

An Electrochemical Studies of Fenitrothion at TiO₂ Nanoparticles Modified Glassy Carbon Electrode

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Abstract - An electrochemical response of Fenitrothion was investigated using cyclic voltammetric technique with the aid of TiO₂ nanoparticles modified glassy carbon electrode. The voltammetric response was evaluated in 0.02 ML⁻¹ acetate buffer solution (ABS), the TiO₂ nanoparticles modified glassy carbon electrode showed a significantly enhanced current peak indicating its (M-GCE) catalytic activity towards Fenitrothion. The parameters such as effect of pH, scan rate, concentration were studied. The increase in the reduction peak current with increase in scan rate was found, the linear regression equation, correlation co-efficient (R²), limit of detection (LOD) and limit of quantification were found to be 0.684mg/ml and 2.2805mg/ml respectively.

Key Words: Fenitrothion, cyclic voltammetry, titanium dioxide nanoparticles, glassy carbon electrode, SEM and XRD characterization.

1. INTRODUCTION

Organophosphorus pesticides (OPs) are most widely used in agriculture due to their high toxicity to insects and limited persistence in the environment, but this use has resulted in a serious risk to human health and the environment worldwide. Many efforts have been made to develop sensitive, convenient and effective methods for OP residues analysis in environment and other samples [1-2]. Gas chromatography (GC) [3-4], GC- Mass Spectrometry (MS) [5], and high performance liquid chromatography (HPLC)-MS [6-8] are commonly used methods to successfully detect OP residues in practical samples with high selectivity, sufficient sensitivity and precision.

Fenitrothion (o,o-dimethyl o-3-methyl-4-nitrophenylphosphorothioate) is one member of organophosphate pesticide class. The structure of Fenitrothion (FT) was represented in Fig.1.

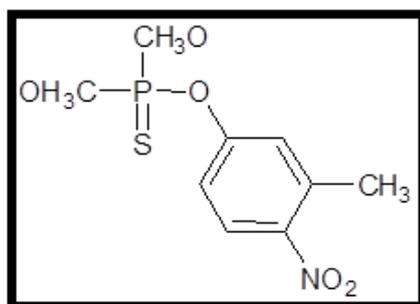


Fig. 1.The structure of Fenitrothion

Many of the OPs are commonly used in agriculture, home and garden. For example, diazinon and chlorpyrifos have been widely used by consumers who may contaminate themselves or their food by not understanding the precautions necessary for safe use. Cases have been reported of acetyl cholinesterase inhibition by a wide variety of drugs, alkyl sulphates and sulphonates, for example neostigmine, physostigmine, pethidine, some immunosuppressants and various cytostatic agents.

Organophosphorous compounds owe their toxic effect to the inhibition of cholinesterase enzyme activity in the nervous tissue. There are different types of cholinesterase in the human body, which differ in their location in tissues, the substrate affinity and physiological function. The principal ones are acetyl cholinesterase, which besides nervous tissues is also present in red blood cells, and serum cholinesterase which are a group of enzymes present in glial cells, plasma and liver. The effects induced by OP compounds in the organism are due to the AChE, Acetylcholinesterase, under normal physiological conditions, performs the breakdown of acetylcholine, which is the chemical mediator responsible for physiological transmission of nerve impulses at different sites. In the presence of OP, AChE is phosphorylated and is no longer able to breakdown acetylcholine into choline and acetic acid. The resulting accumulation of acetylcholine in the parasympathetic nerve synapses (muscarinic-like action), the motor end-plate (nicotine-like action) and in the central nervous system is responsible for all typical symptoms occurring after acute poisoning with OP [9-11].

At present, the electrochemical sensor has been developed for sensitive, reproducible and rapid determination of OPs. In particular, nanoparticle fabrication on glassy carbon electrode has advantage of low cost, easy to prepare, less time consuming [12]. Here, the choice of nanoparticle is titanium dioxide because it can provide significant effect for enhancing catalytically process [13].

1.1 MATERIALS AND METHODS

1.2. Chemicals and apparatus

Fenitrothion, titanium dioxide nanoparticle was purchase from Sigma-Aldrich, other chemicals used for preparing supporting electrolyte are of analytical grade and double distilled water was used throughout. Stock solution of Fenitrothion (5mg /500ml) was prepared by dissolving in 15ml of ethanol and diluting it to 500ml with double distilled water, stored in refrigerator at 4°C and used it as a stock solution.

All the Voltammetric measurements were taken from electro analyzer Model EA-201 with computer interface supplied by chemilink systems, Mumbai. A three electrode system was employed, consisting of Ag/AgCl as reference, platinum electrode as counter electrode and modified glassy carbon electrode (2mm diameter) as a working electrode. pH of supporting electrolyte was adjusted by pH meter supplied by systronics (India).

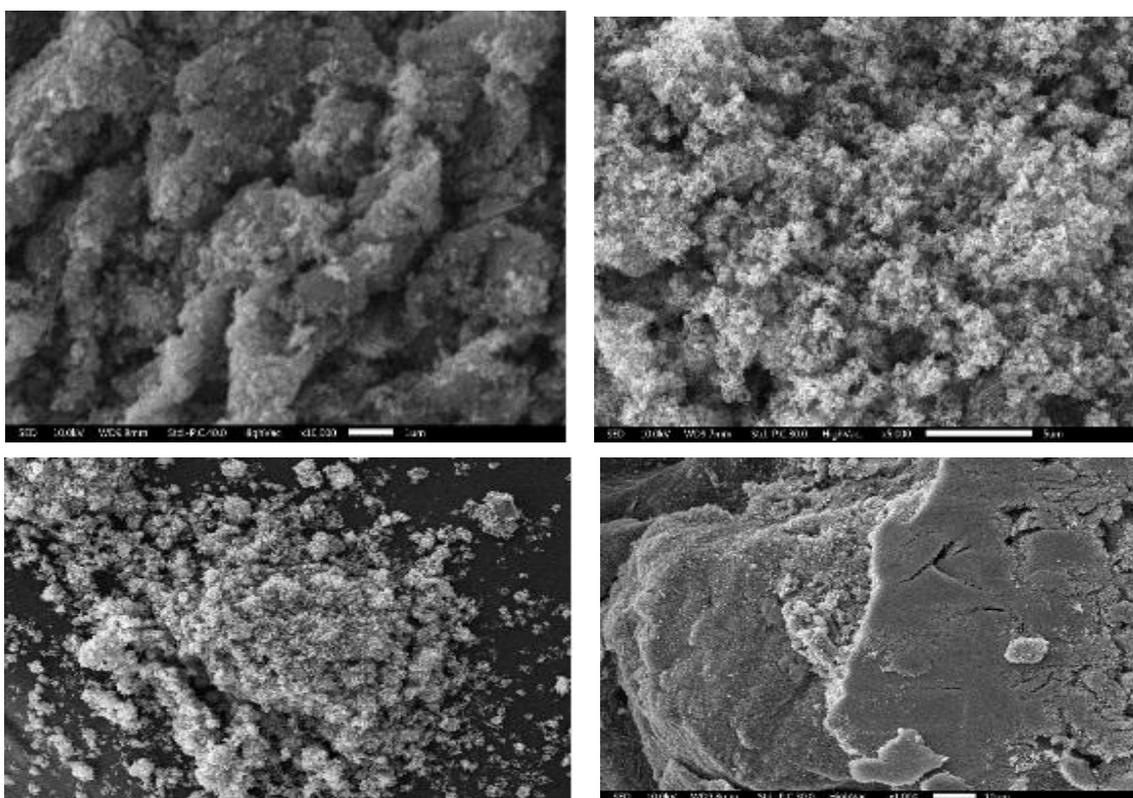
1.3. Pretreatment and Modification of Glassy carbon electrode

The glassy carbon electrode was polished by using alumina powder of different particle size viz., 1.0, 0.3 and 0.05µ m respectively to get clean and glassy finishing. The polished glassy carbon electrode was activated by electrochemical pretreatment method. [14]. A nanoparticle dispersion was prepared by sonicating 5µg of nanoparticle in 1ml of ethanol for 20-30 minutes in hot condition. Then, a drop 5µl of previously prepared nanoparticle dispersion solution was dropped on to the polished surface of electrode dried under IR lamp for 30 minutes, rinsed in distilled water and used as it is.

2. RESULTS AND DISCUSSION:

2.1. Scanning electron microscope (SEM) and X-ray Diffraction (XRD) Characterization of Ti(IV)O₂ Nanoparticles at Different Magnifications.

Fig.2, shows the scanning electron microscopy images it confirms the surface morphology of the Ti(IV)O₂ nanoparticles and xrd images confirms the Ti(IV)O₂ nanoparticles size.



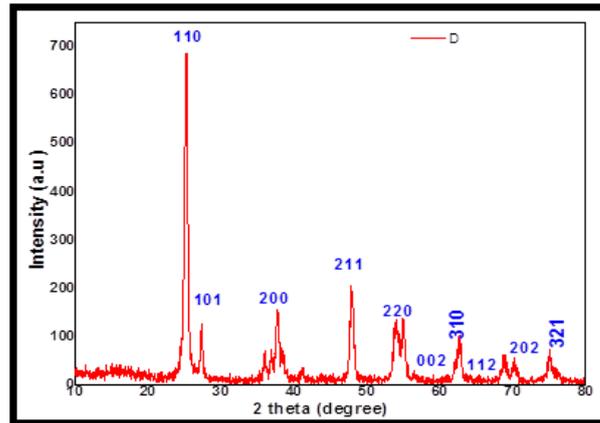


Fig.2. Explain the surface morphology of Ti(IV)O₂ NP at different magnifications using scanning electron microscope SEM and Xrd images of Ti(IV)O₂ NP.

2.2. Electrochemical response of modified glassy carbon electrode [Ti(IV)O₂-NP MGCE]

Fig.3, shows that cyclic voltammograms of 1mM ferricyanide at bare glassy carbon electrode (curve a) and Ti(IV)O₂ nanoparticles modified GCE (curve b) in KCl as supporting electrolyte between potential scan -200 to 600 mV. From the voltammograms we can clearly see that there is great enhancement of current upon the modification of GCE with nanoparticles which indicating varies increase in surface area of electrode after modification.

MGCE $E_{pa} = 284$ mV, $I_{pa} = 20.6$ μ A, $E_{pc} = 178$ mV and $I_{pc} = 15.97$ μ A.
 BGCE $E_{pa} = 296$ mV, $I_{pa} = 15.92$ μ A, $E_{pc} = 173$ mV and $I_{pc} = 10.52$ μ A.

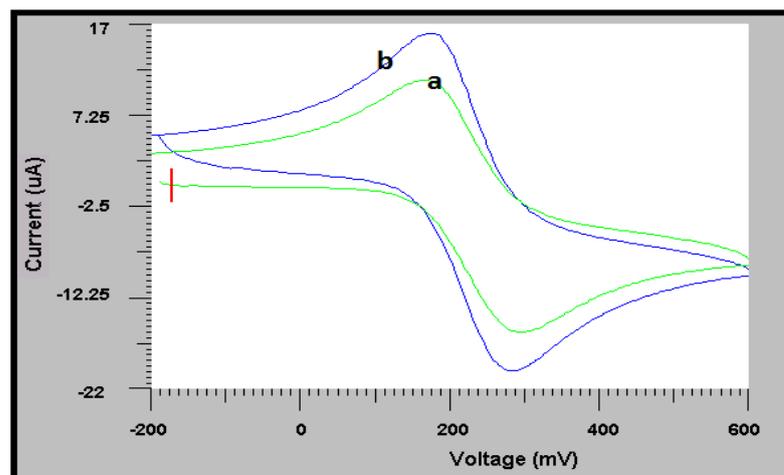


Fig.3. Cyclic voltammograms of 0.1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution at Ti(IV)O₂-NP MGCE (b) and at bare GCE (a) at scan rate 50 mVs⁻¹.

2.3. Electrochemical Behavior of Fenitrothion

Fenitrothion showed a good signal with Ti (IV)O₂ NPMGCE when compared to that of bare GCE. 100 μ L of Fenitrothion stock solution and 20mL of acetate buffer (pH-5.0) were added to the electrochemical cell. Then Ti(IV)O₂ NPMGCE (working electrode) with reference and auxiliary electrodes were dipped in the test solution and potential is applied in the range of +1000 mV to -1300 mV. And the tested sample range was between 25 ng/mL – 250 ng/mL.

Cyclic voltammograms of Fenitrothion in acetate buffer is shown in Fig.4, curve 'b' for bare glassy carbon electrode not showing any reduction peak indicating the low sensitivity of the bare glassy carbon electrode. Curve 'a' shows the reduction peak of Fenitrothion at potential E_{pc} 971 mV and peak current I_{pa} -24.4 μ A indicate the sensitivity of Ti(IV)O₂ NPMGCE. Surface area of modified electrode is calibrated with the help of potassium ferricyanide.

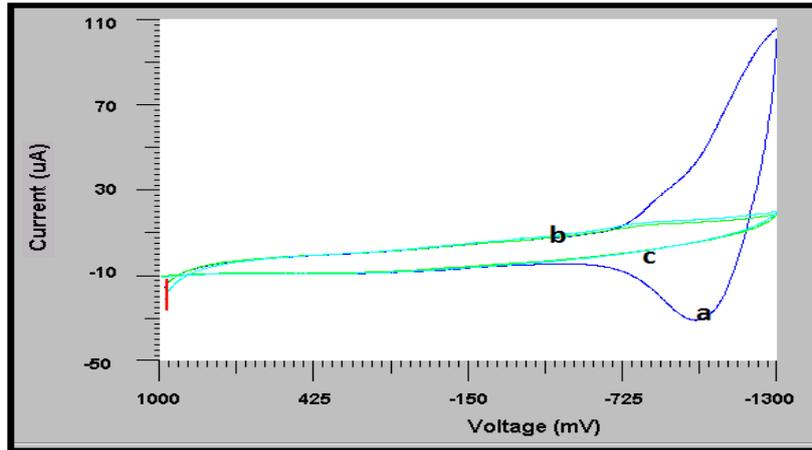


Fig. 4. Cyclic Voltammograms of 25 mg/ml Fenitrothion at TiO₂ NPMGCE (a), Bare CPE (b) and blank solution in acetate buffer pH-5 (c) at scan rate 50 mVs⁻¹.

3. Effects of pH on the Fenitrothion Voltammograms

The electro-reduction of Fenitrothion was studied at 25mg/ml solution in acetate buffer over a pH range from 3 to 9 at scan rate of 100 mV/s Ti(IV)O₂MGCE using cyclic Voltammetric technique. The reduction peak current increases with increase of pH from 3 to 5 and become maximum 971 mV and peak potential shifted to 946 mV as shown in Fig.5, while beyond pH-5, a great a decrease of reduction peak has been observed.

The corresponding linear regression equation is

$$I_{pc} = 0.06178 \times 10^{-5} + 0.47583 - - - - - R = 0.99712$$

The slope of pH versus current 0.04048 indicates that the electron and proton involves in the reduction process as shown in Fig.6,

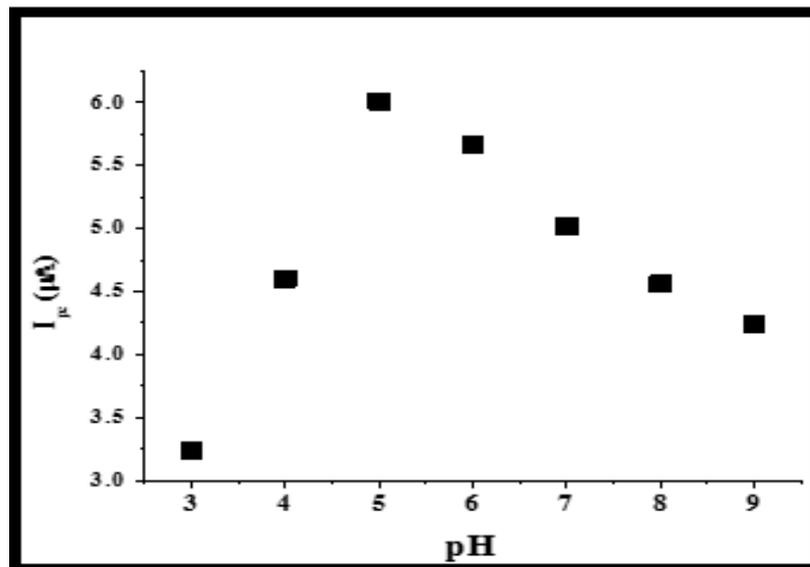


Fig.5, Dependence of reduction peak current on the acetate buffer solution pH 3-9.

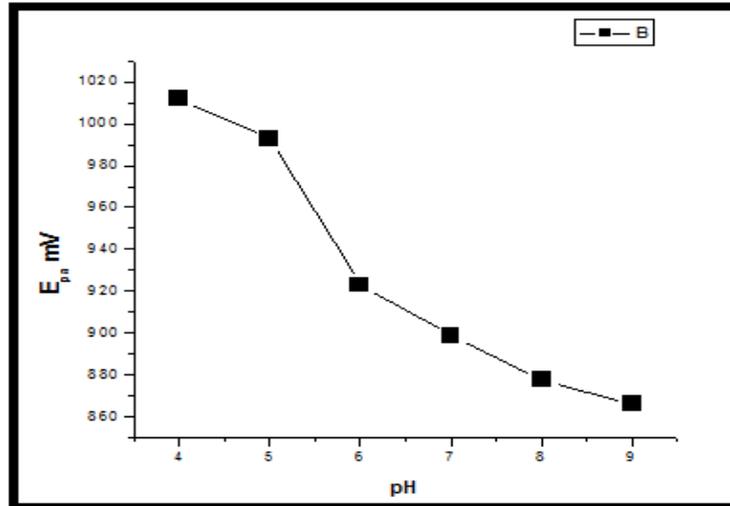


Fig.6, Plot of Cathodic peak potential vs. pH (3.0-9.0) of 25mg/ml Fenitrothion at TiO₂ NPMGCE.

4. Effect of Scan Rate

The effect of scan rate on the electrochemical response of 25mg/mL of Fenitrothion at Ti(IV)O₂ MGCE was studied at the range of 10 to 100 mV/s⁻¹ as shown in Fig. 7, On plotting current versus rate as shown in Fig. 8, It was found that the reduction peak current linearly increases with increase in the scan rate which indicates the process is diffusion controlled. From the Fig. 9, it was found that the reduction peak current increases linearly with the increase in the square root of scan rate with a correlation coefficient R=0.99712 and A=0.47583 B=0.06178

The linear regression equation is

$$I_{pc} = 0.06178 \times 10^{-5} + 0.47583 \text{ --- } R = 0.99712.$$

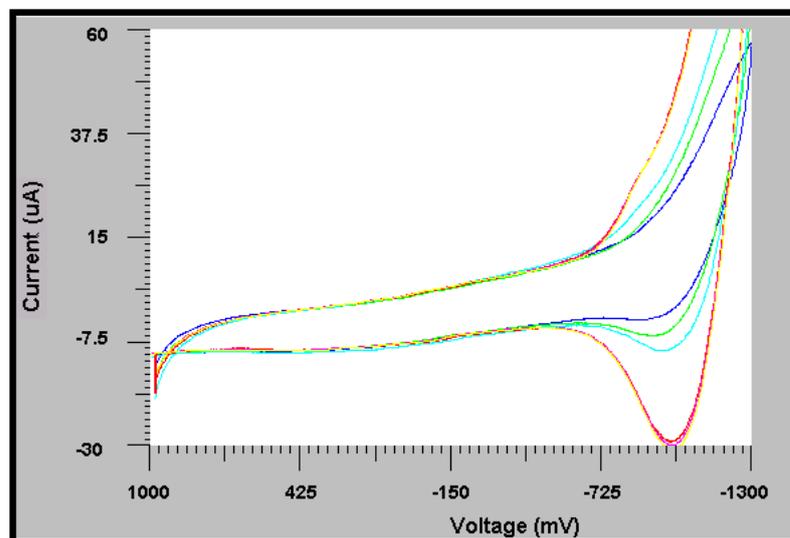


Fig.7, Cyclic voltammograms of 25mg/ml Fenitrothion at TiO₂ NPMGCE GCE in ABS (pH-5) with different scan rates were 10,20,30,40,50,60,70,80,90,100, mVs⁻¹ respectively.

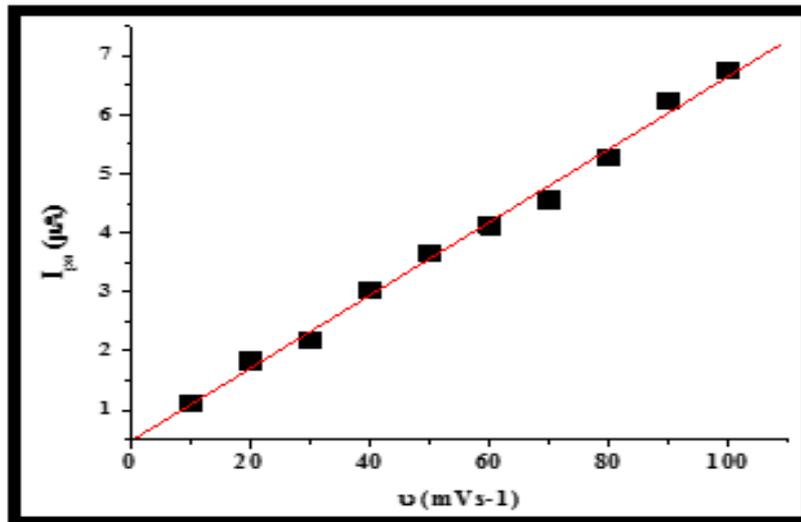


Fig. 8, Plot of reduction peak current versus scan rate

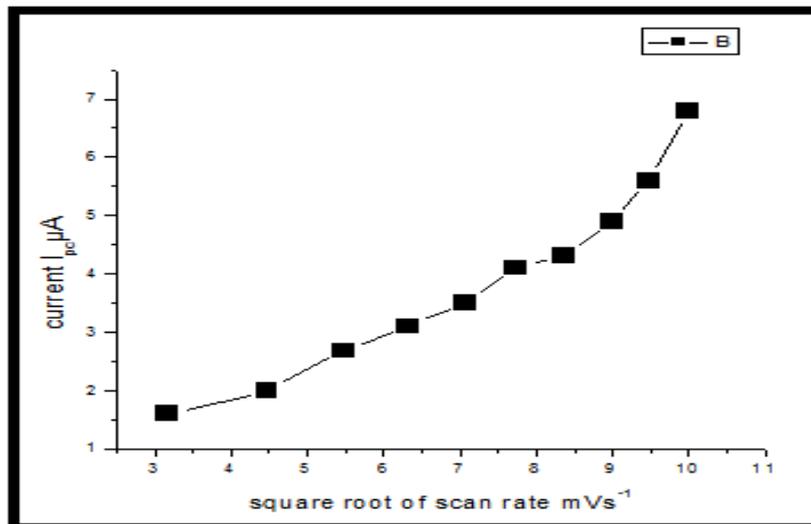
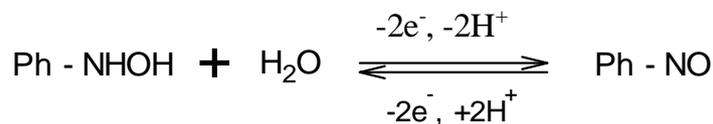
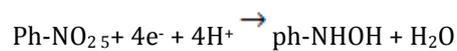


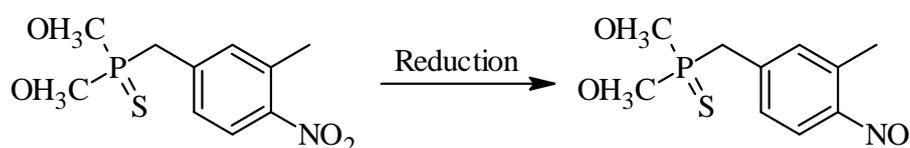
Fig. 9. The plot of Fenitrothion reduction peak current v/s. the square root of scan rates ($r=0.99712$).

A probable reaction mechanism involved the reduction of Fenitrothion also proposed.

Reduction of fenitrothian at electrode surface



Probable oxidation reaction of Fenitrothion



5. Effect of Fenitrothion Concentration

The variation of concentration of Fenitrothion was studied at modified glassy carbon electrode (Ti(IV)O₂ MGCE) using ABS of pH-5 at a scan rate of 100 mV/s⁻¹. Fig. 10, shows the cyclic voltammograms of Fenitrothion at Ti(IV)O₂ MGCE. Fig. 11, shows the plot of I_{pc} versus concentration of Fenitrothion showed the linear relationship between the Cathodic peak current I_{pc} and the Fenitrothion concentration range of 25mg/ml to 200mg/ml with a correlation co- efficient of R=0.99781, A=5.4 and B=0.0404. Limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.684mg/ml and 2.2805mg/ml respectively.

$$I_{pc} = 0.0404 \times 10^{-5} + \dots - R = 0.997812$$

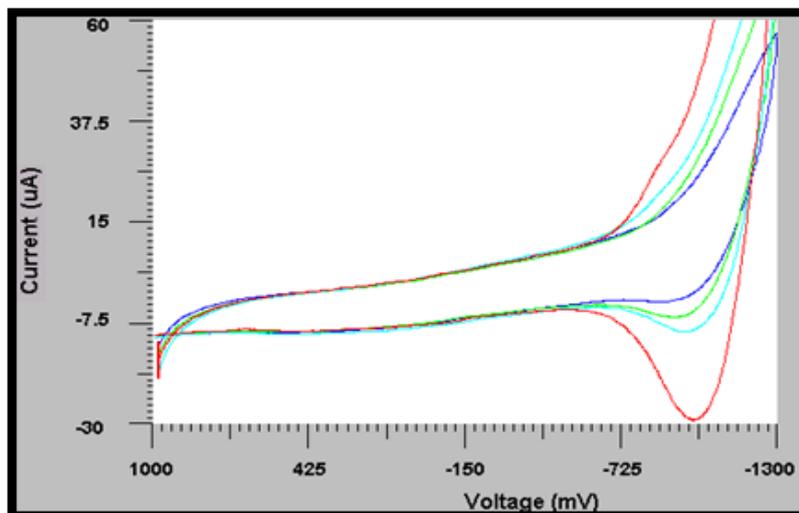


Fig.10, Cyclic voltammograms of variation of concentration of Fenitrothion 25 ng/mL to 200 ng/mL at Scan rate of 100 mV/s⁻¹.

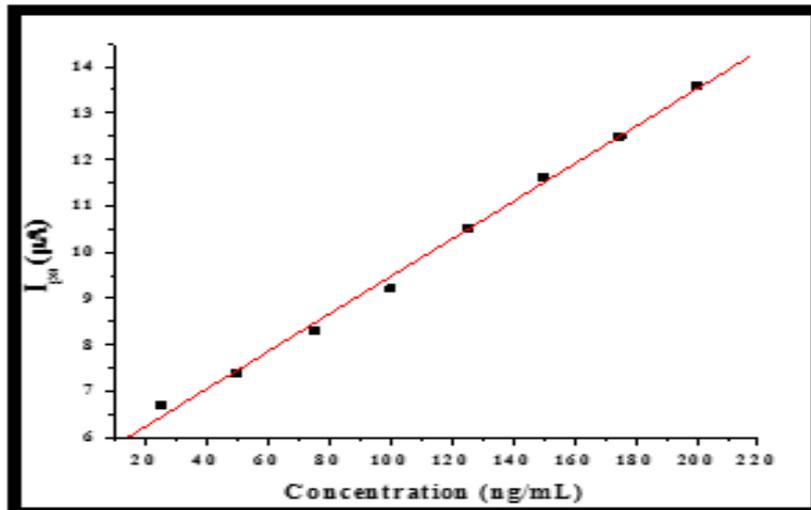


Fig.11, The plot of reduction current versus concentration Fenitrothion.

CONCLUSION:

In the present work Titanium (IV) oxide nanoparticles modified glassy carbon electrode [Ti(IV)O₂NPMGCE] has been prepared for the electrochemical detection of Fenitrothion. Well defined reduction peak of Fenitrothion was obtained at Ti(IV)O₂ NPMGCE, whereas no reduction peak was obtained at bare glassy carbon electrode. Ti(IV)O₂ NPMGCE is more sensitive than bare glassy carbon electrode. The electrochemical response is diffusion controlled and irreversible in nature.

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