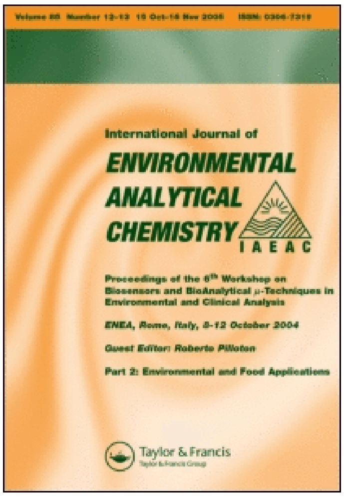

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Utilisation of polypyrrole modified electrode for the determination of pesticides

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Cyclic voltammetric studies of isoproturon and carbendazim using polypyrrole modified glassy carbon electrode were carried out. The electrode and reaction conditions, which yielded maximum current signal, were selected for the development of stripping voltammetric procedure for the determination of the pesticides. The oxidation peak around 1.3 V obtained for isoproturon and carbendazim while employing polypyrrole modified electrode showed maximum current response. This peak was chosen for stripping analysis using square wave mode. The experimental parameters were optimized and the calibration plot was obtained. The LOD was $0.5\,\mathrm{ng\,mL^{-1}}$ for isoproturon and $5\,\mathrm{ng\,mL^{-1}}$ for carbendazim. The relative standard deviation for 5 identical measurements was 2.81% and 3.33% for isoproturon and carbendazim respectively. The applicability of the method was verified by determining the pesticides in spiked soil and water samples.

Keywords: Isoproturon; Carbendazim; Polypyrrole; Stripping voltammetry; Electroanalysis

1. Introduction

Pesticides are highly toxic chemicals owing to their bioaccumulation properties. Trace contamination of these toxic organic compounds present in the natural aquatic systems is of special concern [1, 2]. Techniques such as TLC, HPLC/UV, GC/MS, UV and colorimetry have been used for the determination of residues of pesticides [3–12]. Isoproturon, a selective herbicide, is very stable to light and acid. It is listed in toxicity class III pesticides. Carbendazim is a benzamidazole fungicide that plays very important role in plant disease control for a long time. Its resistance is a very serious problem and it is listed in toxicity class IV pesticides. Apart from a recent indirect electrochemical method reported for the determination of isoproturon [13–15], perusal of literature

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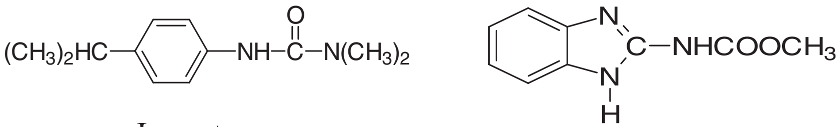
reveals that only little work has been done with regard to electroanalysis of the two pesticides.

Usage of conducting polymer as a modifier is a promising area [16–18] in electroanalytical chemistry. Coating a metallic or semiconductor electrode with a thin film of electroactive polymer has proved to be a simple and convenient method for preparation of modified electrodes. Polypyrrole film itself acts as an internal redox probe for pollutant [19]. Molecular recognition using conducting polymers is the basis of a new electrochemical sensing technology [20]. By employing the modified electrodes the sensitivity is increased and the limit of determination is considerably lowered. In this study, the electroactive nature of two different pesticides, isoproturon and carbendazim was ascertained using polypyrrole modified glassy carbon electrode. Studies were made to develop stripping voltammetric procedure for the determination of the pesticides.

2. Experimental

2.1. *Apparatus and reagents*

EG&G M273A Electrochemical Analyzer (Princeton Applied Research Corporation) was employed mainly for carrying out electroanalytical studies. The two pesticides of technical grade were obtained from the Bureau of Indian Standards and recrystallised in chloroform and used (Scheme 1).



Isoproturon

Carbendazim

A 1.0×10^{-2} mol dm^{-3} stock solution was made up in ethanol. For studies in aqueous media, Britton Robinson Buffers, 0.1 mol dm^{-3} KOH, KCl and 0.1 mol dm^{-3} H_2SO_4 in 50% aqueous alcohol were used as the medium for the analysis. Pyrrole (AR-Merck) and tetra butyl ammonium perchlorate (Sigma) were used for electropolymerisation. Amberlite XAD-4 resin (Fluka), ethanol, diethyl ether, dichloromethane were purchased from Merck AR grade.

2.2. *Procedure*

Purging and blanketing of nitrogen were done for analyte solution placed in the electrochemical cell of 15-mL capacity for 15 min under stirred conditions. Then various voltammograms were recorded. To get reproducible results, great care was taken in the electrode pretreatment. The glassy carbon electrode was pretreated in two ways: Mechanical polishing over a velvet micro-cloth with an alumina suspension and electrochemical treatment by applying a potential of 1.5 V for 2 s. The electrochemical pretreatment was done in the same supporting electrolyte solution in which the measurements were carried out.

2.3. *Preparation of polypyrrole coated glassy carbon electrode (Ppy/GCE)*

The polypyrrole deposition was done with modifications in the already reported methods [21, 22]. Polypyrrole films were obtained by the electrooxidation of 0.1 M pyrrole in acetonitrile containing 0.1M tetrabutyl ammonium perchlorate and cetyl trimethyl ammonium bromide at +0.90 V (vs. Ag/AgCl) applied potential. Thickness of the films was controlled coulometrically and 0.1 μ thick films were used in all cases.

Care was taken to remove the coating and clean the glassy carbon electrode after every experiment in 1:1 HCl/water and 1:1 H_2O_2/acetic acid mixture before usual surface treatment. Nitric acid (6 M) solution was used to clean the cell.

3. Results and Discussions

3.1. *Cyclic voltammetric (CV) studies*

Cyclic voltammograms of isoproturon and carbendazim were recorded using unmodified and polypyrrole modified glassy carbon electrode in acid, neutral and alkaline conditions at different sweep rates ranging from 0.025 to 0.300 V s^{-1}. The background current was recorded for all sweep rates and subtracted properly in calculating the peak currents. The potential window at various pH under zero pesticide conditions was found out and employed. Since the pesticides undergo hydrolysis above pH 10.0, influence of pH on the electrochemical response was studied by varying the pH from 1.0 to 10.0. As an illustration, the cyclic voltammograms pesticides at pH 1.0, 7.0 and 10.00 for isoproturon and carbendazim are presented in figure 1 and 2 respectively. The blank cyclic voltammograms obtained at polypyrrole modified glassy carbon electrode and the cyclic voltammograms obtained at unmodified glassy carbon electrode are also included in the figures. In all cases one main anodic peak is observed above 1.2 V. The peak potential and current of this well-defined anodic peak were considered for the study of effect of pH. Figure 3 show the variation of peak potential with pH. Protonation followed by oxidation leads to the dependence of peak potential with pH for isoproturon. As the pH increases the proton involvement decreases and hence higher potentials are required for the oxidation of isoproturon. In the case of carbendazim, the oxidation followed by the nucleophilic attack of the solvent or hydroxide ion takes place. Hence as the pH increases the oxidation is facilitated and it takes place at lower potentials. The peak current showed a decreasing trend with increasing pH. The peak current exhibits maximum value at pH 1.0 for both pesticides. The cyclic voltammograms of the pesticides on unmodified and polypyrrole modified glassy carbon electrodes exhibit only one oxidation peak and reveal that the modified electrode system at pH 1.0 is more suited for the electrochemical studies. The development of electroanalytical determination procedure for the two pesticides on polypyrrole modified glassy carbon electrode is chosen owing to higher peak current responses. The increase in peak current may be due to increase in the electroactive surface area in modifying the glassy carbon surface with doped polypyrrole.

3.2. *Electrochemical studies of isoproturon (ISO) on polypyrrole modified electrode*

The effect of sweep rate was studied by recording cyclic voltammograms at different sweep rates from 0.025 to 0.300 V s^{-1} at a pesticide concentration of

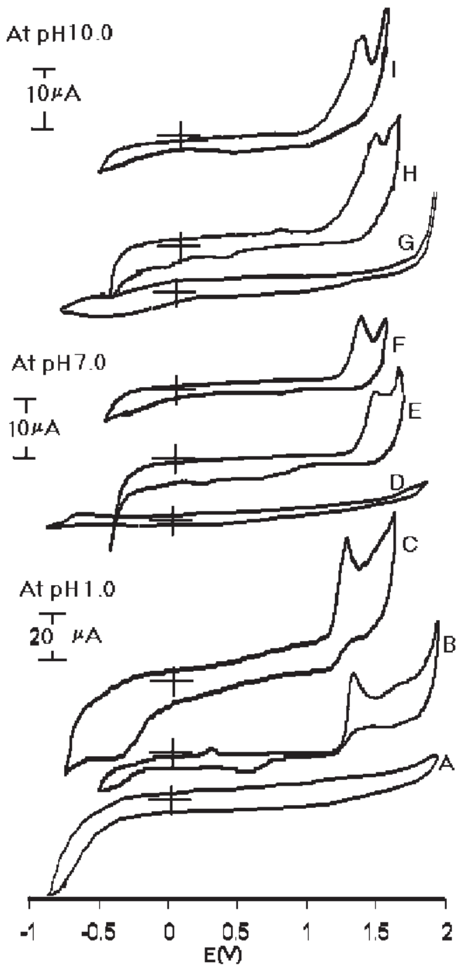


Figure 1. Cyclic voltammogram of (A) zero pesticide on Ppy/GCE at pH 1.0 (B) 9.9×10^{-4} mol dm^{-3} isoproturon (ISO) on GCE at pH 1.0 (C) 9.9×10^{-4} mol dm^{-3} ISO on Ppy/GCE at pH 1.0 (D) zero pesticide on Ppy/GCE at pH 7.0 (E) 9.9×10^{-4} mol dm^{-3} ISO on GCE at pH 7.0 (F) 9.9×10^{-4} mol dm^{-3} ISO on Ppy/GCE at pH 7.0 (G) zero pesticide on Ppy/GCE at pH 10.0 (H) ISO on GCE at pH 10.0 and (I) 9.9×10^{-4} mol dm^{-3} ISO on Ppy/GCE at pH 10.0; Scan rate100 mV/sec.

9.9×10^{-4} mol dm^{-3}. The anodic peak around +1.3 V was well shaped with higher current. As the sweep rate increased, the current of the main oxidation peak also increased. There was a good linear correlation obtained between i_p and ν ($i_p = 0.6811\,\nu + 81.179$, $r^2 = 0.990$) suggesting adsorption-controlled reaction.

The multiple cyclic voltammograms at unmodified GCE (figure 4), showed one main anodic peak, another small anodic peak and a reduction peak in the first cycle. As the cycle increased, the main anodic peak current decreased and the other two peak currents increased. The suffering of main anodic oxidation may be due to the adsorption of the intermediate whose redox behaviour is facilitated. Very interesting features were obtained only in the multiple run cyclic voltammetric studies at Ppy modified GCE. The multiple run voltammogram was started and the progress of the cycle was

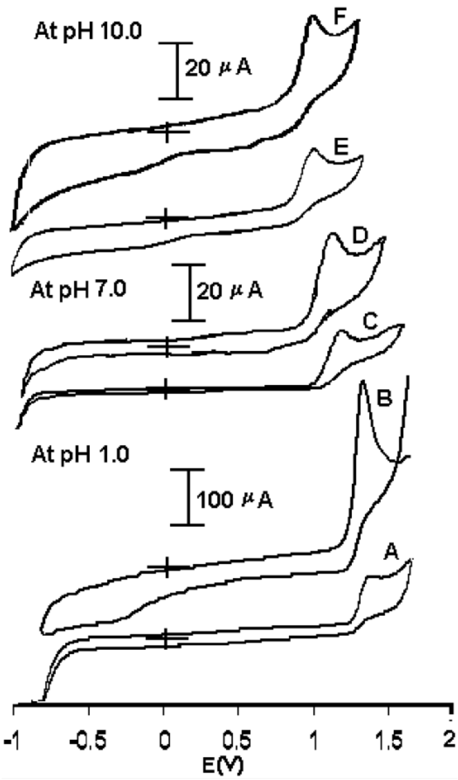


Figure 2. Cyclic voltammogram of $9.9 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ carbendazim (A) on GCE at pH 1.0 (B) on Ppy/GCE at pH 1.0 (C) on GCE at pH 7.0 (D) on Ppy/GCE at pH 7.0 (E) on GCE at pH 10.0 and (F) on Ppy/GCE at pH 10.0; Scan rate100 mV/sec.

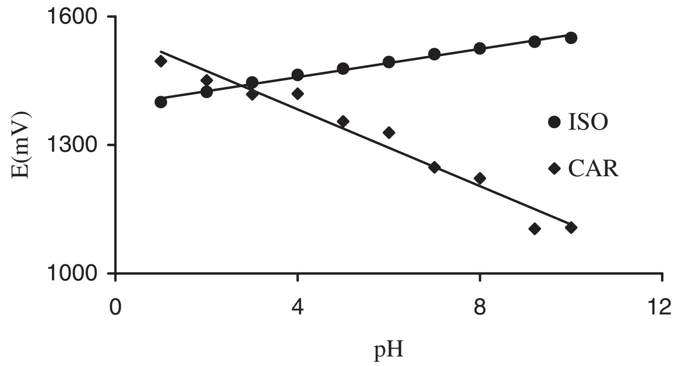


Figure 3. Plot of potential vs. pH ISO-Isoproturon, CAR-Carbendazim.

monitored (figure 5). Apart from the anodic peak around +1.3 V, another anodic peak around +0.85 V and cathodic peak around +0.58 V with lesser current and sharpness were observed. The two peaks around +0.85 and +0.58 V were noticed only after the third cycle and when the initial potentials were switched from or above 1.0 V; otherwise

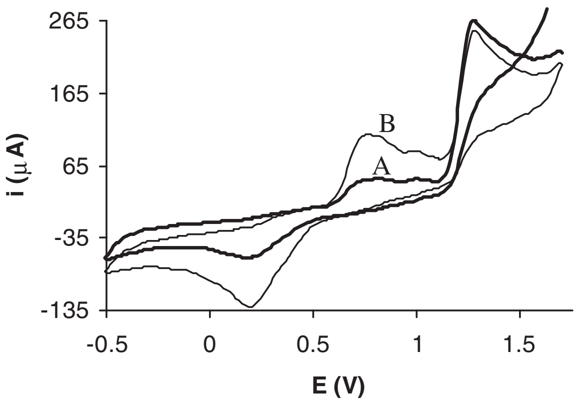


Figure 4. Cyclic voltammograms of 9.9×10^{-4} mol dm^{-3} isoproturon at pH 1.0 on GCE Scan rate: 100 mV/sec. A – first cycle B- 10th cycle.

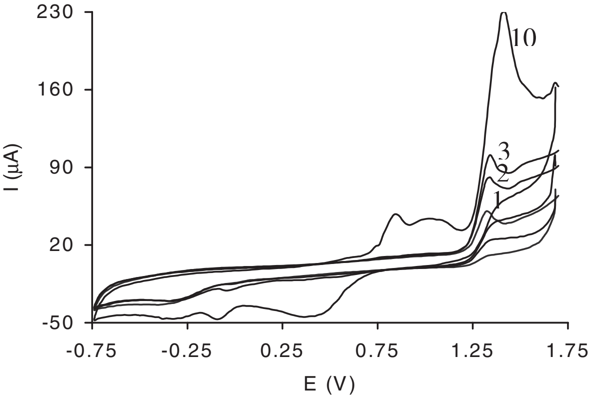


Figure 5. Cyclic voltammograms of 9.9×10^{-4} mol dm^{-3} isoproturon at pH 1.0 on Ppy/GCE Scan rate: 100 mV/sec. 1 – first cycle, 2- second cycle, 3- third cycle, 10-tenth cycle.

these two peaks were absent. This might be due to the reduction followed by the oxidation of the intermediate produced in the main oxidation step. Up to 3 cycles the voltammograms were as usual. After that a sudden switching appeared and the peak currents increased steadily for all the peaks. The cyclic voltammograms resembled that of polyaniline with extra peak at higher potential. Such type of cyclic voltammograms is different from that obtained with unmodified electrode. This may be explained as follows. In the initial scans, the isoproturon adsorbed and accumulated on the pores of the polypyrrole film undergoes oxidation and produces 4–isopropylaniline. As the cycle increased and as soon as the concentration of the 4-isopropylaniline reached sufficient levels for polymerization, then polymerization of 4-isopropylaniline started. Because of the conducting polymer formed on the pores of the polypyrrole film, more conductivity was observed. Hence more and more oxidation of isoproturon took place. This was confirmed from the SEM studies also. The SEM photographs of polypyrrole modified electrode (figure 6A) and isoproturon accumulated surfaces

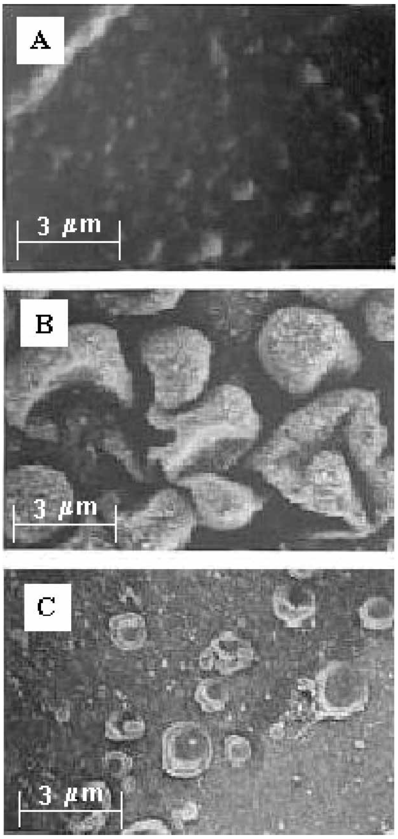
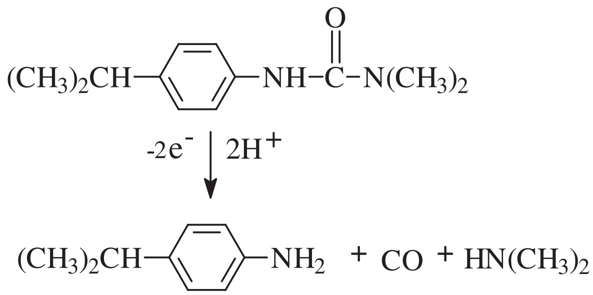


Figure 6. SEM photographs of (A) Ppy/GCE surface prepared from 0.1 M pyrrole with CTAB (B) 9.9×10^{-4} mol dm^{-3} of isoproturon on Ppy/GCE (C) 9.9×10^{-4} mol dm^{-3} of carbendazim on Ppy/GCE surface.

(figure 6B) showed well-developed crystalline deposits on the polypyrrole film of the later suggesting the formation of poly-4-isopropylaniline. Because of the composite conducting electrode surface, the oxidation of isoproturon was facilitated and hence this electrode system was considered as the best system for the development of stripping voltammetric determination procedure.

The number of electrons transferred was calculated from controlled potential coulometric studies. The controlled potential coulometry was carried out using the polypyrrole modified glassy carbon electrode at the appropriate potential at pH 1.0 to determine the number electrons involved in the oxidation. The charge consumed with respect to time and the number of electrons transferred was found to be 2. This is comparable with the already published results [1, 13].

Bulk electrolysis was carried out using a piece of glassy carbon plate of area 18 cm^2 at pH 1.0 and potential 1.3 V. The deposition of polypyrrole on a glassy carbon electrode of larger area might not be uniform. The proposed product from the electrolysis would be a polymer. Hence the electrolysis of isoproturon was carried with bare glassy carbon electrode. The electrolysis was proceeded up to a minimum value of current. The post-electrolysis solution was neutralized with dilute ammonia and the pH was brought to neutral (pH 7.0). The organic compounds liberated were extracted with ether, the ether solution was dried and the ether was distilled. The residual oil was distilled and the structure of the product was confirmed through the following data. ^{1}H-NMR (360 MHz – Bruker WH-360) δ-scale: 6.88 (2H, dd, $J_{\mathrm{ortho}} = 7.6$ Hz & $J_{\mathrm{meta}} = 1.8$ Hz), 6.38 (2H, dd, $J_{\mathrm{ortho}} = 7.6$ Hz & $J_{\mathrm{meta}} = 1.8$ Hz), 4.1 (1H, s), 3.12 (1H, hep) and 1.29 (6H, d). The ^{1}H-NMR data shows two doublet of doublet accounting each for 2 protons in the aromatic region. The doublet of doublet centered at 6.88 δ may be due to two aromatic hydrogens ortho to isopropyl group and coupling may be ortho and meta. Another doublet at 6.38 δ may be due to two hydrogens ortho amino group and the coupling may be ortho and meta. A heptet accounting for 1 proton at 3.12 δ may be due to methine proton in the isoprpyl group. A doublet accounting for 6 protons at 1.29 δ may be due to two methyl groups in the isopropyl group. These assignments suggest the presence of an isopropyl group and the compound is para-disubstituted benzene. Apart from this a small peak around 4.1δ represents NH_2 group. From this, it is concluded that 4-isopropyl aniline is produced during electrolysis. Anodically deposited polypyrrole on the glassy carbon electrode is present in the oxidized state. The protonated isoproturon undergoes oxidative cleavage and the polypyrrole is changed in to reduced form. The electrons are transmitted to the bare electrode. On the basis of the above results, the following probable mechanism is proposed (Scheme 2).



The 4-isopropylaniline formed may undergo polymerization on polypyrrole surface. The conducting electrode surface facilitated the polymerization. The crystalline structure seen on the surface was evident for the polymerization on the pores of the polypyrrole surface. Hence it is concluded that isoproturon molecules are specifically oxidized on the polypyrrole film and the product is accumulated on the cavities. The oxidized product 4-isopropylaniline undergoes redox reaction and the corresponding polymer is formed on the cavities.

3.3. *Electrochemical studies of carbendazim (CAR) in polypyrrole modified electrode*

Carbendazim showed only one well-defined anodic peak around 1.5 V in the cyclic voltammogram (figure 4). A linear relationship ($i_p = 0.7061\,\nu + 142.35$, $r^2 = 0.9914$) between the peak current and sweep rate was observed when i_p was correlated with sweep rate suggesting adsorption of carbendazim on the modified electrode surface. The multiple run cyclic voltammogram (figure 7) showed a gradual decrease in the peak current in the successive CV runs. There was no polymerization noticed as in the case of isoproturon because of the formation of non-conducting intermediate.

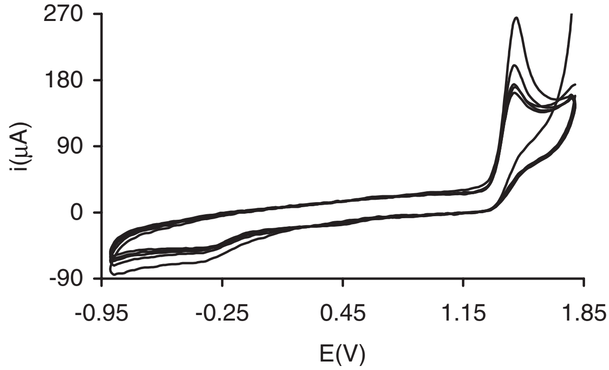
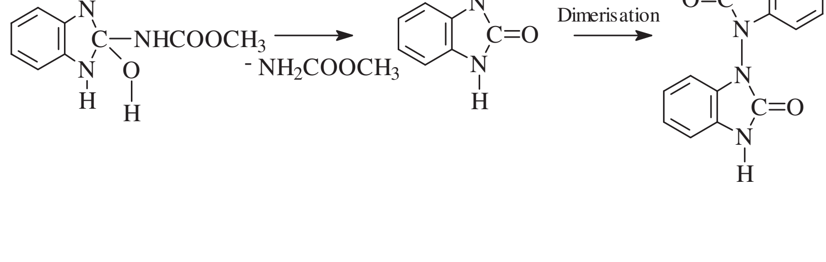


Figure 7. Cyclic voltammogram (multiple run) of 9.9×10^{-4} mol dm^{-3} carbendazim at pH 1.0 on Ppy/GCE Scan rate 100 mV/sec.

Hence the adsorption of substrate may passivate the electrode surface and cause a decrease in peak current. The SEM photograph (figure 6C) of the surface after 20 numbers of cycles confirmed the absence of polymerization as in isoproturon. Hence it is concluded that the compound is adsorbed on the polypyrrole surface.

The calculations of number of electrons transferred and bulk electrolysis were done as in isoproturon. The number of electrons transferred was found to be one. After electrolysis, the solution was neutralized and the organic component was extracted with chloroform. The solvent was dried and removed under vacuum. The residue was chromatographed on silica gel column using benzene/ethyl acetate eluent in the ratio 2:1. Here also oxidative cleavage takes place. The oxidation product was confirmed as 3H,3′H-[1,1′]bibenzoimidazole from ^{1}H-NMR spectral results. ^{1}H-NMR data are as follows:

^{1}H-NMR (360 MHz – Bruker WH-360) δ-scale: 7.56 (2H, dd, $J_{\text{ortho}} = 7.8$ Hz and $J_{\text{meta}} = 2$ Hz), multiple centered at 6.65 (6H) and 6.2 (2H, s). The NMR data showed one doublet of doublet accounting for 2 protons in the aromatic region. The multiplet centered at 6.65 δ might be due the rest of the 6 aromatic protons. Another singlet accounting for 2H at 6.2 δ might be due to two amino hydrogens within the ring. These assignments partially suggested the presence of urea group in a ring having one NH group and two aromatic rings. The assignment of aromatic protons may suggest the possibility of dimmer (Scheme 3). The melting point is 162–164°C and the yield is 51%.



3.4. *Square wave stripping voltammetry*

Square wave stripping voltammetric experiments were carried out to ascertain the best conditions for the adsorption process. Many preconcentration-stripping experiments were performed for accumulation potentials (E_{acc}) varying from −0.25 to 1.0 V and at an accumulation time (t_{acc}) of 5 s, to evaluate the electrostatic attraction/repulsion between electrode surface and the pesticide substrate. Maximum peak current was found at 0.9 V accumulation potential for isoproturon (figure 8A). This might be due to the electrostatic interaction between the positive nature of electrode at this potential and the electron rich substrate. In a similar manner, carbendazim showed maximum peak current at 0.25 V accumulation potential. The accumulation times 20 and 10 s led to the maximum peak current for isoproturon and carbendazim respectively

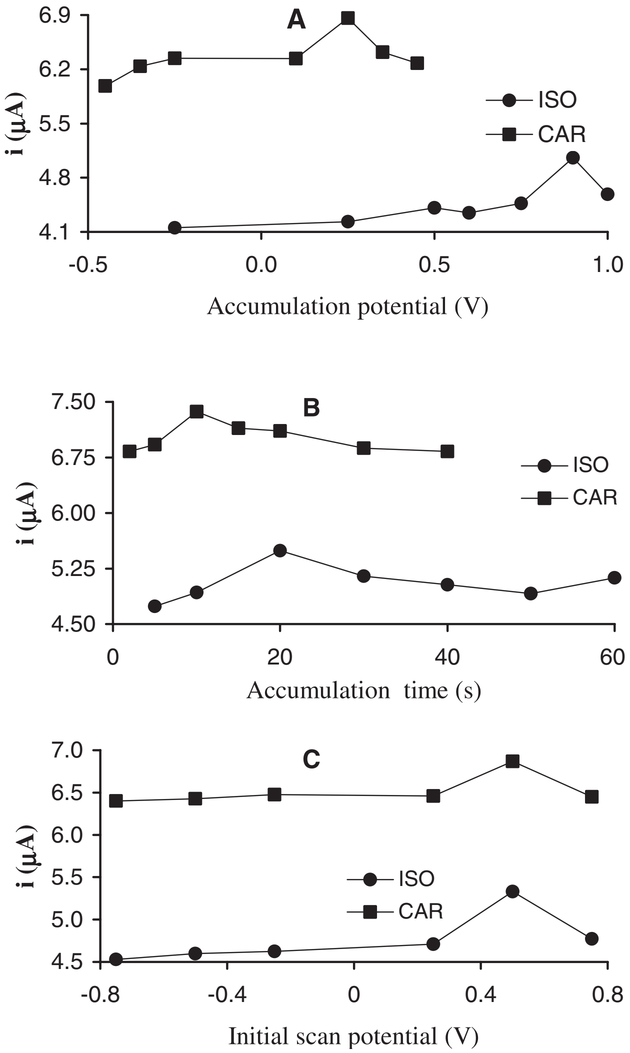


Figure 8. Plot of current vs (A) Accumulation potential (B) Accumulation time (C) Initial scan potential.

Table 1. Optimum experimental conditions arrived in SWSV.

	Optimum value	
Variable	ISO	CAR
Ph	1.0	1.0
Accumulation potential (V)	0.90	0.25
Accumulation time (s)	20	10
Initial scan potential (V)	0.50	0.50
Square wave amplitude (mV)	100	100
Frequency (Hz)	70	70
Step potential (mV)	5	5
Rest period (s)	5	5

(figure 8B). The maximum current signal condition was due to maximum electrode surface coverage under these conditions.

The initial scan potential, (E_{is}), is also an important parameter in controlling the peak characteristics. The initial potential was varied between −0.75 to 0.75 V and an initial scan potential of 0.5 V (figure 8C) was chosen for stripping voltammetric studies of the pesticides because of maximum current signals. The stripping peak current increased with an increase in square wave amplitude from 25 to 150 mV and decreased above 150 mV. However, amplitude of 100 mV was selected owing to maximum current peak response. The dependence of the peak current on the frequency was studied between 10 and 100 Hz. This experiment was carried out for a constant value of the step potential 4 mV and the results showed the maximum peak current at 70 Hz. Lower current response was observed for higher frequency values between 80 and 100 Hz. At higher frequencies, the background current increased sufficiently and hence the peak shape is affected. Broadening of the peak was also seen. When the step potential was varied between 2 and 10 mV, a decrease in peak current was observed above 5 mV. Hence, a frequency of 70 Hz and a step potential of 5 mV were used which provided sufficiently sensitive analytical signal at a reasonable scan rate of 350 mV s^{-1}. The effects of stirring rate (100 to 2000 rpm) and rest period (2 to 30 s) were studied. The optimum values were found to be 300 rpm and 5 s respectively. The experimental conditions for maximum signal from square wave stripping voltammetry are given in table 1. A representative stripping voltammogram of the pesticides are given in figure 9.

3.5. *Analytical characteristics*

Square wave stripping voltammograms at different concentrations of isoproturon and carbendazim were recorded using their maximum signal conditions. The peak current linearly increased with an increase in concentration. The calibration plots of i_p vs. Conc. ($i_{p(\mathrm{ISO})} = 0.312$ conc. –0.7254; $R^2 = 0.984$, $i_{p(\mathrm{CAR})} = 0.1761x + 0.0257$; $R^2 = 0.993$) are presented good linear correlation. The range of determination was from 0.5 to 300 ng mL^{-1} for isoproturon and 5 to 500 ng mL^{-1} for carbendazim. The LOD was 0.5 ng mL^{-1} for isoproturon and 5 ng mL^{-1} for carbendazim. The relative standard deviation found for five identical measurements of the stripping current at

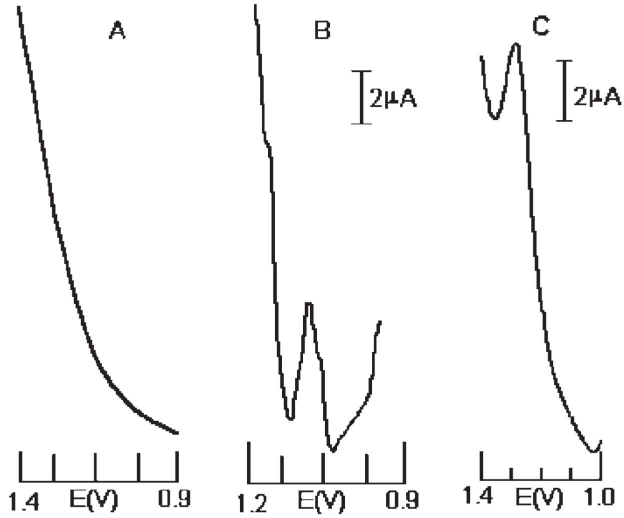


Figure 9. Square wave stripping voltammetric behaviour of (A) Ppy (B) isoproturon (C) carbendazim under optimum conduction.

Table 2. Tolerance limit of anions and other pesticides in the determination of $200\,\mathrm{ng\,ml^{-1}}$ isoproturon and carbendazim on Ppy/GCE by SWSV.

Anions	Tolerance limit in $\mathrm{ng\,mL^{-1}}$	Other pesticides	Tolerance limit in $\mathrm{ng\,mL^{-1}}$
Cl^-	500	Phenol	550
Br^-	450	Malathion	650
I^-	450	Methyl parathion	600
SO_4^{2-}	500	Endosulfan	500
NO_3^-	300	–	–

$100\,\mathrm{ng\,mL^{-1}}$ analyte concentration was 2.81% for isoproturon and 3.33% for carbendazim.

The effect of other coexisting substances and anions were studied. Known amounts of these species were added to a standard solution containing $200\,\mathrm{ng\,mL^{-1}}$. The solutions were analyzed by the proposed method. The results obtained are shown in table 2. The results show that the foreign species tested do not interfere in the analysis under the reported conditions. This indicates the validity of the method.

3.6. *Proposed method for the determination of pesticides in soil sample*

The soil sample analyzed was collected from a paddy field in Karaikudi and was washed repeatedly with water and exposed to the atmosphere. Approximately 50 g of the sieved soil was spiked with 10 mL of $10\,\mathrm{ng\,mL^{-1}}$ isoproturon stock solution by shaking in a closed bottle for about 30 min. Isoproturon was extracted using 100 mL 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

Table 3. Isoproturon and carbendazim percentage of recovery from soil samples.

Compounds	Added in ng mL^{-1}	Found* in ng mL^{-1}	Recovery in %	RSD*
Isoproturon	10	8.09	80.90	2.93
	50	44.39	88.78	3.32
	100	93.71	93.71	2.95
	200	182.70	91.35	2.63
Carbendazim	25	20.23	80.92	2.71
	75	61.38	81.84	2.96
	100	88.98	88.98	3.53
	250	219.18	87.57	3.07

*n = 6

Table 4. RSD value and percentage of recovery from water spiked samples of isoproturon and carbendazim.

Compounds	Added in ng mL^{-1}	Found* in ng mL^{-1}	Recovery in %	RSD*
Isoproturon	10	8.99	89.90	2.63
	50	43.89	87.78	3.02
	100	94.41	94.41	2.85
	200	183.65	91.83	2.53
Carbendazim	25	19.63	78.52	2.92
	75	63.31	84.41	2.84
	100	90. 89	90.89	3.47
	250	220.78	88.31	2.87

*n = 6

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 H_2SO_4 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 the 10 ng mL^{-1} isoproturon stock standard solution was added to the solution prepared as described above. Square wave stripping voltammetry was recorded under the maximum current signal conditions for the determination of isoproturon in the soil samples. Similar soil samples analyses were done for other concentrations of isoproturon and carbendazim. Six identical measurements were made and the relative standard deviations of isoproturon and carbendazim were given in table 3.

3.7. *Determination of pesticides in spiked water sample*

The spiked water sample was prepared by adding known amount of isoproturon (10–200 ng) stock solution and pesticide-free water and then allowing them to stand 24 h. A glass column was filled with Amberlite XAD-4 resin up to a height of 20 cm. The column was washed with ethanol, diethyl ether and distilled water. Then the spiked water was filtered through the column at an average rate of 10 mL min^{-1}. After completed this process the tap was closed and dichloromethane filled with column and then allowing them to stand 20 min after the column was drained into a beaker. The extract was 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. The isoproturon was determined by square wave stripping voltammetric method. Similar way the carbendazim also determined. The recovery percentage of pesticides and relative standard deviations were found out and presented in table 4.

4. Conclusions

Isoproturon and carbendazim were electroactive and gave good responses at pH 1.0 when polypyrrole modified glassy carbon electrode was employed. Isoproturon was oxidised to 4-isopropylaniline, which underwent polymerisation in continuous cycling and increased the conductivity of the electrode surface and reactivity of isoproturon. Carbendazim was adsorbed on the surface and oxidised to a dimer. Based on the enhanced electroactivity on the polypyrrole-modified electrode, the stripping voltammetric determination procedure was developed. The presence of PPY film leads to wide range of determination and the limit of determination is also lower than that with bare glassy carbon. The procedure is simple and it leads to the limits of determination down to ppb levels. High sensitivity, good reproducibility, and simple instrumentation were the added advantages. This method may be easily applied for the determination of these pesticides in spiked soil and water samples.

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