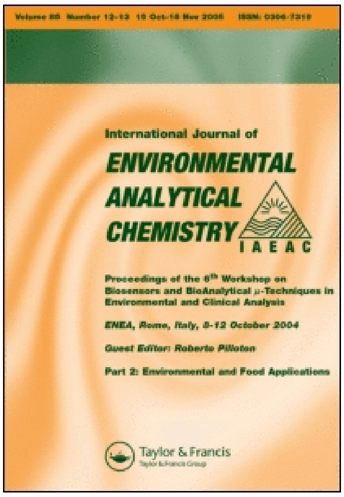

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Electroanalysis of Endosulfan and o -Chlorophenol in Polypyrrole Coated Glassy Carbon Electrode

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ELECTROANALYSIS OF ENDOSULFAN AND *o*-CHLOROPHENOL IN POLYPYRROLE COATED GLASSY CARBON ELECTRODE

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Electroanalysis of endosulfan, an important organochlorine pesticide and *o*-chlorophenol, a toxic pollutant was carried out with polypyrrole coated glassy carbon electrode. Pyrrole was electropolymerised on glassy carbon electrode potentiostatically at 0.9 V. Cyclic voltammogram, square wave voltammogram, differential pulse stripping voltammogram and square wave stripping voltammogram under their optimum experimental conditions were obtained for the determination of both compounds. On polypyrrole coated electrode, higher peak current response was observed with differential pulse and squarewave stripping techniques. Comparatively better analytical signal was noticed with square waveform than the differential pulse form. Optimum stripping voltammetric conditions were arrived and the calibration plot was made. The determination limit is 2.457×10^{-3} and 23.346 mM for endosulfan and 7.779×10^{-3} and 26.916 mM for *o*-chlorophenol.

Keywords: Endosulfan; *o*-Chlorophenol; Stripping voltammetry; Modified electrode; Polypyrrole

INTRODUCTION

The most interesting family of organochlorine pesticide is that of cyclodiene type owing to their neurotoxic activity [1]. One such pesticide, endosulfan, [6,7,8,9,10,10a-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide] is a brownish solid readily absorbed by the mammalian skin and causes primary nervous stimulation, reflex excitations, convolutions, brachycardial and vasodepressions (Table I). It is included in the US Environmental Protection Agency [EPA] list of priority pollutants. *o*-Chlorophenol is another compound included in the EPA list of priority pollutants and is readily absorbed through skin in toxic amounts (Table I). In continuation to our earlier reports [2,3], we report here the voltammetric and stripping analysis of endosulfan and *o*-chlorophenol using polypyrrole coated electrode.

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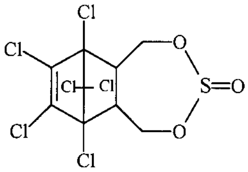
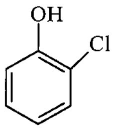
TABLE I Chemical structure and toxicity of pollutants

Name	*Structure*	*Toxicity*
Endosulfan		Insecticide/acaricide toxicity class I Tech: oral LD_{50} 160 mg/kg (male), 22.7 mg/kg (female); Dermal LD_{50} > 500 mg/kg
o-Chlorophenol		Corrosive, harmful LC_{30}: 10–500 mg/kg for aquatics. Readily adsorbed through skin

EXPERIMENTAL

Instruments

A Bio Analytical System [BAS-100A] Electrochemical Analyser was employed for most of the electroanalytical techniques and a BAS CV 27 Voltammograph instrument was used in certain experiments related to the preparation of polypyrrole coated electrode. BAS-MF-2012 model glassy carbon working electrode of area 0.0774 cm^2 was used.

Reagents

Endosulfan of technical grade was obtained from the Bureau of Indian Standards [IS: 4344]. A 1.0×10^{-2} mol dm^{-3} endosulfan stock solution was made up in acetonitrile. Stock solutions of 1.0×10^{-1} mol dm^{-3} *o*-chlorophenol in 50% aqueous acetonitrile were prepared. For the voltammetric studies, Britton Robinson buffers, 0.1 mol dm^{-3} KOH, 0.1 mol dm^{-3} KCl and 0.1 mol dm^{-3} H_2SO_4 in 50% aqueous acetonitrile were used as the medium for the analysis. Pyrrole (AR – Merck) and tetrabutylammonium perchlorate (TBAP) (Sigma) were used for electropolymerisation.

Preparation of Polypyrrole Coated Electrode

The polypyrrole deposition was done with modifications in the already reported methods [4–8]. Polypyrrole film was obtained by electrooxidation of 0.1 M pyrrole solution in acetonitrile containing 0.1 M TBAP at +0.90 V *vs.* Ag/AgCl. Thickness of the films was controlled coulometrically and 0.1 μm thick film was 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-mol dm^{-3}] solution was used to clean the cell.

RESULTS AND DISCUSSION

Voltammetric Studies of Endosulfan in Polypyrrole Coated GC Electrode

Endosulfan showed one well-defined reduction peak in the pH range 1.0–13.0. The peak current [i_p] decreased at higher pH values. This may be due to the hydrolysis of endosulfan in basic medium to form endosulfandiol [9]. The peak potential [E_p] values remained almost constant over the whole pH range studied, suggesting that hydrogen ion is not involved in the rate-determining step or in any prior chemical process. Increased current responses were observed at pH 1.0 (Fig. 1a). In this medium, cyclic voltammetric peak potential varied linearly with the scan rate and a 28 mV cathodic shift in the peak potential was noted for a scan rate change from 25 to 100 mV/sec. The peak current was dependent on the scan rate (ν) and a straight line with good correlation was observed in the i_p *versus* $\nu^{1/2}$ plot. The height of the peak decreased as the scan cycle increased. In square wave voltammetry, the square wave response was a single peak (Fig. 1b) and its peak potential was almost identical with the forward current curve peak potential; no peak was seen in the reverse current curve. The forward current response was lower than the difference current response. E_p was directly related to the frequency and a 69 mV cathodic shift was noted for a frequency change from 10 to 100 Hz. i_p was directly related to the frequency. The log i_p *versus* log ν [$\log i_p = 0.81 \log \nu - 1.02$] and log i_p *versus* log frequency [$\log i_p = 0.73 \log \mathrm{Hz} - 0.32$] plots yielded slopes of 0.81 and 0.73, respectively. This type of behaviour is associated with diffusion controlled adsorption as reported by Osteryoung and O'Dea [10].

Differential Pulse Stripping Voltammetry

Various experiments were carried out to ascertain the best conditions for the adsorption process. Hence, several preconcentration-stripping experiments were performed for accumulation potentials [E_{acc}] varying from 1.0 to −0.4 V and at an accumulation time [t_{acc}] of 15 s, to evaluate the electrostatic attraction/repulsion/reduction behaviour between electrode surface and the endosulfan substrate. Maximum peak current was

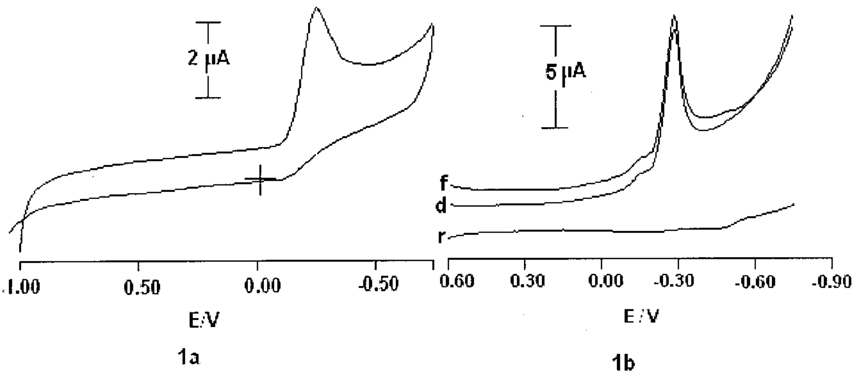


FIGURE 1 Cyclic voltammogram (1a) and Square wave voltammogram (1b) for 18.185 mM of endosulfan in 0.1 M H_2SO_4–50% (v/v) acetonitrile–water at polypyrrole coated glassy carbon electrode under optimum experimental conditions given in Table II. [*f*, forward current; *r*, reverse current; *d*, difference current curves].

found for an accumulation potential in the negative region [−0.2 V], but a decrease in the peak height was observed for potentials in the positive region. This may be due to the electrostatic interaction between the negative nature of electrode at −0.2 V and radical cation formed by the elimination of one chlorine atom from the endosulfan molecule. Hence, E_{acc} of −0.2 V was chosen as optimum. The initial scan potential, [E_{is}], is also an important parameter [11]. It also influences both peak potential and peak height in the stripping voltammogram. Differential pulse stripping signal exhibited maximum peak current at initial scan potential 0.2 V. Experiments carried out for different pulse amplitudes between 25 and 200 mV have demonstrated the existence of linear relationship. Hence, pulse amplitude of 200 mV was used hereafter due to increased current response. The effects of pulse period and pulse width demonstrated that the stripping peak current decreased with an increase in pulse width from 25 to 100 ms and increased with an increase in pulse period from 50 to 200 ms. Hence, a pulse period of 200 ms and a pulse width of 25 ms were used further. The influence of scan rate on the stripping signal was studied between 25 and 200 mV/s and maximum peak current was obtained at 50 mV/s. Similarly the effect of deposition time was studied and the optimum conditions (Table II) were arrived. The stripping voltammogram under optimum experimental conditions was given in Fig. 2.

TABLE II Optimum experimental conditions for differential pulse and square wave stripping voltammetric for the determination of endosulfan on polypyrrole coated glassy carbon electrode

Variable	*Range examined*	*Optimum value*
pH	1.0–11.5	1.0
Initial scan potential/V	1.5–0.0	0.6
Accumulation potential/V	1.0– −0.4	−0.2
Stir rate/rpm	10–2000	1000.0
Reset period/ms	2–30	4.0
Pulse amplitude/mV	10–200	100.0
Pulse period/ms	50–250	200.0
Pulse width/ms	25–200	25.0
Scan rate/mV/s	10–200	50.0
Square wave amplitude/mV	10–250	150.0
Frequency/Hz	5–2000	50.0
Step potential/mV	2–40	4.0
Scan rate [freq. × step]/mV/s	10–80000	200.0

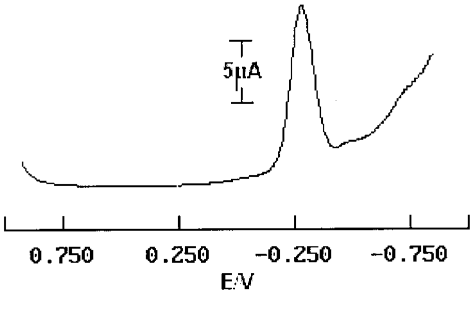


FIGURE 2 Differential pulse stripping voltammogram for 18.185 mM of endosulfan on polypyrrole coated glassy carbon electrode under optimum experimental conditions given in Table II.

Square Wave Stripping Voltammetry

The effects of E_{acc} and E_{is} on the square wave stripping mode were studied. A similar current response with respect to the differential pulse mode was obtained (Table II). The stripping peak current increased sharply with increasing square wave amplitude from 50 to 150 mV. There was a decrease in stripping peak current at higher square wave amplitudes above 200 mV. The peak potential shifted from −0.37 to −0.31 V for a square wave amplitude change from 50 to 250 mV. The dependence of the peak intensity on the frequency was studied between 10 and 2000 Hz. This study was performed at a constant value of the step potential at 4 mV and the results showed the maximum peak current at 50 Hz. Decrease in stripping peak current and broadening of the peak was observed at higher frequency values above 60 Hz. When the step potential was given higher values [6–40 mV], a decrease in peak current was observed. Hence, a frequency of 50 Hz and a step potential of 4 mV were selected. The use of higher frequency and step potentials led to distorted peak resulting in a poor resolution. The effects of stir rate [100–2000 rpm] and rest period [2–30 s] were studied and the optimum values obtained were 1000 rpm and 10 s, respectively. The stripping voltammogram under optimum experimental conditions was given in Fig. 3.

Voltammetric Studies of *o*-Chlorophenol on Polypyrrole Coated GC Electrode

Cyclic Voltammetry

The effect of pH on E_p and i_p using cyclic voltammetry was examined. The peak potentials, E_p suffered cathodic shift with increase in pH from 1.2 to 11.5. There was a maximum shift when the pH was changed from 10.0 to 11.5. Maximum peak current was observed at pH 11.5. This suggests the operation of different oxidation mechanisms at different pH for *o*-chlorophenol. This may be due to easy oxidation of *o*-chlorophenoxide ion, which is possible under alkaline conditions. Hence, alkaline pH 11.5 was chosen for analytical studies. *o*-Chlorophenol showed an oxidation peak

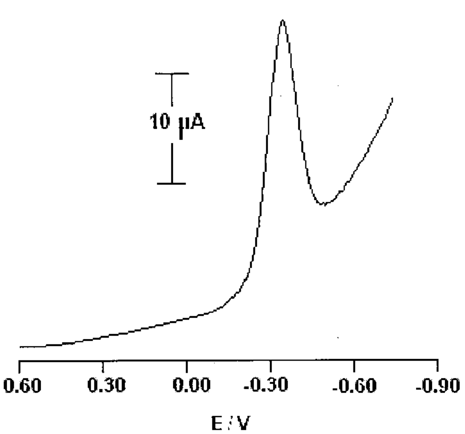
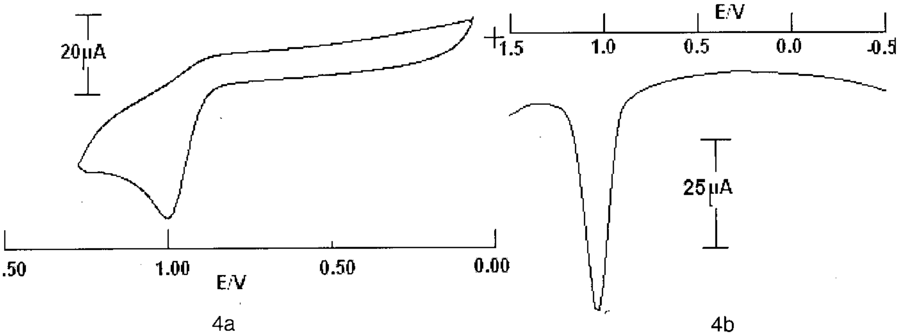


FIGURE 3 Square wave stripping voltammogram for 18.185 mM of endosulfan on polypyrrole coated glassy carbon electrode under optimum experimental conditions given in Table II.



4a 4b

FIGURE 4 Cyclic voltammogram (4a) and Square wave voltammogram (4b) for 18.047 mM of *o*-chlorophenol in 0.1 M aqueous KOH on polypyrrole coated glassy carbon electrode under optimum experimental conditions given in Table III.

in 0.1 mol dm^{-3} KOH medium [pH 11.5] on the glassy carbon electrode (Fig. 4a). The reaction was irreversible, since in CV, it showed a clear anodic peak and there was no cathodic peak. Among the supporting electrolytes in 100% aqueous, 50% aqueous alcohol and in 50% aqueous acetonitrile solutions, the maximum peak current was obtained in 0.1 mol dm^{-3} KOH aqueous medium only. In 0.1 mol dm^{-3} KOH medium, the cyclic voltammetric peak potential varied linearly with the logarithm of the scan rate and the current of the peak was dependent on the scan rate. Peak current [i_p] was proportional to the square root of scan rate for *o*-chlorophenol concentration at 2.32 mg/ml. The current function [$i_pACv^{1/2}$, where A = area of the working electrode and C = concentration of analyte] value initially increased and then decreased in this medium for a scan rate change from 25 to 250 mV/s. The log i_p *versus* log v [log $i_p = 0.781\log v + 0.0027$] plot has yielded a slope value of 0.78. The height of the peak decreased as the sweep cycle increased. These clearly explain the adsorption behaviour. The ratio of peak current to concentration decreased with increasing *o*-chlorophenol concentration. Thus the reaction could be described as total irreversible oxidation of adsorbed reactant. In square wave voltammetry, similar trend was obtained (Fig. 4b). Peak potential was directly proportional to the logarithm of the frequency and peak current was directly proportional to the square root of frequency. Here also diffusion-controlled adsorption is observed.

Differential Pulse Stripping Voltammetry

Experiments were carried out to find the parameter for the preconcentration-stripping steps. Voltammograms performed for accumulation potentials [E_{acc}] varying from 0.0 to 0.8 V and at accumulation time [t_{acc}] of 5 s showed the best peak current for an accumulation potential in the positive region [0.4 V]. Thus, the strong alkaline pH and an E_{acc} of 0.4 V were chosen as optimum for further studies. Similarly, other parameters were varied and the optimum conditions were arrived. The optimized conditions (Table III) that resulted in good peak response were used to study the effect of concentration. A typical stripping voltammetric response under optimum experimental condition for *o*-chlorophenol concentration at 18.047 mM is given in Fig. 5.

TABLE III Optimum experimental conditions for differential pulse and square wave stripping voltammetric for the determination of *o*-chlorophenol on polypyrrole coated glassy carbon electrode

Variable	*Range examined*	*Optimum value*
pH	1.2–11.5	11.5
Initial scan potential/V	−1.0–−0.4	−1.0
Accumulation potential/V	0.0–0.8	0.4
Stir rate/rpm	10–2000	1000.0
Reset period/ms	2–30	4.0
Pulse amplitude/mV	10–200	100.0
Pulse period/ms	50–250	100.0
Pulse width/ms	20–200	20.0
Scan rate/mV/s	10–200	100.0
Square wave amplitude/mV	10–250	60.0
Frequency/Hz	5–2000	140.0
Step potential/mV	2–40	10.0
Scan rate [freq. × step]/mV/s	10–80000	1400.0

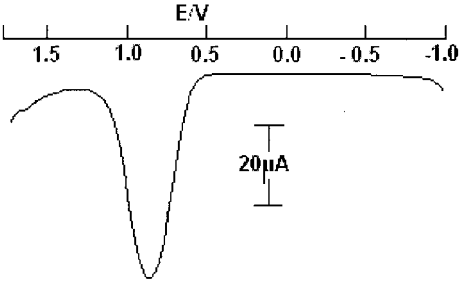


FIGURE 5 Differential pulse stripping voltammogram for 18.047 mM of *o*-chlorophenol on polypyrrole coated glassy carbon electrode under optimum experimental conditions given in Table III.

Square Wave Stripping Voltammetry

The influences of E_{acc}, E_{is}, square wave amplitude, frequency and step potential etc., on the square wave stripping were studied. The square wave stripping voltammogram obtained under optimum experimental conditions for 18.047 mM *o*-chlorophenol concentration is given in Fig. 6.

Analytical Characteristics

The study of effect of concentration on the stripping signal using both DPSV and OSWSV leads to linear calibration plots for endosulfan at a concentration between 2.457×10^{-3} and 23.346 mM (Fig. 7). The reproducibility of the stripping signal was calculated in terms of relative standard deviation for 10 measurements carried out at a concentration of 18.185 mM as 3.2% in DPSV and 2.8% in OSWSV.

A linear calibration plot was obtained for *o*-chlorophenol at a concentration between 7.779×10^{-3} and 26.916 mM (Fig. 8). The reproducibility of the stripping signal was calculated in terms of relative standard deviation for 10 measurements carried out at a concentration of 18.047 mM as 3.0% in DPSV and 2.05% in OSWSV.

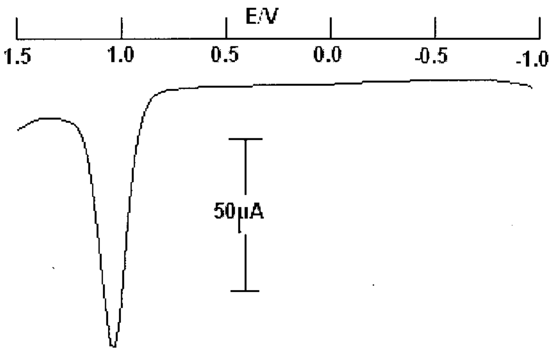


FIGURE 6 Square wave stripping voltammogram for 18.047 mM of *o*-chlorophenol on polypyrrole coated glassy carbon electrode under optimum experimental conditions given in Table III.

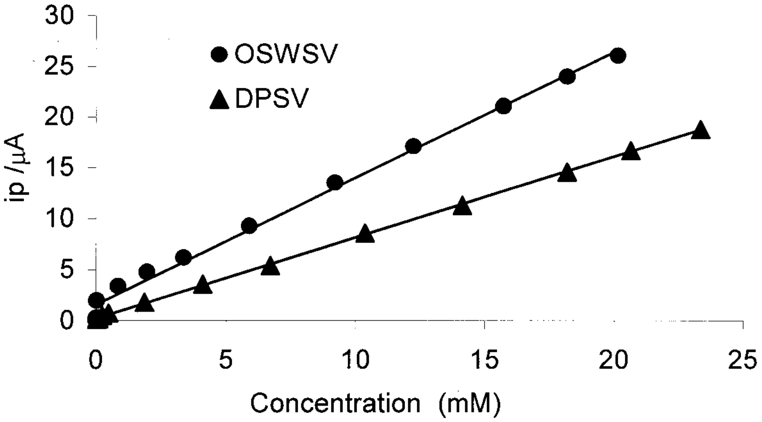


FIGURE 7 Calibration graph for endosulfan (OSWSV, Osteryoung square wave stripping voltammetry and DPSV, differential pulse stripping voltammetry) under optimum conditions given in Table II.

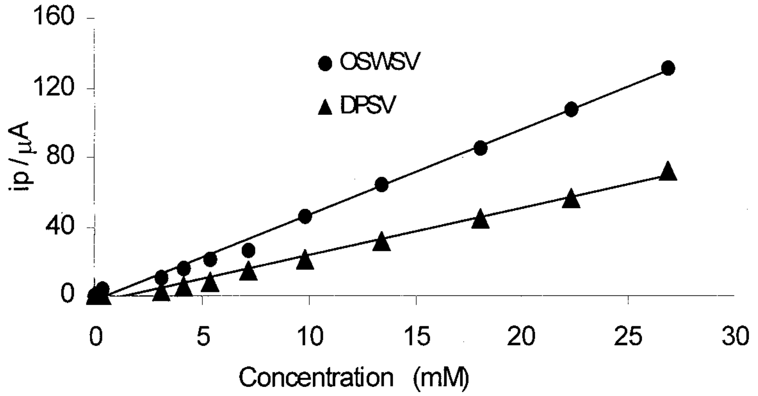


FIGURE 8 Calibration graph for *o*-chlorophenol (OSWSV, Osteryoung square wave stripping voltammetry and DPSV, differential pulse stripping voltammetry) under optimum conditions given in Table III.

TABLE IV Peak current and peak potential values for 18.185 mM of endosulfan and 18.047 mM of *o*-chlorophenol on bare and polypyrrole coated glassy carbon electrode under optimum experimental condition given in Tables II and III

Analyte		*Bare electrode*			*Coated electrode*		
		CV	*DPSV*	*OSWSV*	*CV*	*DPSV*	*OSWSV*
Endosulfan	$i_p/\mu A$	15.8	18.4	21.0	3.7	14.6	24.9
	E_p/V	−0.33	−0.35	−0.40	−0.25	−0.28	−0.35
o-Chlorophenol	$i_p/\mu A$	10.0	16.5	20.4	34.7	45.8	85.4
	E_p/V	0.50	0.55	0.60	0.85	0.85	1.00

Comparison of Coated Electrode Behaviour with Bare Electrode

On a pretreated glassy carbon electrode, it is possible to obtain good cyclic voltammogram [CV], differential pulse stripping voltammogram [DPSV] and Osteryoung square wave stripping voltammogram [OSWSV] under their optimum experimental conditions for endosulfan and *o*-chlorophenol [2,3]. After polypyrrole coating on the electrode, the peak currents decreased in CV and increased in both DPSV and OSWSV techniques. The peak potential in DPSV shifted towards anodic side, which resulted in a potential difference of about 0.15 V (Table IV). In the case of *o*-chlorophenol, the peak currents increased in CV, DPSV and OSWSV techniques on the polypyrrole coated GC electrode. The peak potential in DPSV and OSWSV shifted towards anodic side, which resulted in potential differences of about 0.30 and 0.40 V, respectively (Table IV).

CONCLUSION

Polypyrrole coated glassy electrode showed better selectivity and sensitivity than bare glassy carbon electrode for the determination of endosulfan and *o*-chlorophenol using stripping voltammetry technique. Of the two stripping methods the OSWSV method is better than DPSV. Polymer coated glassy carbon electrodes have allowed efficient preconcentration of organic analytes even at low and high concentration levels. Based on the present study, it is possible to conclude that the progressive electroanalytical methods that are the primary part of monitors and analyzers can be used for environmental pollution control and monitoring of organic pollutants. Particularly, the adsorptive square wave stripping voltammetry with polypyrrole coated electrode may be of greater usage for this task.

Acknowledgement

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