A Comparitive Study on the Electrode Kinetics and Mechanism of Pesticides Having Different Electro Active Centres at Carbon Nano Tubes Paste Electrode

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Strictly as per the compliance and regulations of :

A Comparitive Study on the Electrode Kinetics and Mechanism of Pesticides Having Different Electro Active Centres at Carbon Nano Tubes Paste Electrode

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I. Introduction

Although pesticides have many harmful effects on environment they have been used in agriculture field to increase yield, improve food quality and save time and money. But the uniform use of pesticides can cause soil, water and food contamination. Their detection concerns agriculture health care professionals and regulatory agencies. At present, they are mostly determined in the laboratory by methods such as chromatographic and spectroscopic methods. Although they have high sensitivity, these methods suffer from many disadvantages, in requiring skilled technicians, being complex, costly and time consuming and their use online for continuous monitoring is impractical. Because large number of samples have to be measured, the development of fast automated and inexpensive methods are of great interest. voltammetric methods are suitable, sensitive and reproducible and can be applied for the analysis of pesticides in environmental matrices[1-10].

More recently electrochemical techniques become extremely useful for the monitoring of pesticides in environmental samples. This can be attributed to the introduction of highly sensitive commercial instrumentation, which yields easily interpretable data for routine quantitation at low levels. The approach has been demonstrated to have utility for number of hygienic and toxicological problems. The early voltammetric methods experienced number of difficulties making them less ideal for routine analytical uses. However, in the 1960's and 1970's significant advances were made in all areas of voltammetry, which enhanced the sensitivity and expanded repertoire of analytical methods. The coincidence of these advances with the advent of low cost operational amplifiers also facilitated the rapid commercial development of relatively inexpensive instrumentation. The common characteristic of all voltammetric techniques is that involve the application of potential (E) to an electrode and monitoring the resulting current (i) flowing through the electrolytic cell. In many cases, the applied potential is varied or the current is monitored over a period of time (t). Thus, all voltammetric techniques can be described as some function of E, i and t. Concentration of electro active species is forced to change by the applied potential which electrochemically reduce or oxidizes it's activity at the electrode surface. Thus, they are considered as active techniques.

Phenothrin containing >C=C< as electro active group is broad spectrum pyrithroid ester insecticide which is widely used for weed control in many agricultural crops.

Chlorpropham containing >C=O as electro active group is a plant growth regulator used for the pre-emergence control of grass weeds in falfa, Lima and snap beans, blueberries, cane berries, carrots, cranberries, ladino clover, garlic, eed grass, onions, spinach, sugar beets, tomatoes, safflower, soybeans, gladioli and woody ursery stock. It is also used to inhibit potato sprouting and for sucker control in tobacco.

Fenclorim containing >C=N- as electro active group is broad spectrum herbicide which is widely used for weed control in many agricultural crops like corn, wheat, maize and barley.

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II. Experimental

a) Apparatus and electrodes

Voltammetric determinations were performed using a model Meterohm Auto Lab 101 PG stat (Netherlands)Fig I. CNTPE was used as working electrode for differential pulse adsorptive stripping voltammery and cyclic voltammetry. pH measurements were carried out with an Eutech PC_510 cyber scan. Meltzer Toledo (Japan) Xp26 delta range micro balancer were used to weigh the samples during the preparation of standard solutions. All the experiments were performed at 250C.

Fig 2 : Meterohm Auto Lab 101 PG stat (Netherlands)

b) Reagents and solutions

All reagents used were of analytical reagent grade. Double distilled water was used throughout the analysis. In the present investigation universal buffers of pH range 2.0 to 6.0 are used as supporting electrolytes and are prepared by using 0.2 M boric acid, 0.05M citric acid and 0.1Mtrisodium orthophosphate solutions. Samples obtained from nagarjuna agrichem and syngat india limitted

c) Calculation of Ep And Ip

Cyclic voltammetry is perhaps a most versatile electroanalytical technique for the study of electroactive species. Its versatility combined with ease of measurement has resulted in the extensive use of cyclic voltammetry in the field of electrochemistry, inorganic chemistry, organic chemistry, and biochemistry. It is rarely used for quantitative determinations, but it is widely used for the study of the redox process, for understanding reaction intermediates and for obtaining stability of reaction products.

In this technique, the potential applied between the working electrode and the reference electrode is varied with time in known fashion in a triangular sweep mode. The forward or cathode potential sweep gives a reduction wave where as backward or anodic potential sweep gives an oxidation wave. Generally linear diffusion conditions are employed in cyclic voltammetry. Fast scan rates minimize diffusion problems.

This technique is based on varying the applied potential at working electrode in both forward and reverse directions (at some scan rate) while monitoring the current for example. The initial scan could be in the negative direction to the switching potential. At the point, the scan would be reversed and run in the positive direction. Depending on the analysis, one or more potential cycles can be performed, hence the term 'Cyclic Voltammetry'. The potential of working electrode (usually CNTPE) is controlled verses a reference electrode such as saturated calomel electrode or silver electrode. The controlling potential, which is applied across these two electrodes, can be considered in excitation signal. The excitation signal for cyclic voltammetry is liner potential scan with triangular wave form. If only a single anodic / cathodic sweep is performed the technique usually called linear potential sweep voltammetry.

The peak current in a reversible process is quantitatively expressed by

$$i_p = KACD^{1/2} V^{1/2} n^{3/2}$$

where, i_p = peak current in microamperes

K = Randles-Sevcik constant

A = area of working electrode in cm^2

C = concentration of the depolarizer in mM

D = diffusion coefficient of electroactive species in cm^{2}s^{-1}

V = scan rate in mVs^{-1}

n = number of electrons

Delahay indicated 2.75 x 10^5 as the reliable value for the 'K' in the case of reversible process.
For an irreversible processes

$$i_p = 3.01 \times 10^5 n\, (\alpha\, na)^{1/2}\, AD^{1/2}\, CV^{1/2}$$

where, α = transfer coefficient.

n_a=number of electrons involved during the rate determining step and other terms have their usual significance.

The above equations are used for evaluating diffusion coefficient values of reversible and irreversible electrode processes respectively.

The nature of the irreversible process is known from following equations

(i) $\quad E_{p/2} - E_p = 0.0565/n$ volts

(ii) $\quad (E_p)_{anodic} - (E_p)_{cathodic} = 0.058/n$ volts

where, $\quad E_p$=peak potential in volts

$E_{p\backslash2}$=half-peak potential in volts

Any deviation from the above equations leads to irreversible nature of the electrode process. Absence of anodic signal on the reverse scan indicates irreversible nature of the electrode process.

α_{na} values can be evaluated from the equation

$E_{p/2} - E_p = 0.048/\alpha_{na}$ volts

The forward rate constant values for all irreversible processes can be evaluated using the equation

$$E_p = \frac{-1.14RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \frac{k^0_{f,h}}{D^{1/2}} - \frac{RT}{2\alpha n_a F} \ln(\alpha n_a v)$$

where, all the terms have their usual significance.

The most useful aspects of cyclic voltammetry[11-15] is, its application to the qualitative diagnostic of the electrode reactions which are coupled to the homogeneous chemical reactions. Cyclic voltammetry provides a particularly convenient means to study adsorption phenomena in detail. For adsorption controlled waves, the current function ($i_p / Cv^{1/2}$) increased rapidly with an increase in scan rate.

III. RESULT AND DISCUSSION

Based on the nature of the peak it is found to be diffusion controlled and adsorbed on the electrode surface in the buffer systems taken, as shown by the linear plot of ip vs $v^{1/2}$ (Fig. III) which is found to pass through origin. The irreversibility of the electrode process was confirmed by log plot analysis of the peak. The variability of the peak potential with scan rate also indicates the irreversible nature of the electrode process. Further Ep values are observed to have shifted towards more negative values with increasing concentration of the depolarizer. The Ep values were found to be dependent on pH and shift towards more negative values with the increase in pH of the buffer solutions, indicating proton involvement in the electrode process.

The values for transfer coefficient (α), diffusion coefficient (D) and heterogeneous forward rate constant ($k^0_{f,h}$) at various pH values in cyclic voltammetry technique were given in Table I. The variation of diffusion current and peak current with the pH of the supporting electrolyte influences the diffusion coefficient values. Because the slight variation in diffusion coefficient values with increase in pH for isopropalin may be attributed to the decrease in the availability of protons. The forward rate constant ($k^0_{f,h}$) values were found to decrease with increase in pH. This trend shows that the electrode process becomes more irreversible with increase in pH of the solution.
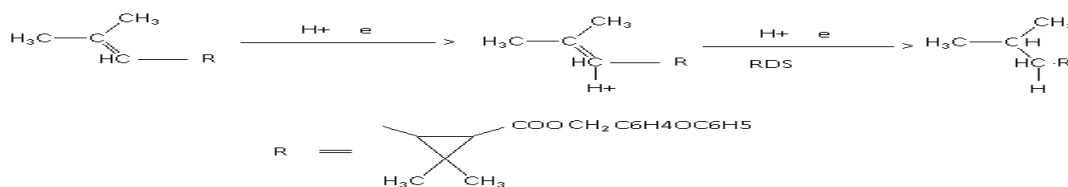
Scheme I : Electrode mechanism of Phenothrin (at pH 4.50)
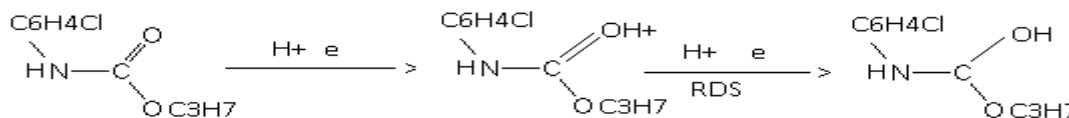
Scheme II : Electrode mechanism of Chlorpropham (at pH 4.50)
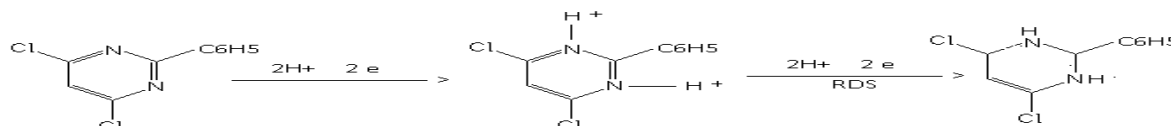
SchemeIII : Electrode mechanism of Fenclorim (at pH 4.50)

Cyclic voltammetry is mainly employed to study the mechanism and nature of the electrode process (Scheme I, II and III). Cyclic voltammetry has been specially used for the detection of reactive

intermediates, if any during the electrode process. Apart from general applications of all the techniques, differential pulse adsorptive stripping voltammetry has been extensively used to establish experimental and instrumental parameters for analytical estimations of the above said pesticides and their determination. Controlled potential electrolysis has been used for the isolation of the reduction products. Determination of total number of electrons participated in the electrode process has been carried out by milli coulometric technique. The experimental data obtained from these techniques has been used to evaluate the kinetic parameters such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constant values to understand the mechanistic nature and kinetics of the electrode process in universal buffer systems.

Information concerning the voltammetric properties and electron stoichiometry of pesticide and the knowledge of the reduction behaviour of similar classes of pesticides reported in literature should permit us to propose a reasonable mechanism for the reduction of the studied compounds. The reduction mechanisms proposed for the electrode processes studied are presented in Schemes I, II and III.

Phenothrin exhibits a single well-defined wave / peak obtained in pH 2.0 to 6.0 in all the techniques, corresponding to the reduction of >C=C< group in two electron process.

Chlorpropham exhibits only one voltammetric wave / peak over the pH range 2.0 to 6.0 with all techniques. This wave / peak is attributed to the simultaneous reduction of carbonyl group involving 2 electrons.

Fenclorim exhibits a single well-defined wave / peak obtained in pH 2.0 to 6.0 in all the techniques, corresponding to the reduction of azomethine group in two electron process. Typical cyclic voltammograms for three samples are shown in Fig. 1.0.

IV. Recovery Experiments

a) Analysis

Based on the results obtained with Dp Asv at a CNTPE, differential pulse adsorptive stripping voltam-mery has been used for quantitative estimation of samples using both calibration and standard addition methods.

Investigated compounds was found to exhibit well resolved peak at pH 4.0, and the sharp well resolved peak was chosen for quantitative studies. Peak currents were linear over the concentration range of 10^{-7} M to 10^{-12} M with lower detection limits of 1.02×10^{-11} M. The relative standard deviation and correlation coefficients for phenothrin, chlorpropham and fenclorim are found to be 1.30%, 0.998, 1.25%, 0.996 and1.26%, 0.997respectively for 10 replicates.

b) Recommended analytical procedure

Standard solutions (1.0×10^{-8}M) prepared in dimethyl formamide[16-18]. 1 mL of standard solution were transferred into a voltammetric cell and made up with 9 mL of supporting electrolyte (pH 4.50) and de oxygenated with nitrogen gas for 10 min, subjected to voltammetry. After obtaining the voltammogram, a small increment of standard solution of samples is added to voltametric cell and deoxygenated for 10 min and voltammogram recorded under similar conditions. In the same manner 10 voltammograms are recorded for 10 standard additions. The optimum conditions for analytical determination were found to be at pH.4.50.

c) Determination of samples in spiked water samples

To the filtered water known amount of samples are added. Aliquots of water samples were taken in a 25mL graduated tube buffer solution is added and analysed as described above. The recoveries of samples ranged from 99.60 to 99.80% and the results are summarized in Table II.

V. Conclusion

From the results, it is concluded that phenothrn, cloropropham and fenclorim are found to exhibit a single well resolved wave / peak in the buffer systems studied (pH 4.50) owing to the reduction of electro active group. It can be seen from the above mentioned results and findings that modern electro analytical methods may even today play a very useful role in the field of monitoring the persistence of various pesticides having different electro active groups in different matrices such as environmental samples, food and drinks, aquatic samples etc. Remarkably new electrode materials and arrangements can greatly stimulate further development in this field.

Table I : Typical cyclic voltammetric data of phenothrin, chlorpropham and fenclorim at pH:4.50

Sample	-Ep/V	Ip/nA	αn_a	$DX10^6/cm^2S^{-1}$	$K^0_{f,h}/cm\ S^{-1}$
Phenothrin	1.60	6.5	0.42	2.12	7.20×10^{-2}
Chlorpropham	0.60	5.8	0.30	1.60	3.32×10^{-3}
Fenclorim	1.15	7.5	0.52	2.10	6.89×10^{-6}

Table II : Recoveries of phenothrin, chlorpropham and fenclorim in spiked water samples

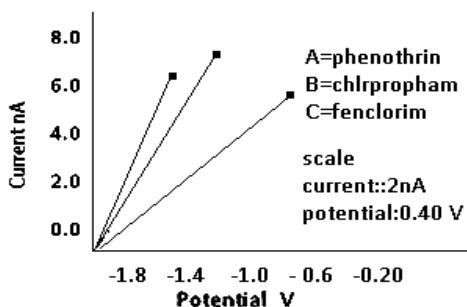| Name of the sample	Amount added (μg/mL)	Amount found (μg/mL)	*Recovery (%)	Standard deviation%
Phenothrin	3.0	2.97	99.80	0.30
Chlorpropham	5.0	4.89	99.60	0.25
Fenclorim	7.0	6.95	99.70	0.26

Average of 10 replicates

Fig. I : Peak current Vs half wave potential curves of samples at CNTPE , pH 4.50, Concentration: 0.5 mM; scan rate : 45 mVs^{-1}
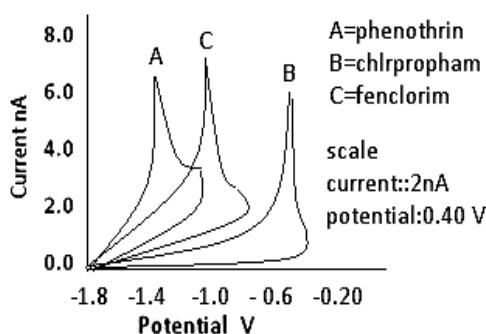

Fig. II : Typical cyclic voltammogram of samples at CNTPE, pH 4.50,Concentration: 0.5 mM; scan rate : 45 mVs^{-1}

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