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Determination of pesticides using heteropolyacid montmorillonite clay-modified electrode with surfactant

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Abstract

Redox behavior of three pesticides, namely isoproturon, carbendazim and methyl parathion was investigated electrochemically using hetropolyacid montmorillonite clay-modified glassy carbon electrode in the presence and absence of a surfactant, cetyl trimethyl ammonium bromide. A solution of 0.1 M H_2SO_4 in 50% aqueous alcohol (pH 1.0) was found to be suitable medium for electroanalysis. Isoproturon exhibited one well-defined oxidation peak around 1.2 V along with one more oxidation and reduction peaks. Carbendazim showed only one well-defined anodic peak around 1.4 V. Methyl parathion exhibited one well-defined reduction peak around −0.26 V and the oxidation peak appeared around 0.510 V. In the second cycle, a new cathodic peak was found around 0.420 V. The presence of surfactant enhanced the peak current and hence stripping voltammetric determination procedures for all the three pesticides were developed. Square wave stripping mode was employed and the maximum current experimental conditions were arrived at. Calibration plot was made for all the three pesticides. The determination limit and standard deviations were arrived at. The applicability of the method was also verified in a soil sample and water analyte.

Keywords: Isoproturon; Carbendazim; Methyl parathion; Clay; Electrochemical; Stripping

1. Introduction

Trace contamination of pesticides present in the natural aquatic systems creates lot of pollution problem due to their toxicity and bioaccumulation property [1–5]. Techniques, such as TLC, HPLC, GC/MS, UV, capillary electrophoresis and colorimetry have been used for the determination of pesticides [6–17]. A recent indirect electrochemical method of determination of isoproturon was also reported [1–4]. Isoproturon, a toxic class III pesticide, is a selective herbicide. Carbendazim, a toxic class IV pesticide, is a benzamidazole fungicide that plays an important role in plant disease control. Methyl parathion [*O*,*O*-dimethyl-*O*-(4-nitrophenyl) phosphorothioate] is a selective insecticide, very stable to light and acid and it is listed in the toxicity class I insecticide. Electrochemical redox mechanisms were already studied in detail for isoproturon and carbendazim [1–4,18,19]. We already reported the electrochemical redox behaviour and electroanalysis of methyl parathion in soil suspension [19]. Trace determination of carbendazim in water by application of multivariate calibration to cross-sections and parallel factor of three-dimensional excitation–emission matrix fluorescence and signal-based method are reported [20–22]. The development of newer method with more sensitivity for the determination of these pesticides is warranted always. Clay minerals are cheap, widely available and naturally occurring materials. Their well-defined layered structures [23–25], flexible adsorptive properties and potential as catalysts or catalytic supports [26–29] make them interesting materials compared to other modifications. Determination

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of pollutants using clay-modified electrode has attained importance recently because of the available clay stacks, which helps in more accumulation. Synthetic layered double hydroxides of anion-exchanged clay-modified electrodes have the tendency to intercalate with electroactive organic anions. Utilization of clay-modified electrodes for different species was summarized well by Mousty and co-workers [30,31]. Differential pulse adsorptive stripping voltammetric determination of herbicides and organic pollutants at a clay-modified electrode has been studied by many researchers [32,33]. The clay modification on the electrode surface is one of the promising areas in the development of sensors. This paper reports the development of an electrochemical determination of three pesticides, namely isoproturon, carbendazim and methyl parathion using heteropolyacid montmorillonite clay (HPMM) modified glassy carbon electrode.

2. Experimental

EG&G M 273A Electrochemical Analyzer (Princeton Applied Research Corporation) was employed mainly for the electroanalytical techniques. All the pesticides of technical grade were obtained from the Bureau of Indian Standards and purified [19]. Their structure and physical status are presented in Table 1. A 1.0×10^{-2} M stock solution was made up in ethanol. Montmorillonite KSF clay was purchased from Acros organics, Belgium. Britton Robinson Buffers, 0.1 M KOH, 0.1 M KCl and 0.1 M H_2SO_4 in 50% aqueous alcohol were used as the medium for the analysis. Electrochemical method was adopted using a three-electrode system. Clay-modified glassy carbon working electrode, Pt foil counter electrode and saturated calomel (SCE) reference electrode were used. Purging and blanketing of nitrogen were done for analyte solution placed in the electrochemical cell of 15 mL capacity for 20 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 as reported by us earlier [1–4]. The background current was recorded for all sweep rates and subtracted properly in calculating the peak currents.

2.1. *Preparation of clay-modified glassy carbon electrode*

Ultrasonication of 1 g of Montmorillonite KSF clay, 5 mL of 0.5 M phosphotungstic acid and 20 mM CTAB for 4 h was done and kept for 1 h. The formed HPMM clay was centrifuged, washed thoroughly with water, dialyzed to remove the salt and dried. Ultrasonication of about 0.1 g of heteropolyacid montmorillonite in 10 mL of water and 100 mg of carboxy methylcellulose (CMC) was done for 1 h to prepare uniform solution. About 50 μL of this solution was spread evenly on the polished electrode surface and dried at room temperature. It shows no peak in CV. Care was taken to remove the coating and clean the glassy carbon electrode after each experiment in distilled water before usual surface treatment. Nitric acid (6 M) solution was used to clean the cell.

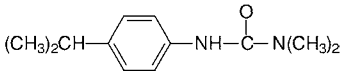
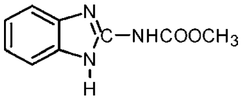
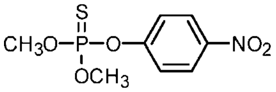
3. Results and discussions

3.1. *Cyclic voltammetric studies of pesticides*

Cyclic voltammetric studies of the isoproturon on HPMM clay-modified glassy carbon electrode were carried out at various pH media from 1.0 to 10.0. Since isoproturon was unstable above pH 10.0 [1], influence of pH on the electrochemical response was not studied above pH 10.0. One main oxidation peak with higher current above 1.2 V and two smaller peaks arising due to the redox behavior of intermediate were observed in all pH. Fig. 1 showed the variation of peak potential of the well-defined anodic peak above 1.2 V with pH. Lowest peak potential was observed only at pH 1.0 revealing easy oxidation due to prior protonation of the amino group in the substrate, which facilitated oxidative cleavage. Fig. 2 exhibited the variation of peak current with pH showing maximum peak current at pH 1.0. Thus, pH 1.0 was selected as the suitable medium for the electrochemical studies of isoproturon.

Fig. 3 represents the cyclic voltammogram recorded for isoproturon using HPMM clay-modified glassy carbon electrode in the presence and absence of a surfactant, cetyl trimethyl ammonium bromide at pH 1.0. The main oxida-

Table 1
Structure and physical status of the selected pesticides

Name	Physical nature at 25 °C	Chemical structure	Category
Isoproturon	Colourless crystalline solid, m.pt. 155–156 °C		Herbicide
Carbendazim	Colourless and odourless crystalline solid, m.pt. ca. 155 °C		Fungicide
Methyl parathion	Colourless crystalline (15) solid, m.pt. 35–36 °C		Insecticide

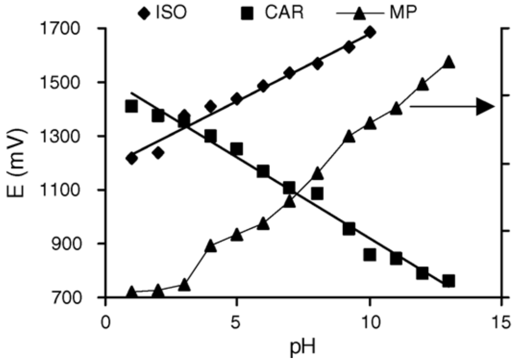


Fig. 1. Plot of pH vs. potential.

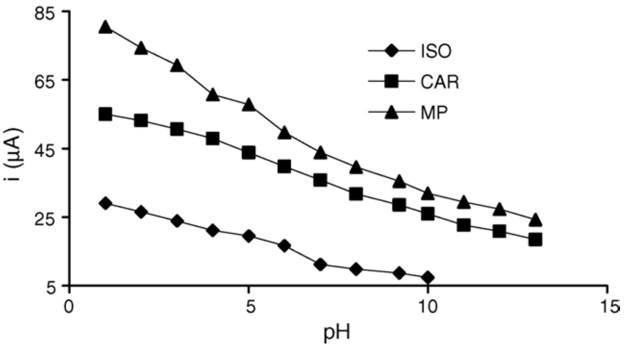


Fig. 2. Plot of pH vs. current.

tion peak seen in the cyclic voltammogram between 1.20 and 1.23 V was considered for the electroanalytical studies because of higher current response. Various cyclic voltammograms of 0.99 mM of isoproturon were run at various sweep rates from 0.025 to 0.400 V s^{-1} in the presence and absence of surfactant. The peak potentials are correlated with logarithm of sweep rate. Straight lines with good correlation were obtained. The results of correlations are presented in Table 2. From the slope, the transfer coefficient (α) values were calculated. The fractional value of α (0.618 without CTAB and 0.634 with CTAB) confirms the irreversibility of the electron transfer in oxidation of isoproturon. The peak current

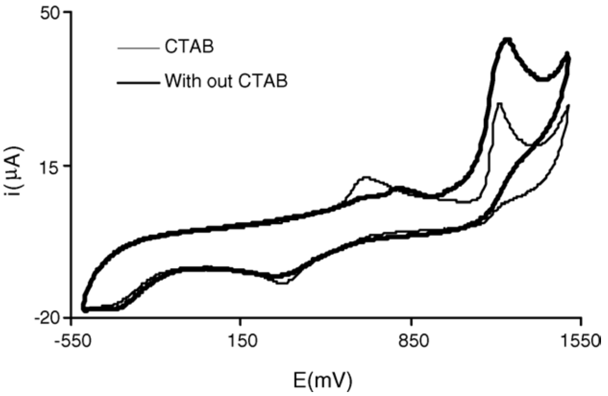


Fig. 3. Cyclic voltammetric behaviour of 0.99 mM of isoproturon in with and without CTAB at pH 1.0, scan rate 100 mV s^{-1}.

linearly varied with square root of sweep rate. The plot of i_p versus $v^{1/2}$ led to straight lines. The $\log i_p$ versus $\log v$ plot also showed straight lines with slopes 0.3396 with CTAB and 0.3784 with CTAB. These facts suggest diffusion-controlled mass transfer. Comparison of the peak current response in the presence and absence of CTAB led to the selection of the former due higher current. There was no appreciable shift in the peak potentials. The micellar effect of the surfactant CTAB enhances the accumulation of the pesticide in the clay pores and increases the electron transfer rate. Hence, higher peak current is observed in the presence of CTAB.

Since carbendazim is stable at strong alkaline medium, the influence of pH on the cyclic voltammetric response was studied between pH 1.0 and 13.0. Only one oxidation peak around 1.4 V was observed at all the pH studied. Here also acid pH 1.0 was chosen as the best pH because of maximum current (Fig. 2.) signals. At 0.99 mM concentration of carbendazim, the sweep rate was varied between 0.025 and 0.250 V s^{-1}. Typical cyclic voltammogram is presented in Fig. 4. The peak potentials were correlated with logarithm of sweep rate. The plot of E_p versus $\log v$ yields a straight line (Table 2). From the slope, α, transfer coefficient values (0.377 without CTAB and 0.976 with CTAB) were calculated and they were fractions suggesting the irreversible nature of electron transfer.

Table 2
The results of correlations employed in this study

Compound	Without CTAB	With CTAB
Isoproturon	$E_p = 24.25 \log v + 1166.3$; $r^2 = 998$ $i_p = 1.902\, v^{1/2} + 9.997$; $r^2 = 0.997$ $\log i_p = 0.340 \log v + 0.7905$; $r^2 = 0.998$	$E_p = 23.676 \log v + 1202$; $r^2 = 0.994$ $i_p = 3.309\, v^{1/2} + 10.655$; $r^2 = 0.999$ $\log i_p = 0.378 \log v + 0.8923$; $r^2 = 0.995$ $i_p = 0.2629$ concentration $+ 0.0271$; $r^2 = 0.999$
Carbendazim	$E_p = 79.575 \log v + 1248.9$; $r^2 = 0.996$ $i_p = 3.4692\, v^{1/2} + 21.198$; $r^2 = 0.995$ $\log i_p = 0.2935 \log v + 1.1677$; $r^2 = 0.986$	$E_p = 30.746 \log v + 1304.6$; $r^2 = 0.992$ $i_p = 4.1583\, v^{1/2} + 31.381$; $r^2 = 0.996$ $\log i_p = 0.2817 \log v + 1.3079$; $r^2 = 0.991$ $i_p = 0.1861$ concentration $+ 0.0217$; $r^2 = 0.993$
Methyl parathion	$-E_p = 58.07 \log v + 194.94$; $r^2 = 0.9917$ $i_p = 6.2775\, v^{1/2} - 11.014$; $r^2 = 0.9974$ $\log i_p = 0.5774 \log v + 0.5574$; $r^2 = 0.9957$	$-E_p = 26.858 \log v + 207.5$; $r^2 = 0.9935$ $i_p = 6.2297\, v^{1/2} - 4.576$; $r^2 = 0.9978$ $\log i_p = 0.5331 \log v + 0.6935$; $r^2 = 0.9985$ $i_p = 0.6185$ concentration $+ 0.0362$; $r^2 = 0.999$

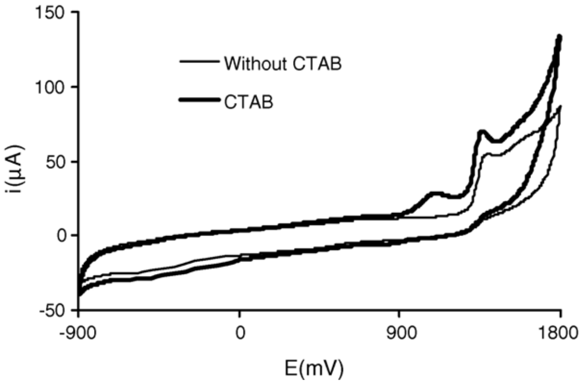


Fig. 4. Cyclic voltammetric behaviour of 0.99 mM of carbendazim in with and without CTAB at pH 1.0, scan rate 100 mV s^{-1}.

The peak currents were correlated with sweep rate. Linearity of i_p versus $v^{1/2}$ plot resulted in straight line indicating diffusion-controlled reaction. The log i_p versus log v plot also resulted in straight lines with slopes 0.2935 for without CTAB and 0.2817 for with CTAB confirming diffusion-controlled reaction. In presence of CTAB, increase in peak current and decrease in potential were observed when the results were compared with that in the absence of CTAB. The micellar effect could be the reason for this.

On contrary to isoproturon and carbendazim, methyl parathion underwent reduction in one step at acid and neutral media and two steps in basic medium leading to the formation of hydroxylamine. The electrochemical reduction showed maximum peak current at acid pH 1.0. From the cyclic voltammetric results, this pH is chosen as the best pH (Figs. 1 and 2) for electroanalytical studies. Cyclic voltammograms at various sweep rates ranging between 0.025 and 0.400 V s^{-1} in acid pH were recorded and the results were collected. A representative cyclic voltammogram is given in Fig. 5. The main reduction peak in the first cycle appeared around −0.260 V and the oxidation peak appeared around 0.510 V. In the second cycle, a new cathodic peak was found around 0.420 V. The cathodic peak in the second cycle and the anodic peak in the first cycle are due to the redox couple between hydroxylamine and nitrosobenzene. For the correlation studies, the main reduction peak of the substrate was considered. A linear correlation between peak current and the square root of sweep rate was observed. The log i_p versus log v plot also exhibited straight line with slope around 0.5. These facts suggest a diffusion-controlled reaction. There was no corresponding anodic peak observed in the reverse scan. The E_p versus log v plot yielded straight lines and α values (0.279 without CTAB and 0.129 with CTAB) were calculated from the slope. The fractional value of α confirmed the irreversible electron transfer. Here also the peak response was higher in the presence of CTAB. The results of correlations are presented in Table 2.

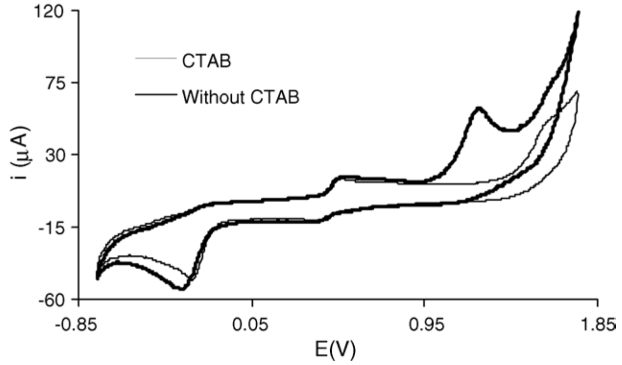


Fig. 5. Cyclic voltammetric behaviour of 0.99 mM of methyl parathion in with and without CTAB at pH 1.0, scan rate 100 mV s^{-1}.

The above cyclic voltammetric studies led to the selection of HPMM clay-modified electrode as the indicator electrode, pH 1.0 as the medium in the presence of CTAB for the development of stripping voltammetric procedure for the determination of the three pesticides.

3.2. 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. 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 and methyl parathion showed maximum peak current at −0.25 V and −0.20 V accumulation potential, respectively. The accumulation times 20, 10 and 20 s led to the maximum peak current for isoproturon, carbendazim and methyl parathion, respectively. 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 −0.25 and 0.75 V and an initial scan potential of 0.9 V was chosen for stripping voltammetric studies of isoproturon because of maximum current signals. In a similar manner, 1.0 and −0.7 V were found out for carbendazim and methyl parathion, respectively. The stripping peak current increased with an increase in square wave amplitude from 25 to 200 mV and decreased above 200 mV. However, amplitudes of 50, 25 and 100 mV were selected for isoproturon, carbendazim and methyl parathion, respectively, 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 25 Hz for all the three pesticides. Lower current response was observed for higher frequency

Table 3
Optimum experimental conditions in SWSV

Variable	Optimum value		
	ISO	CAR	MP
pH	1.0	1.0	1.0
Accumulation potential (V)	0.900	−0.250	−0.200
Accumulation time (s)	20	10	20
Initial scan potential (V)	0.900	1.00	−0.700
Square wave amplitude (mV)	50	25	100
Frequency (Hz)	25	25	25
Step potential (mV)	2	2	2
Stirring rate (rpm)	300	300	300
Rest period (s)	5	5	5

values. 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 2 mV. Hence, a frequency of 25 Hz and a step potential of 5 mV were used which provided sufficiently sensitive analytical signal at a reasonable scan rate of 50 mV s^{-1}. The effects of stirring rate (100–2000 rpm) and rest period (2–30 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 3. A representative stripping voltammograms of the pesticides are given in Fig. 6.

3.3. Analytical characteristics

Square wave stripping voltammograms at different concentrations of isoproturon, carbendazim and methyl parathion were recorded using their maximum signal conditions. The peak current linearly increased with an increase in concentration. The calibration plots of i_p versus concentration lead to good linear correlation. The calibration results are presented in Table 2. The limit of detection (LOD) is determined as 1, 10 and 20 ng mL^{-1} for isoproturon, carbendazim and methyl parathion, respectively. The range of determination was found out as 1–300, 10–500 and 20–700 ng mL^{-1} for isoproturon, carbendazim and methyl parathion, respectively. Five identical measurements of the stripping current at 100 ng mL^{-1} analyte concentration were made and the relative standard deviation was determined. It is 2.67%, 2.93% and 2.91% for isoproturon, carbendazim and methyl parathion, respectively (Fig. 7).

3.4. Proposed method for determination in soil sample

The soil sample analysed 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 25 mL of 1.0×10^{-2} mM isoproturon stock solution by shaking in a closed bottle for about 30 min. Isoproturon 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 H_2SO_4 containing 50% aqueous ethanol was used to dilute the contents

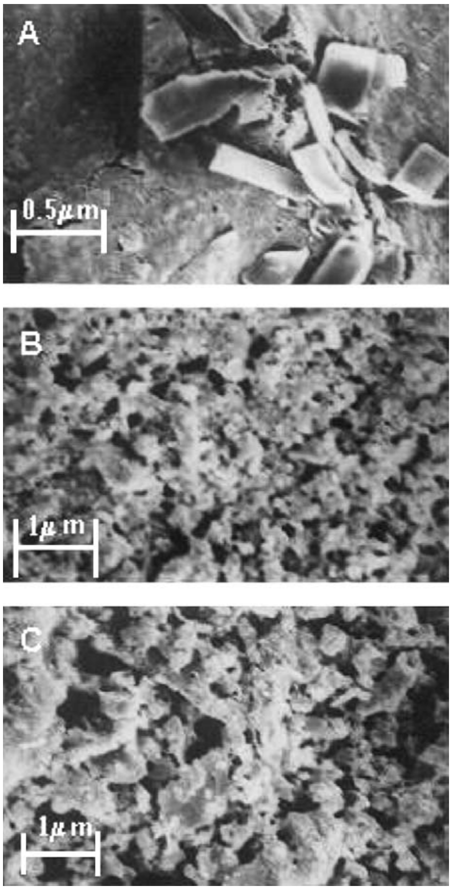


Fig. 6. SEM photographs of pesticide accumulation on clay modified electrode surface: (A) isoproturon; (B) carbendazim; (C) methyl parathion.

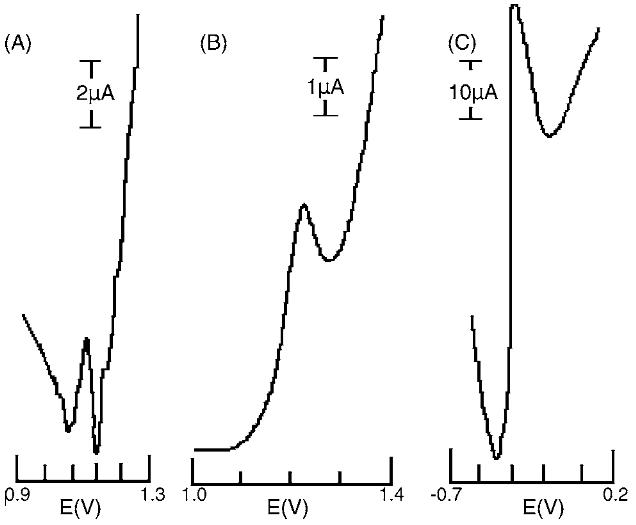


Fig. 7. SWSV of (A) isoproturon; (B) carbendazim; (C) methyl parathion under maximum experimental condition.

Table 4
Pesticides percentage of recovery from soil samples

Compound	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)	R.S.D.[a]
Isoproturon	10	8.59	85.90	2.73
	50	46.31	92.62	3.02
	100	92.81	92.81	2.85
	200	181.78	90.89	2.87
	250	228.85	91.54	2.91
Carbendazim	25	22.23	88.92	2.88
	75	68.13	90.84	2.91
	100	91.08	91.08	3.01
	200	78.84	89.42	3.14
	250	223.93	89.57	3.37
Methyl parathion	50	44.77	89.54	3.27
	100	91.54	91.54	3.12
	200	181.7	90.85	2.91
	300	265.92	88.64	3.24
	400	357.08	89.27	2.98

[a] $n = 6$.

of the flask to the required volume. The standard addition method was used. 0.05 mL aliquot of the 1.0×10^{-2} mM isoproturon stock standard solution was added to the solution prepared as described above. Square wave stripping voltammetry under the optimum experimental conditions carried out the determination of isoproturon in the soil sample. Similar soil samples analysis was done for carbendazim and methyl parathion also. Six identical measurements were made and the relative standard deviations of isoproturon, carbendazim and methyl parathion are given in Table 4.

3.5. Determination of pesticides in spiked water sample

The spiked water sample was prepared by adding known amount of isoproturon 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 completion of this process, dichloromethane was filled in the column and then allowing them to stand for 20 min. The extract of dichloromethane was then 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 voltammetry method. In a similar manner, carbendazim and methyl parathion were also determined. The pesticide percentage of recovery and relative standard deviation were determined and are presented in Table 5.

Table 5
R.S.D. value and percentage of recovery from water spiked samples of pesticides

Compound	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)	R.S.D.[a]
Isoproturon	10	8.19	81.9	2.52
	50	46.89	93.78	2.66
	100	93.41	93.41	2.95
	200	188.62	94.31	2.73
	250	227.08	90.83	2.79
Carbendazim	25	20.63	82.52	2.82
	75	67.64	90.19	2.76
	100	91.43	91.43	3.07
	250	230.38	92.15	2.77
Methyl parathion	50	46.17	92.34	3.45
	75	67.24	89.65	3.29
	100	91.45	91.45	3.07
	200	176.78	88.39	2.99
	300	279.36	93.12	2.91

[a] $n = 6$.

4. Conclusions

HPMM clay electrode was found to be suitable for the electroanalytical studies of three pesticides, isoproturon, carbendazim and methyl parathion. All the three pesticides exhibited good responses at pH 1.0 in the presence and absence of a surfactant, CTAB. They underwent irreversible electron transfer and the overall process was controlled by diffusion. The electroactive behavior was used and stripping voltammetric procedures for the determination of the three pesticides were developed after optimizing all the experimental parameters. This procedure led the limits of determination down to ng mL^{-1} levels. High sensitivity, good reproducibility and simple instrumentation were the added advantages. The suitability of the method was understood from the applications for the determination of these pesticides in spiked soil and water samples.

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