Global Journal of Science Frontier Research: a
Physics and Space Science
Volume 18 Issue 2 Version 1.0 Year 2018
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Reduction Electrode Mechanism of Pesticides Having Different Electro Active Centres at Carbon Nano Tubes Paste Electrode

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GJSFR-A Classification : *FOR Code: 240504*

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I. Introduction

Despite the fact that 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. In present investigation two pesticides having >C=C< and >C=N- as electro active centres are examined.

a) Binapacryl

Binapicrylis registered as dinitrophenol acaricide (bird repellenent) Mauro De Paoli, M. Taccheo Barbina[1] determined pesticide by using Solid-phase extraction and gas chromatographic determination acaricide residues in honey. Bissacot DZ, Vassilieff [2] applied HPLC determination of binapicryl., deltamethrin, cypermethrin, and cyhalothrin residues in the milk and blood of lactating dairy cows. Zhou J, Xue X, et.al[3] employed Rapid and sensitive determination of two degradation products of binapicryl in honey by ultrasonically assisted extraction and gas chromatography with electron capture detection. Bissacot, et.al[4] employed HPLC Determination of Flumethrin, Deltamethrin, Cypermethrin, and Cyhalothrin Residues in the Milk and Blood of Lactating Dairy Cows. Sassine et al. [5] employed cypermethrin Residues Determination in the Milk of a Lactating Dairy Cow by Gas Chromatography-Ion Trap Mass Spectrometry. Ravi et al. [6,7] employed Negative Ion Chemical Ionization-Gas Chromatographic–Mas Spectrometric Determination of Residues of Different pesticides in Whole Blood and Serum. Wang [8] subjected Chromatographic methods for the determination of pesticide residues in crops, foods and environmental samples. Sanghavi et al.[9-13] reported voltammetric determination of pesticides having various electro active groups.

b) Isoxadifen

Isoxidifen is registered as herbicide which leads to accumulation in soil and crops that have been treated directly[14]. Prevention of negative effects of herbicides requires a systemic control of their residues in agricultural products, food, soil and water. Several analytical methods have been developed for the determination of herbicides in soil, water and agricultural products. Tanogai et al.[15] developed chromatographic method for the determination of a herbicides in food crops. Tanabe et al.[16] developed a GC/MS method for the determination of residues Gas chromatography with atomic emission [17-21].

II. Experimental

a) Apparatus and Electrodes

Voltammetric determinations were performed using a model meterohm Auto Lab 101 PG stat (Netherlands). 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

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(Japan)Xp26 delta range micro balancer were used to weigh the samples during the preparation of standard solutions. All the experiments were performed at 25^{0}C.

Fig. 1

b) Reagents and Solutions

All reagents used are 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 limited.

III. Characterisation of Peaks/Waves

Binapycril and isoxydefen are found to a give a single well defined peak in acidic solutions (2 < pH < 6). Increase of pH from 4.0 leads to decrease of the peak current. In the acidic medium, the peak of the compound is due to the reduction of >C=C< and-C=N- group in two electron process(scheme-1). Typical cyclic voltammograms of Binapycril and isoxydefen are shown in Fig.1.0

IV. Nature of the Electrode Process

The reduction process in Binapycril and isoxydefen found to be diffusion controlled and adsorption on the electrode surface in the buffer systems studied as evidenced from linear plot $i_p$vs $v^{1/2}$ passing through origin (Fig.2.0.).The shift of peak potential (E_p) towards more negative values with increase in concentration of depolarizer, shows that the electrode process is irreversible. This is further confirmed by log-plot analysis. The variation of peak potentials with scan rates and absence of anodic peak in the reverse scan in cyclic voltammetry indicates the irreversible nature of the electrode processes. The dependence of i_p/pH curves shows a behaviour in accordance with a process in which a proton transfer provides the reduction of the acid form to form an electroactive species. The number of protons taking part in the rate determining step is two.

V. Identification of Reduction Products

Millicoulometry employed to find out the number of electrons involved in the electrode process. The results obtained from millicoulometry have shown that the number of electrons is two for Binapycril and isoxydefen. The number of protons involved in the rate determining step of the electrode process is two. Controlled potential electrolysis experiments were carried out at -0.80 V vs. SCE at pH 4.0.

VI. Kinetic Data

Kinetic data such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constants obtained with different methods for Binapycril and isoxydefen summarised in Table 1.0. The diffusion coefficient values were noticed to be in good agreement from cyclic voltammetry. The heterogeneous forward rate constants were decreasing with an increase in pH of the supporting electrolyte, which may responsible for the shift of reduction potentials towards more negative values with increase in pH. This trend is particularly evident where the proton transfer is involved in the electrode process.

VII. Differential Pulse-Adsorptive Stripping Voltammetric Studies

DP-AdSV peaks of Binapycril and isoxydefen at CNTPE (Fig.3.0) is attributed to two electron reduction of Binapycril and isoxydefen this peak followed to establish the optimum conditions. The standard addition and calibration methods have been employed to estimate the compound in water and soil samples.

a) Analysis

Well defined and well resolved AdSV waves/ peaks obtained at pH 4.0 were used for the quantitative estimation of Binapycril and isoxydefen in water samples. Both calibration and standard addition

methods were used for the quantitative determination of the Binapycril and isoxydefen. From the calibration method, it is observed that the peak current shows a trend found to be linear over the concentration range 3.0 x 10^{-8}M to 1.0 x 10^{-4} with lower detection limit 0.89 x 10^{-6} M for Binapycril and isoxydefen for 6 replicates, relative standard deviation and correlation coefficient were found to be 0.95% , 0.994 and 0.94%,0.985 respectively for Binapycril and isoxydefen

b) Recommended Analytical Procedure

The stock solution (1.0 x 10^{-3} M) of samples prepared by dissolving the required quantity of the electroactive species in methanol. Standard solutions prepared by dilution of stock solution with fitting amount of methanol. 1 mL of the standard solution is transferred into voltammetric cell and added with 9 mL of the supporting electrolyte and then de gasified by bubbling oxygen free nitrogen gas for 10 min. After recording the voltammogram, small amout of standard solutions added and then voltammograms recorded for each addition under similar experimental conditions.

c) Determination Binapycril and Isoxydefen in Spiked Water Samples

The above mentioned procedure has been successfully applied for the determination of pesticides in water samples. A100 mL sample of water is spiked with known concentrations pesticides and shaken for few minutes and filtered through a Whatman Nylan® membrane filter (0.45 nm pore size) and filtrate passed through a sep-pakc_{18} cartridge previously activated with 10 mL of methanol. Elution carried out with 30 mL of methanol. The organic phase was evaporated. The residues dissolved in methanol and added to cell containing a buffer solution. The average recoveries obtained for two samples ranged from 97.00% to 99.46% and are given in Table 2.0.

VIII. Conclusion

Though several methods reported regarding pesticide analysis in the reported less tedious method consumption of sample is reduced in quantitie and pollution arises due to heavy metal electrodes is avoided.

Table 1: Typical cyclic voltammetric data at CNTPE concentration: 0.5 mM, scan rate: 50 mVs^{-1} pH=4.0.

Sample	-Ep/V	Ip/nA	$\alpha\, n_a$	$\frac{D \times 10^6}{cm^2\ s^{-1}}$	$\frac{k^0_{f,h}}{cm\ s^{-1}}$
Binapicryl	1.04	5.80	0.44	1.50	2.13 x 10^{-10}
Isoxydefen	1.08	7.80	0.36	1.41	1.32 x 10^{-10}

Table 2: Recoveries of pesticides at CNTPE in spiked water samples

Sample	Amount added (μg/mL)	Amount found (μg/mL)	Recovery%	Standard deviation
Binapicryl	10.0	9.70	97.00	0.021
Isoxydefen	10.0	9.91	99.10	0.014

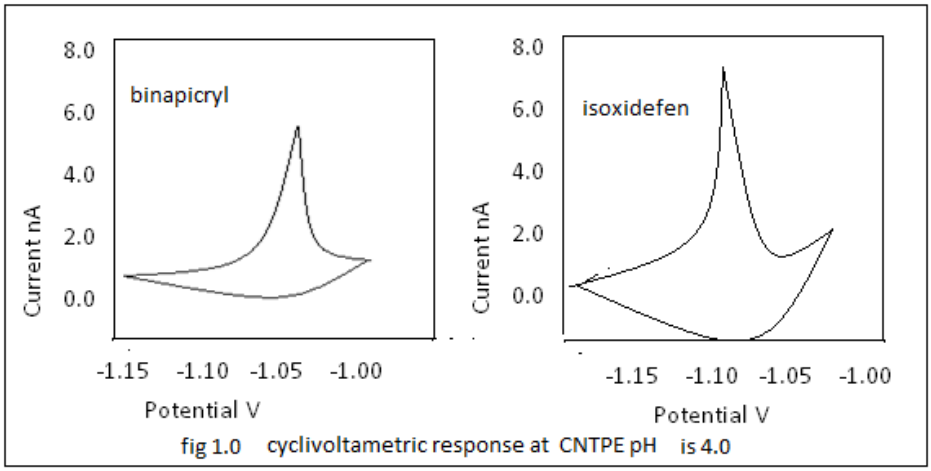

Fig. 2

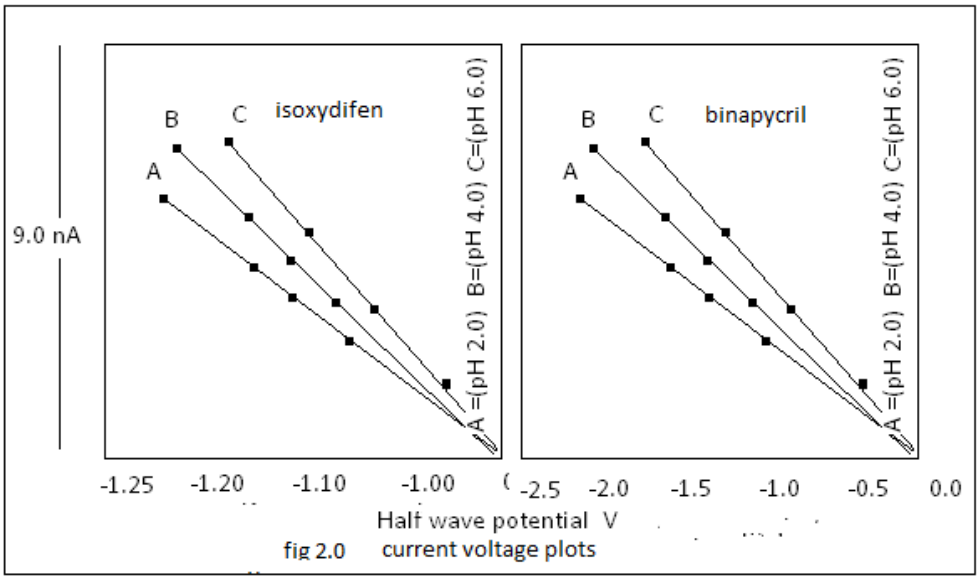

Fig. 3

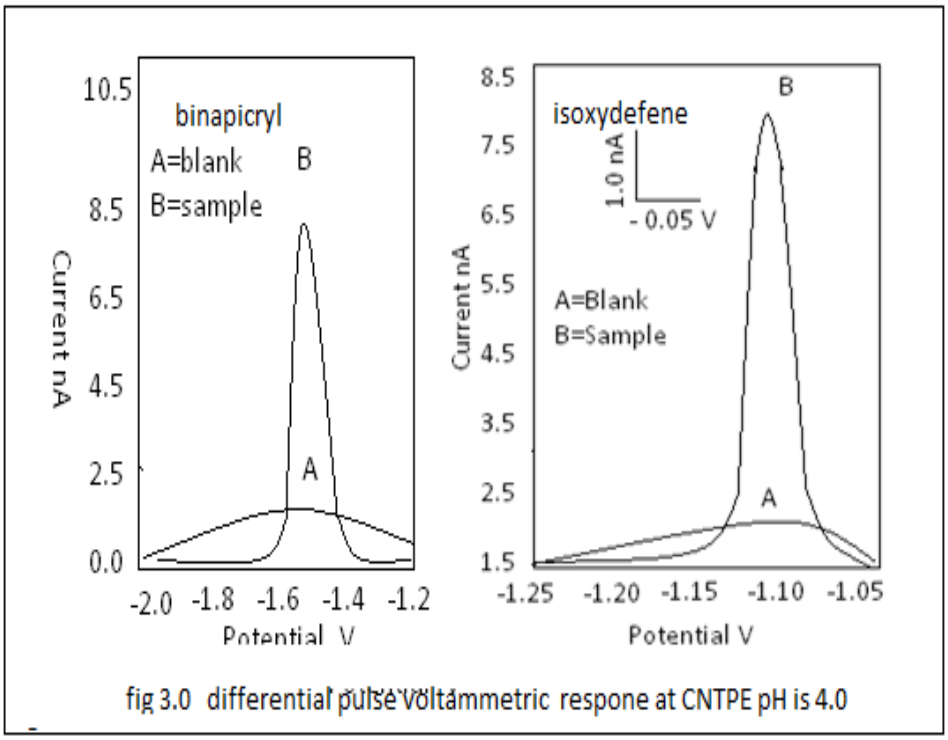

Fig. 4

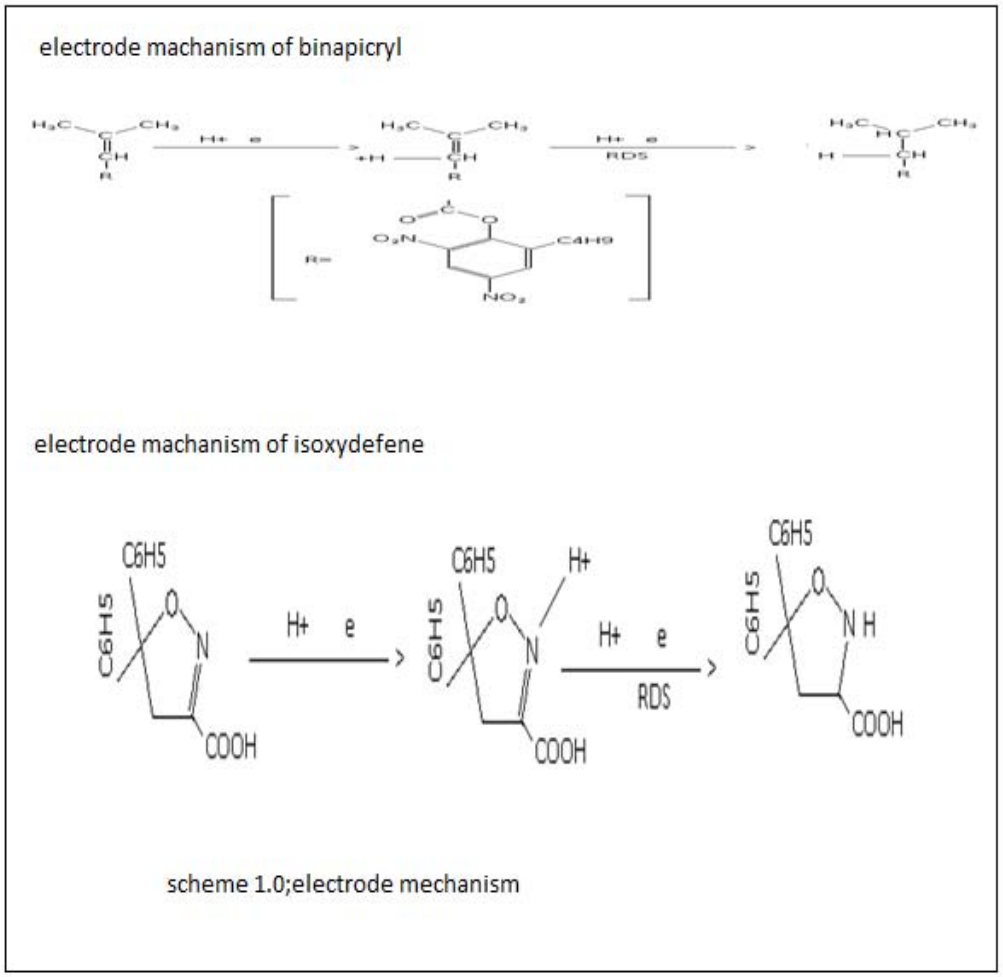

Fig. 5

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