Reduction behavior and determination of herbicides at Bare Carbon Electrode

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***Abstract*—In the present work, agriculturally important azomethine group containing herbicides Fenclorim, Isoxadifen, Fenchlorazole, was chosen to get clear information on the reduction groups present in their nuclei and electrode kinetics was studied by employing electrochemical techniques such as cyclic voltammetry, differential pulse adsorptive stripping voltammetry at bare carbon electrodes. Adsorptive stripping voltammetry method has been used for quantification of these herbicides in grains and water samples. Universal buffer with pH range2.0-6.0 was used as supporting electrolyte. The peak heights are in linear trend over the concentration range of 10^{-11} to 10^{-5} M. The relative standard deviation and correlation coefficient for the compounds was 0.97, 0.95, 0.98% and 0.978, 0.986, 0.988 respectively. The lower detection limit for the compounds under investigation was 1.03 x 10^{-9} M.**

***Index Terms*—Fenclorim, Isoxadifen, Fenchlorazole, Differential Pulse Adsorptive Stripping Voltammetry, bare carbon electrodes, Grains and Water Samples.**

1. INTRODUCTION

Now a days agro yields is based on the use of herbicides to control weeds in crops. Many herbicides are potentially toxic to higher animals. The increasing use of herbicides exerts their toxic effects through repeated exposure. The azomethine group containing herbicides were introduced in agriculture in 1954[1-10]. The azomethine group containing herbicides are used worldwide as selective pre and postemergence herbicides for the control of weeds.

2. EXPERIMENTAL

2.1Istrumentation

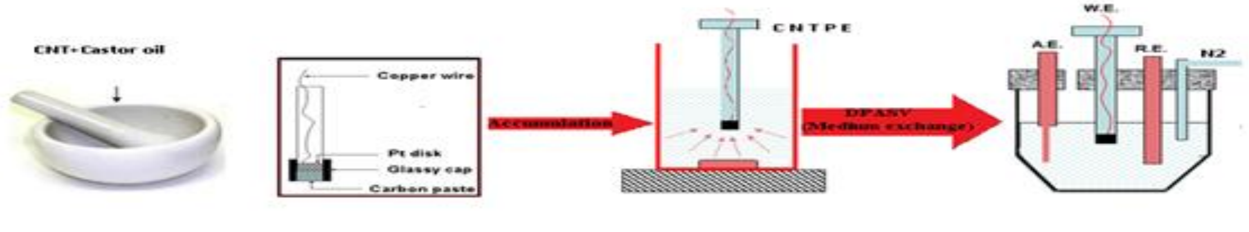
Experiments were conducted with Autolab PGSTAT 101 supplied by Metrohm, Netherlands. All electrochemical experiments were performed using an Electrochemical workstation, having a conventional three -electrode cell configuration with a bare carbon electrode as the working electrode, saturated calomel electrode (SCE) as a reference electrode and platinum wire as a counter electrode. Electrochemical experiments were carried out in a 2- mL voltammetric cell at room temperature (250) all potentials are referred to the Ag/AgCl reference electrode.
All potentials are quoted vs. SCE reference electrode. All pH measurements were made with the aid of a digital pH meter using a combined glass electrode.

2.2 Reagents

Reagents used were analytical grade.

2.3 Preparation and purification of electrode

The carbon paste electrode (CNTPE) was prepared by mixing castor oil in an agate mortar with pestle. Suitable amount of carbon and casterol oil were weighed in order to obtain 40-70% carbon w/w in the paste electrode. Subsequently, the paste was packed into a glass tube (l= 1.2 mm), a copper wire was embedded in the paste for electrical connection(Scheme I).



Sheme I: preparation of bare carbon electrode.

3. RESULT AND DISCUSSION

The effect of pH on the voltammograms has been investigated by recording the current voltage curves for the compounds under investigation at a concentration of 0.5 mM in universal buffer systems over the pH range of 2.0 to 6.0. All the compounds exhibit a single well-defined wave / peak at pH 2.0 to 6.0 in all the techniques, corresponding to the reduction of azomethine group. Typical voltammograms are shown in Fig. 1.0 and 2.0.

3.1 Effect of pH

The peak current i_p, increased gradually with the increase of pH of the solution till it reaches the maximum value at pH 4.0. A shift of the peak potential towards more negative value with increase in pH indicates the existence of a protonation reaction coupled with the reduction process(scheme 2). The best curve and highest peak current are obtained in universal buffer at pH 5.0

4. ANALYSIS

Adsorptive stripping voltammetry is a suitable technique for the analysis of herbicides due to its high sensitivity and resolution. The well resolved stripping voltammetric peak for the analytical purpose was obtained at pH 2.0 to 6.0, because in the buffer solution of higher alkalinity (pH < 8) the reduction of azomethine group is not easily facilitated owing to the less availability of protons. The peak heights are in linear trend over the concentration range of 10^{-11} to 10^{-5} M. The relative standard deviation and correlation coefficient for the compounds was 0.97, 0.95, 0.98% and 0.978, 0.986, 0.988 respectively. The lower detection limit for the compounds under investigation was 1.03 x 10^{-9} M.

4.1 Recommended analytical procedure

Analytical procedure for the voltammetric determination of herbicides as follows. A standard solution of herbicides (0.50 mM) was prepared in methanol.1 mL of standard solution is transferred in to cell and made up with 9 mL of supporting electrolyte and then purged with oxygen free N_2 gas for 10 min. prior to each run. After obtaining the voltammogram, small addition of standard solutions are added and voltammogram recorded after each addition under similar experimental parameters. The optimum conditions for the determination is pH 4.0, scan rate25 mVs^{-1} to 75 $mVs.^{-1}$, accumulation potential from -0.50 V to -1.3 V, accumulation time of 50 to 90 sec.

4.2 Determination of herbicides in spiked grain samples

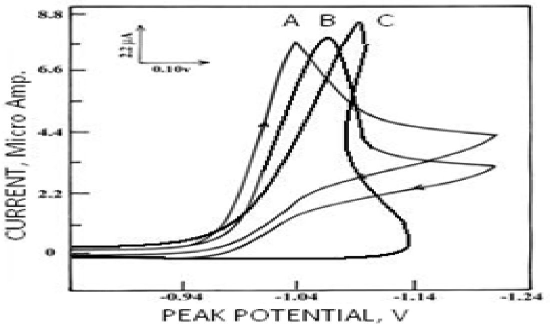
The developed analytical procedure has been applied to the quantitative estimation of herbicides grain samples. Known amounts of herbicides were sprayed on grain (wheat, rice) samples (25 g) and left for 1-2 hours. Then the samples are weighed, crushed and homogenized. The extracts were prepared by treatment of the above sample with two 50 mL portions of acetone and evaporated to dryness. The residue of herbicides dissolved in methanol and transferred to a 100 mL volumetric flask and aliquots were taken and analyzed. The results are shown in Table.1.0

4.3 Determination of herbicides spiked water samples

River water samples, which received run-off water from agricultural field, were collected form swarnamukhi river belt,Vakadu, Nellore district, A.P., India. These samples were filtered through a Whatman No.41 filter paper and added with known amount of herbicides under investigation. Aliquots were taken in a 25mL graduated tube and buffer solution was added and analyzed as described above. The results are shown in Table 2.0.

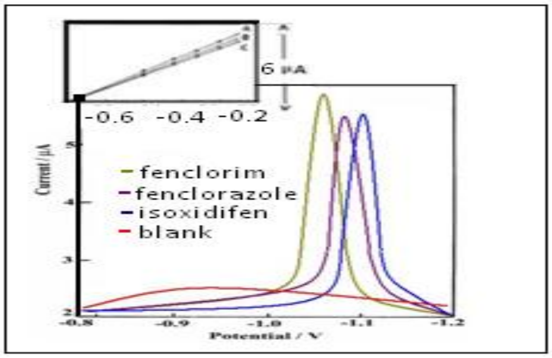
5.0 CONCLUSIÓN

By this aproche we can say that the method undertaken for the determination of pesticides differential pulse adsorptive stripping voltamery is selective and sensitive and low consumption of sample and less tidious compared to chromatography and spectroscopy. Bare carbon electrodes is most conveniente working electrode and polution less when compared to mercury and lead electrodes.



A=Fenchlorim B= Isoxadifen C= Fenchlorazole

Fig. 1.0: Typical cyclic voltammogram at pH5.0, Concentration: 0.5 mM; scan rate :(A) 45,(B)50,(C)40 mVs^{-1} at bare carbon electrodes.



Scheme II:Reduction mechanism at pH 5.0.

Fig 2.0. i_p vs $V^{1/2}$ plot of Fenclorim, concentration : 0.5 mM, scan rate for :(A) 45,(B)50,(C)40 mVs-1, at CNTPE.(Inlet Callibaration Plot) at bare carbon electrodes.

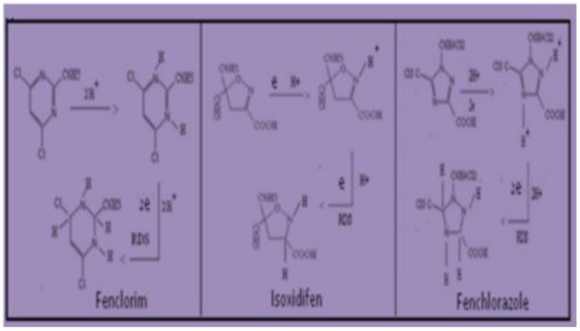


Table 1.0: Recoveries of herbicides in spiked wheat samples

Sample	Amount added (μg/mL)	Amount found (μg/mL)	Recovery (%)	Standard deviation
A.Fenclorim	3.0	2.96	98.00	0.0212
B.Isoxidifen	3.0	2.95	97.50	0.0252
C.Fenchlorazole	3.0	2.98	99.00	0.0282

Table 2.0: Recoveries of herbicides in spiked water samples

Sample	Amount added (μg/mL)	Amount found (μg/mL)	Recovery (%)	Standard deviation
A.Fenclorim	3.0	2.99	99.50	0.0512
B.Isoxidifen	3.0	2.97	98.50	0.0352
C.Fenchlorazole	3.0	2.88	94.00	0.0683

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