rates a linear dependence of peak currents on $\nu^{1/2}$ is observed (Figures 5A and 5B). The slope of the plot of $\log i_p$ with $\log \nu$, 0.49 to 0.56 (Figure 5C) showing reduction of adsorbed reactant was found at all modified systems. Here too, irreversibility in electron transfer was observed owing to fractional αn value (0.60, 0.56, 0.58 and 0.52 at four different electrode systems, respectively).

The cyclic voltammogram of FEN for the scan rate of 0.05 V on bare GCE, MWCNT/GCE, PANI/MWCNT/GCE and PPY/MWCNT/GCE is presented in Figure 1C (a–d). It exhibited a well-defined reduction peak at −1.50 V (5.24 μA), −1.48 V (14.39 μA), −1.49 V (30.68 μA) and −1.46 V (33.35 μA) on all the said electrode systems, respectively. Absence of anodic peak suggested irreversible electron transfer nature of FEN. The plot of peak current versus scan rate resulted in straight line for the variation of scan rate from 0.025 to $0.150\,\mathrm{V\,s^{-1}}$ (Figure 6A). At higher scan rates, the peak current showed linearity with square root of scan rate (Figure 6B). Correlation of log peak current with log scan rate also resulted in straight line with a slope from 0.46 to 0.52 (Figure 6C) for all modified systems. Here also the electrochemical behaviour was similar to that of CYP and DEL. Fractional αn values (0.60, 0.56, 0.58, 0.52 at four different electrode systems, respectively) indicate irreversible electron transfer process. It is to be noted that higher peak current was observed with PPY/MWCNT/GCE than the other two modified systems for all the three insecticides.

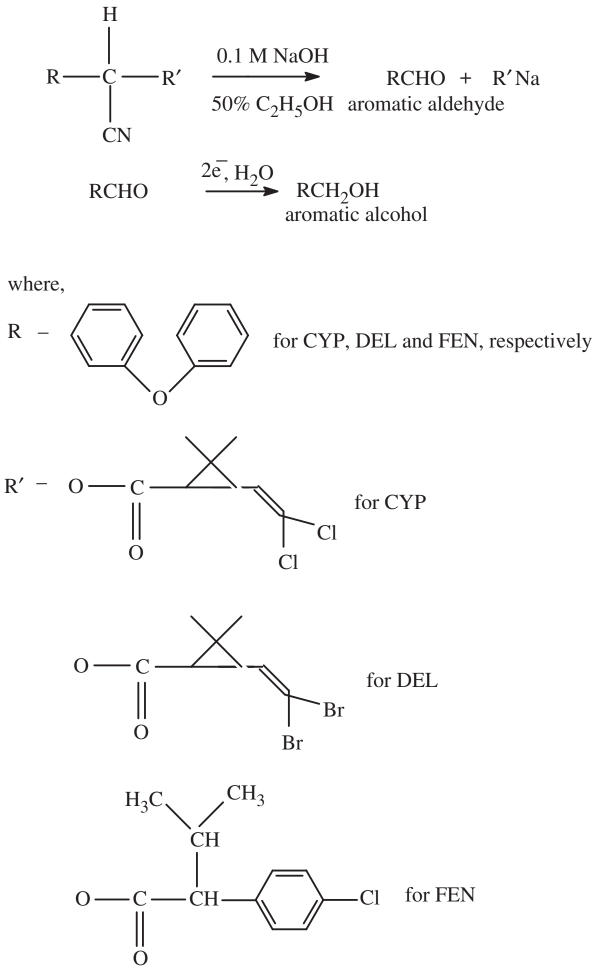
Here, all the reported insecticides responded almost at similar potential in cyclic voltammetry and their electrochemical behaviour was also similar. This is in accordance with the earlier report [42] and suggests that all the insecticides undergo hydrolysis during electrolysis and the resulted 3-phenoxy benzaldehyde undergoes reduction (Scheme 1).

3.2 *Adsorption studies*

Cyclic voltammetric results revealed good electroactivity of the substrate at pH 13 and diffusion-controlled adsorption behaviour. Hence adsorption studies were carried out at optimum accumulation potential. Square-wave mode was employed for stripping voltammetric studies as detailed below.

3.3 *Square-wave stripping voltammetric studies of the insecticides*

Stripping voltammetry involves two steps in which the first step is accumulation of the substrate on the electrode surface and the second step involves stripping. In this process, the accumulation potential (E_{acc}) was varied between −0.5 and 0.5 V and maximum peak current was observed at 0 V for CYP, FEN and 0.1 V for DEL, respectively. The accumulation of the three insecticides on the PPY/MWCNT/GCE modified surface under the optimum accumulation conditions was understood from the changes in the electrode surface before and after accumulation. Scanning electron microscopy (SEM) was performed for the insecticides accumulated on the



Scheme 1. Reduction mechanism of CYP, DEL and FEN.

electrode surface. The surface morphology of PPY/MWCNT/GCE is provided by us in our report [40] previously. Also MWCNT/GCE surface provide nano backbone for the polymerisation of pyrrole. SEM micrographs of adsorbed surfaces were given in Figure 2(A–C). The cluster of insecticide molecules arranged in an orderly fashion is evident from the provided micrographs, which may be due to that of PPY and adsorbed insecticides. This surface morphology is unquestionably distinct from that of MWCNT/GCE and PPY/MWCNT/GCE morphology. This confirms the adsorption process.

After fixing the accumulation potential, accumulation time was varied from 5 to 50 s for all the selected insecticides and maximum peak current was observed at 25 s for CYP, 20 s for DEL and 25 s for FEN. Initial scan potential (Eis) was varied from −0.2 to −1.0 V and optimum value obtained at −0.8 V for CYP, FEN and −1.0 V for DEL, respectively. Above-mentioned parameters are the optimised value and used for further studies. For the optimisation of square-wave conditions, the square-wave frequency and square-wave amplitude were examined by varying one of them and maintaining the others constant.

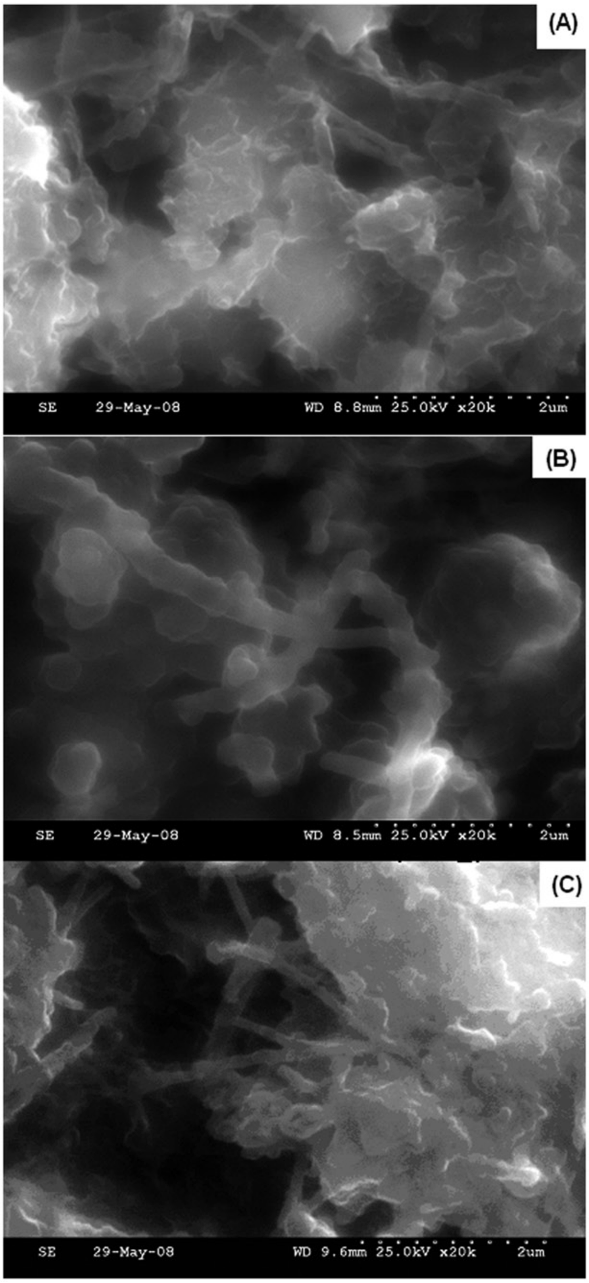


Figure 2. SEM micrograph of (A) CYP; (B) DEL; (C) FEN adsorbed on PPY/MWCNT/GCE.

Stripping peak current decreased with an increase in amplitude from 0.025 to 0.075 V. Hence, amplitude of 0.025 V was selected for all insecticides because of higher peak current response. The dependence of peak intensity on the square-wave frequency was studied between 5 and 50 Hz. Maximum peak current was at 20 Hz for CYP and FEN, 25 Hz for DEL, respectively. As the frequency increased above 50 Hz, peak current decreased and

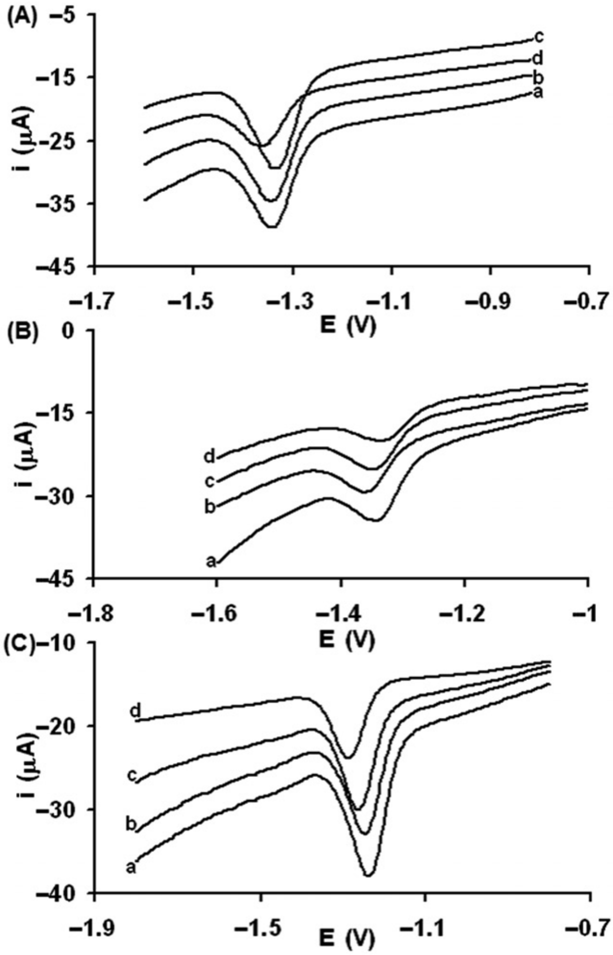


Figure 3. (A) SWSV of CYP; (B) SWSV of DEL; (C) SWSV of FEN for 25 mg L^{-1} at pH 13 (a) PPY/MWCNT/GCE; (b) PANI/MWCNT/GCE; (c) MWCNT/GCE; (d) real sample.

the peak was broadened. The square-wave stripping voltammograms thus obtained under optimum experimental conditions for three insecticides at concentration of 25 mg L^{-1} are given in Figures 3A–C. The experimental conditions that gave maximum current response are given in Figure 7.

3.4 *Analytical characteristics*

The experimental results showed that the peak current increased with increase in the concentration of insecticides. Calibration plots were made and linear dependence of concentration was observed. The regression equations obtained are given in Figure 7F. The reproducibility of the stripping signal was determined in terms of relative standard deviation (RSD) for five identical measurements carried out at a concentration level of 5 mg L^{-1}. Limit of detection (LOD) is the lowest concentration that can be distinguished

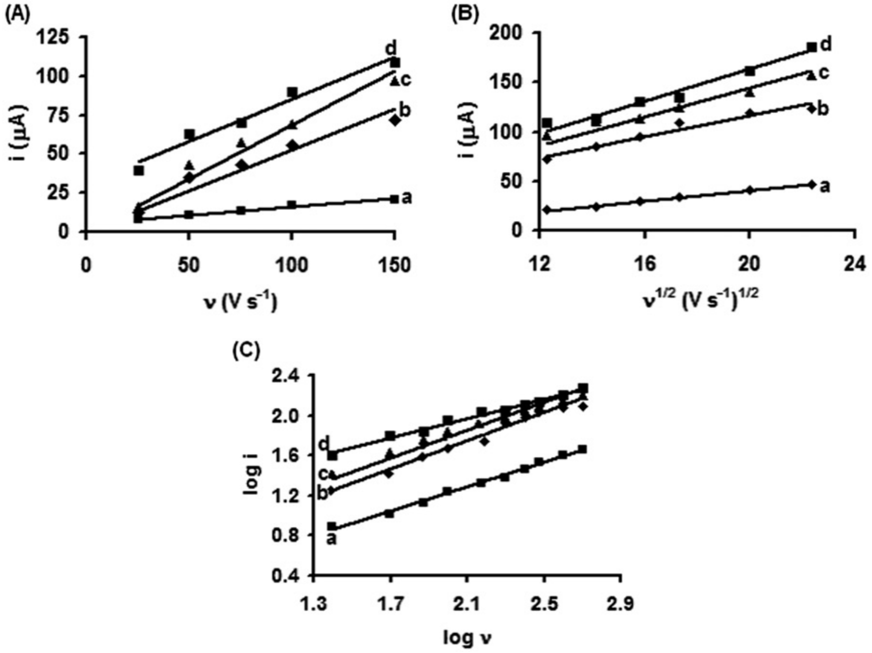


Figure 4. Cyclic voltammetric calibration plots of CYP (a) bare GCE; (b) MWCNT/GCE; (c) PANI/MWCNT/GCE; and (d) PPY/MWCNT/GCE.

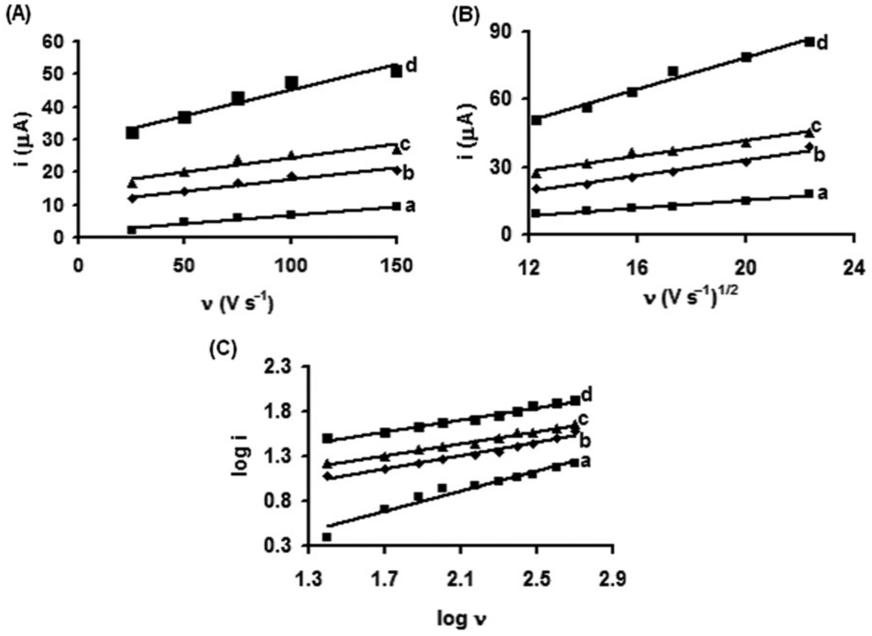


Figure 5. Cyclic voltammetric calibration plots of DEL (a) bare GCE; (b) MWCNT/GCE; (c) PANI/MWCNT/GCE; and (d) PPY/MWCNT/GCE.

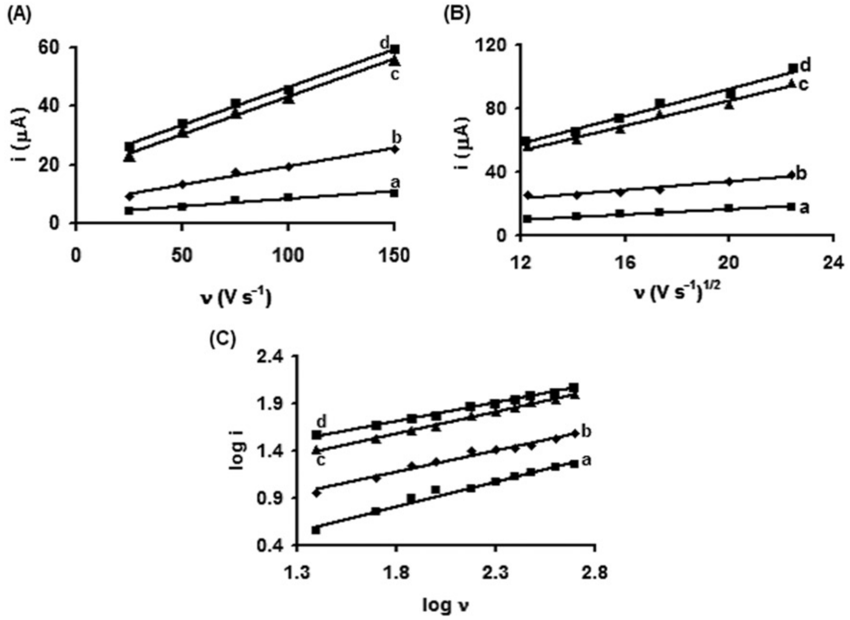


Figure 6. Cyclic voltammetric calibration plots of FEN (a) bare GCE; (b) MWCNT/GCE; (c) PANI/MWCNT/GCE; and (d) PPY/MWCNT/GCE.

from the noise level. The possible smallest peak current was measured in a particular concentration and the ratio between this and the background current measured at the same potential in the absence of analyte. In this study the concentration of insecticides giving signal to noise ratio of 3 : 1 was 1.17, 3.8 and 1.62 µg L^{-1} for CYP, DEL and FEN, respectively. Below this value for the respective insecticide, a hump instead of peak is observed and there is no linearity with concentration. The LOD was determined as 1.17, 3.8 and 1.62 µg L^{-1} for CYP, DEL and FEN, respectively on PPY/MWCNT/GCE system, respectively. The LOD values reported here are comparatively lower than the earlier reports and the values are compared in Table 2 [42–45]. This kind of determination is as per the earlier reports [1,46]. Among the three modified systems, lowest LOD was achieved in PPY/MWCNT/GCE. The effect of other coexisting substances and anions were studied. Known amounts of these species were added to a standard solution containing 250 µg L^{-1}. The solutions were analysed by the proposed method. The results obtained are provided in Table 3. The results showed that the foreign species tested do not interfere in the analysis under the reported conditions. This indicates the validity of the method.

3.5 *Reproducibility*

Five milligram per litre of CYP, DEL and FEN were determined continuously with the same electrode for several times and it was noticed that the height of voltammetric peak decreased greatly for every determination. It implied that species competed for the adsorbing sites, which influenced the height of voltammetric peaks when the analyte adsorbs on the electrode. So it was necessary to renew the electrode surface after every determination. Five milligram per litre of CYP, DEL and FEN were determined

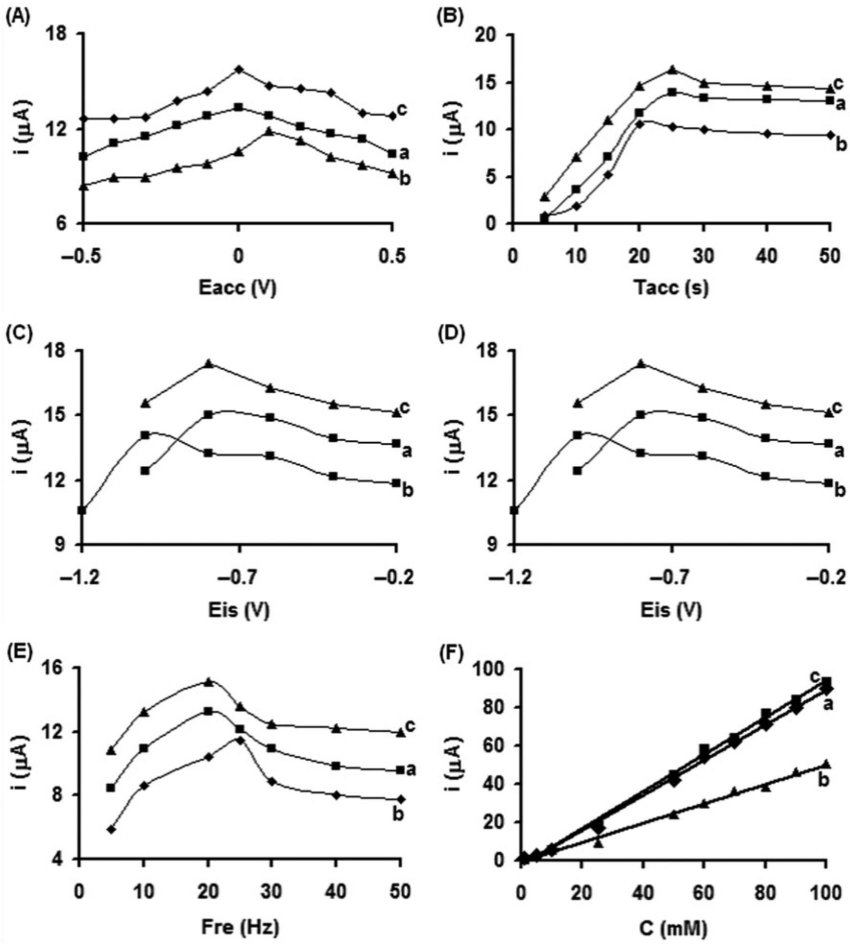


Figure 7. Square wave stripping voltammetric calibration curves of (a) CYP; (b) DEL; (c) FEN on PPY/MWCNT/GCE. (A) Plot of peak current (*i*) *vs*. Accumulation potential (E_{acc}); (B) Plot of peak current (*i*) *vs*. Accumulation time (T_{acc}); (C) Plot of peak current (*i*) *vs*. Initial scan potential (E_{is}); (D) Plot of peak current (*i*) *vs*. Amplitude (*AP*); (E) Plot of peak current (*i*) *vs*. Frequency (*Fre*); (F) Plot of peak current (*i*) *vs*. Concentration (*C*).

Table 2. Merits of comparable methods for the determination of selected insecticides.

		Insecticides			
S. no.	Techniques	CYP	DEL	FEN	Reference(s)
1	Voltammetric method (mg g^{-1})	2.5	2.5	–	[42]
2	Spectrophotometric method (mg mL^{-1})	0.467	0.345	0.273	[43]
3	Chromatography-ion trap mass spectrometry (mg kg^{-1})	0.016	0.013	0.003	[44]
4	GC/MS (mg kg^{-1})	0.10	0.08	0.08	[45]
5	LC/MS (mg kg^{-1})	0.02	0.03	0.02	[45]
6	Voltammetric method (μg L^{-1})	1.17	3.8	1.62	This article

Table 3. Tolerance limit of anions and other pesticides in the determination of 250 μg L^{-1} of CYP, DEL and FEN on modified systems.

Anions	Tolerance limit in μg L^{-1}	Other pesticides	Tolerance limit in μg L^{-1}
Cl^{-1}	550	Phenol	600
Br^{-1}	500	Malathion	700
I^{-1}	500	Methyl parathion	650
SO_4^{2-}	550	Endosulphan	550
NO_3^-	350	–	–

repeatedly with the electrode modified under identical conditions for five times. The relative standard deviation (RSD) of the selected insecticides was 3.5, 2.5, 3.1% for CYP, 2.8, 3.8, 2.3% for DEL, 2.2, 2.1, 1.5% for FEN on MWCNT/GCE, PANI/MWCNT/GCE, PPY/MWCNT/GCE, respectively, suggesting that this method possesses good reproducibility. The lifetime of the modified electrodes were examined and it demonstrated that the electrodes could retain 94.5% of its initial response after 2 weeks storage, suggesting that the modified electrode did possess long-term stability and seemed to be acceptable for most practical applications.

3.6 *Determination of insecticides in soil samples*

The stripping voltammograms obtained from real samples of CYP, DEL and FEN is given in Figures 3A(d)–3C(d) on PPY/MWCNT/GCE. Precision and accuracy of this method was determined after dosing known amount of analytes into environmental sample solution. Recovery percentage of CYP, DEL, FEN for the agrochemical product is 90.9 ± 4.3, 91.5 ± 4.3 and 93.3 ± 7.2 on PPY/MWCNT/GCE. The precision of all pollutants was calculated from five repeated analyses at different intervals. Based on this study, it is possible to conclude that these stripping voltammetric measurements are efficient in the determination of these insecticides. This method can be easily applied for the determination of other electroactive insecticides and pesticides in real samples.

4. Conclusions

A rapid and convenient electrochemical method is described for the determination of some common insecticides. All the selected insecticides exhibited good response in cyclic voltammetry and showed their electroactive nature. The reduction peak currents of used insecticides were strikingly enhanced at the modified electrodes. The electrochemical process was found to be irreversible reduction of adsorbed reactant at all the modified electrode systems. Based on this, square-wave stripping voltammetric procedure was developed for the determination of above said pollutants. PPY/MWCNT/GCE modified system considered to be better sensor than other two modified systems in which higher peak current and lowest LOD is found. This method was proposed for the determination of above-mentioned insecticides in spiked soil samples and the results are satisfactory.

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