ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
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GRADUATE PROJECT

VOLTAMMETRIC STUDY OF FENITROTHION BY USING POLY (CARMINE) MODIFIED GLASSY CARBON ELECTRODE

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Abstract

Attempted has been made to develop a voltammetric sensor for the determination of fenitrothion based on the use of poly (carmine) film electrode. The voltammetric response of poly (carmine) based on previously reported paper is compared with voltammetric response of electrochemically pretreated (EPT) glassy carbon electrode in 0.5M H_2SO_4 and 0.1M (pH 6.0) phosphate buffer used for the preparation of carmine. The response appears to be similar in both poly (carmine) modified and EPT glassy carbon electrodes. Electrochemical behavior of fenitrothion is studied by cyclic voltammetry (CV). One irreversible reductive peak appeared at -0.598 V and a couple of reversible oxidative and reductive peaks appeared at -0.012 V and -0.04 V potentials respectively. The oxidation peak of fenitrothion is studied by linear scan voltammetry (LSV) and it exhibited a well defined peak at a potential of -0.012 V on both poly (carmine) modified and EPT glassy carbon electrodes. Compared with that on a bare glassy carbon electrode, the oxidation peak current of fenitrothion at the modified electrodes is significantly enhanced. The oxidation peak current is linear with the fenitrothion concentration in the range of 5.0×10^{-6} to 1.2×10^{-4} mol L^{-1} for the poly (carmine) modified glassy carbon electrode and 5.0×10^{-6} to 1.0×10^{-4} mol L^{-1} for the EPT glassy carbon electrode.

1. INTRODUCTION

Conducting polymer has now been known for more than 20 years. In 1977 the American scientists Heeger and MacDiarmid discovered that doping of polyacetylene (PA) with iodine endowed the polymer with metallic properties, including an increase in conductivity of 10 orders of magnitude. This promising results simulated worldwide efforts to construct a polymer battery. In the course of these studies, conducting polymers with properties similar to PA were discovered, such as polyphenylene polyphnylelne vinylenes, as pure hydrocarbons, on the one hand, and polypyrrol, polythiophine, and polyaniline on the other hand. Nowadays, a great deal of different monomers are known that from conducting polymers up on chemical or electrochemical preparation techniques. Such starting system include substituted derivatives of the already mentioned hydrocarbons and heterocycles as well as specially tailored novel compounds, such as for generation of small band gap polymers with high transparency in the conducting state (1).

There are several reasons why electrochemists are interested in this field. The method of choice for preparing conducting polymers, with the exception of PA, is the anodic oxidation of suitable monomer species such as pyrrol or thiophine or aniline. Three aspects of electrosynthesis are of relevance for electrochemists. First, there is a deposition process of the polymers at the electrode surface, which involves nucleation and growth stapes. Second to analyze these phenomena correctly, one has to know the mechanism of electropolymerization and third, there is the problem of optimization of the mechanical, electrical, and optical material properties produced by the special parameters of electropolymerization.

Electropolymerization of conducting polymers occur by the electrochemical oxidation of monomers such as pyrrol, thiophine, aniline, etc. or their derivatives, initiates a polymerization process at the electrode/electrolyte interface that promotes the formation of a polymeric film that adheres to the electrode. A similar homogeneous polymerization process can be initiated by chemical oxidation or chemical polymerization. Some monomers can be polymerized as well by electrochemical or chemical reduction (2).

Doping mechanism is not comparable with the classic doping of typical semiconductors. Rather, they correspond to oxidation in the case of p-doping or reduction in the case of n-doping. Thus in electrochemical terminology the doping process corresponds to a redox reaction. Especially for applications, it is important to know the phenomenological details of such redox reactions, for example in which potential range the charging occurs and what is the maximum level of oxidation before the material starts to degrade (2).

A basic property of all conducting polymers is the conjugation of the chain-linked electroactive monomeric units; that is, the monomers interact via a Π-electron system. In this respect, they are fundamentally different from redox polymers. Although redox polymers also contain electroactive groups, the polymer backbone is not conjugated. Consequently, redox polymers are nonconductors.

2. LITERATURE REVIEW

2.1 Conjugated polymers (2-5)

Carbon has the electronic configuration $1s^22s^22p^2$ and forms four nearest neighbor bonds. In σ-boned polymers, as in polyethylene which consists of the monomeric repeated unit of –(CH_2-CH_2)-, the C atoms are sp3 hybridized, and each C atom has four σ-bonds. In such non-conjugated polymers, the electronic structure of the chain of atoms that comprises the backbone of the macromolecule consisted of only σ-bonds. The large energy band gaps in σ-bonded polymers, *Eg* (σ), renders these polymer materials electrically insulating, and generally non absorbing to visible light.

In conjugated polymers, however, there exists a continuous network, often a simple chain, of adjacent unsaturated carbon atoms, i.e., carbon atoms with sp2 hybridized state. Each of these sp2 hybridized C atoms has three σ-bonds, and the remaining pz atomic orbital, which exhibits π-overlap with the pz orbital of the nearest neighbor sp2 hybridized C atoms. This chain of atoms with π-overlap of the atomic pz-orbitals leads to the formation of π-states delocalized along the polymer chain. In a system with one dimensional periodicity, these π-states form the electronic bands, according for optical absorption at lower photon energies.

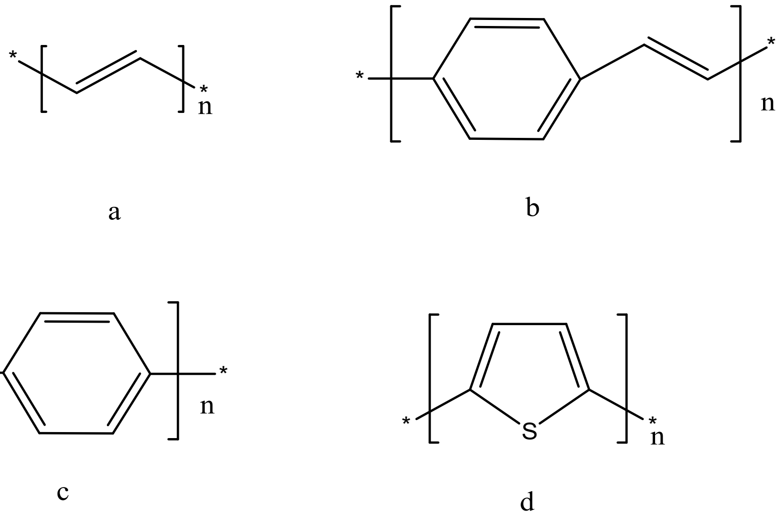


Fig. 1. The structural formula of some common polymer chains. (a) *trans*-polyacetylene, (b) poly(*para*-phenylenevinylene), (c) poly(*para*-phenylene), (d) poly(thiophene)

The essential properties of the delocalized π-electron system, which differentiate a typical conjugated polymer from a conventional polymer with σ-bonds, are the following;

(i) The electronic band gap, *Eg* is relatively small (~1-4eV), leading to low energy electronic excitations and semiconductor behavior,

(ii) The polymer chains can easily be oxidized or reduced, through charge transfer with dopant species,

(iii) Carrier mobilities are large and high electrical conductivities are realized in the doped (chemically/electrochemically oxidized or reduced) state, and

(iv) The mobile charge carriers are not free electrons or holes, but quasi-particles, which may move freely through the material, along uninterrupted polymer chains.

Conjugated polymers are quasi one dimensional, with a covalent bonding within the chains and interactions between chains are of van der Waals type. The intrinsic geometrical structure is dependent upon the ionic state of the polymer, which leads to the existence of the unusual charge carrying species. The charge bearing species are not free electrons or holes, but may be any one of several different entities. The charge bearing species are self localized, and the presence of electronic charge leads to local changes in the geometry (the lattice), which in turn, leads to localized changes in the electronic structure. These species can be generated through optical absorption, or through charge transfer, which later on becomes localized electronic states with energy levels within the forbidden electron energy gap**.**

2.2 Conductivity of conducting polymer (2,5)

Conducting polymers are new materials that are intrinsically electronic conductors at the molecular level. One of the most fascinating aspects of these polymeric materials is that they mimic inorganic metals being oxidized and reduced under electrochemical control. Under oxidation, radical cations (polarons in the dominant physical terminology) accumulate along the polymeric chains before they recombine, by the attraction of new electrons, to give dications (bipolarons). Anions coming from the solution guarantee the electroneutality. The injection of electrons from the metal promotes the electrochemical reduction of the charged species moving to the neutral, uncharged state of the polymeric molecule. A few polymers can be reduced from the neutral state, giving radical anions or dianions (also polarons and bipolarons, from a physical point of view).

Delocalization can be accomplished by forming a conjugated backbone of continuous overlapping orbitals. For example, alternating single and double carbon-carbon bonds can form a continuous path of overlapping p orbitals. In polyacetylene, but not in most other conductive polymers, this creates degeneracy in the frontier molecular orbitals (the highest occupied and lowest unoccupied orbitals named HOMO and LUMO respectively). This leads to the filled (electron containing) and unfilled bands (valence and conduction bands respectively) resulting in a semiconductor.

A neutral polymer contains alternate single and double bonds along its chain. There is a long band gap between II and II* levels. A very low population of electrons can jump, under ambient temperature, from the occupied II band to the unoccupied II* band. The conductivity of a neutral polymer is low. Polymeric oxidation generates empty (electrons are lost) polaronic and bipolaronic bonds in the mid gap. The width of every new band is proportional to the population of polarons or bipolarons, these populations being controlled by the oxidation depth.

Since the new bonds can house electrons because the gap to the valence band is lower than the II - II* gap, increasing amount of electrons can jump, at ambient temperature, between the valance band and the new polaronic and bipolaronic bands. In this way, the width of the polaronic levels (that is, the probability of the electronic jumps increasing the number of carriers (electrons and holes)), and the conductivity increase as oxidation advances. Both initial and final values change from one polymer to another and are different for two films of “the same polymer” synthesized under different conditions. Since most of the polymeric levels are generated during the initial 10 to 20% of variation in composition. The largest change in the conductivity is observed during this change in composition.

2.3 Electrochemical polymerization (4,5,6)

The electrochemical polymerization is carried out with a classical three electrode electrochemical cell, consisting of a working electrode, a reference electrode and a counter electrode and an electrolyte solution containing the monomer in a supporting electrolyte solution. A solvent is used in which the monomer is soluble but not the polymer. The nature of the working electrode is critical for the preparation of these films and depends on the type of polymer to be synthesized and on the electrolyte medium. Since oxidative or reductive processes produce the films, it is important that the electrode should not oxidize reduce concurrently with the monomer.

Electrochemical synthesis of conjugated polymers has the following advantages over the chemical synthesis.

a) The polymeric material is produced in one step, directly grafted on to the electrode surface.
b) There is no need for a catalyst; therefore, the electrodeposited polymer is pure.
c) By controlling the amount of charge supplied, the thickness of the polymer film may be controlled from a few angstroms to many micrometers.
d) By changing the nature of the counter ions in solution, the electrical and physicochemical properties of the polymer may be changed for a particular purpose.
e) It is possible to perform in situ characterization of the growth process of the polymer by electrochemical and/or spectroscopic techniques.

For the synthesis, potentiostatic (fixed potential), galvanostatic (fixed current), or potentiodynamic (varying potential) methods can be used. A preliminary study is necessary in order to find a solvent in which the monomer is soluble and to determine the potential at which the polymerization may be performed. Cyclic voltammetry is a very good technique to determine the best polymerization conditions. The polymerization potential should not be too low, since this causes the polymerization process to be very slow and to form soluble oligomers, nor too high in order to avoid a material having lower conductivity due to overoxidation. In general, the polymerization potential must be chosen not too far (± 0.1 V) from the corresponding oxidation peak potential of the monomer.

The electrodeposition potential is specific for any given electroplymerization process. As the potential needed for monomer oxidation is always higher than the charging of the existing polymer, both polymerization and doping processes may be driven by a single electrochemical operation which, starting from the monomer, first forms the polymeric chain and then induces its oxidation/reduction and deposition on the working electrode can be studied in situ or afterwards in monomer free solution.

2.4 Doping (5,6)

In silicon semiconductors, a few of the silicon atoms are replaced by electron rich (e.g., phosphorus) or electron-poor (e.g. boron) atoms to create n-type and p-type semiconductors, respectively. In contrast, there are two primary methods of doping a conductive polymer, both through an oxidation-reduction (redox) process. The first method, chemical doping, involves exposing a polymer to an oxidant (typically iodine or bromine) or reductant (far less common, but typically involves alkali metals). The second is electrochemical doping in which a polymer-coated, working electrode is suspended in an electrolyte solution in which the polymer is insoluble along with separate counter and reference electrodes. An electric potential difference is created between the electrodes which causes a charge (and the appropriate counter ion from the electrolyte) to enter the polymer in the form of electron addition (n doping) or removal (p doping). Polymers may also be self-doped, e.g., when associated with a protonic solvent such as water or an alcohol.

The reason n doping is so much less common is that Earth's atmosphere is oxygen-rich, which creates an oxidizing environment. An electron-rich n doped polymer will react immediately with elemental oxygen to de-dope (re-oxidize to the neutral state) the polymer. Thus, chemical n doping has to be done in an environment of inert gas (e.g., argon). Electrochemical n doping is far less common in research, because it is much more difficult to exclude oxygen from a solvent in a sealed flask; therefore, although very useful, there are likely to be no commercialized n doped conductive polymers.

2.5 Application of conducting polymers (5-8)

The starting point for applications was the discovery that polyacetylene can function as an active electrode in a rechargeable battery. Since then the prospects of technical applications has grown considerably. The attraction in the development of a rechargeable polymer battery lies in the specific weight of polymers which is considerably lower than that of ordinary inorganic materials, as well as the potential environmental benefit. The polyacetylene cell was most extensively studied. However, due to its chemical instability, it has virtually no commercial prospects. A promising candidate for a polymer battery that does not possess the typical disadvantages of polyacetylene is polypyrrole. Unfortunately, polypyrrol cell has its own disadvantages, that is, during discharging cations are incorporated into the polymeric layer which leads to consumption of the electrolyte and stops the charging/discharging process in tin-layer cells. The reason for this phenomena lies in structural peculiarities of polypyrrol, which forms sigma- dimmers during discharging, producing immobile positive charges correlated with immobile anions.

An important problem encountered with polymers electrodes is that of overoxidation. It occurs after reversible charging of an electrode with high oxidation potentials and leads to the degradation of the polymer. Such degenerative mechanisms are promoted by the nucleophilcity of the solvent.

Apart from the battery electrode, conducting polymers are discussed as potential electrochromic displays, antistatic materials, anticorresives, electrocatalysts, and light-emitting materials.

2.6 Polymer modified electrode (7, 8, 10, 11)

Electroactive monolayers and thicker films on conductive substrates (material that is also used in an unmodified form as an electrode such as Pt, Au, or carbon,) are frequently called chemically modified electrodes. These electrodes are often prepared by the modification of a conductive substrate to produce an electrode suited to a particular function, whose properties are different from those of the unmodified substrate. In the 1970 s, interest arose in the modification of electrode surfaces by covalent attachment of monolayers of different species to electrode surfaces. Electrodes modified with thicker polymeric films and inorganic layers were introduced later. Paralleling this, many of which can be produced electrochemically. More complex structures (bilayers, arrays, biconductive films) have also been produced.

There has long been interest in electrochemistry in the occurrence and consequences of adsorption of ions and molecules on electrode surfaces. Adsorption can have both desirable and deleterious consequences, and adsorption research has been adjunct to numerous fundamental insights into the electrical double layer and the kinetics and mechanisms of electrochemical reactions. Adsorbed layers of molecules or ions can accelerate or (more commonly) retard electrode reaction rates, and leads to passivation of electrodes to corrosion process or promote them, can in the case of so-called brightnes influence the morphology of electrodeposition reaction, can interfere with or be the basis of electroanalytical measurements, among others. A great deal of information has accumulated on what species adsorb on various electrodes, types of electrode materials, and from what solvents and electrolyte media. In some instances the adsorption phenomena are rationally explainable based on chemical reactivity or solubility grounds, adsorption of simple metal complexes on mercury electrodes being a case in point.

Chemically modified electrodes as discussed here diverge sharply from the traditional field of adsorption on electrode surfaces. The most essential difference is that one deliberately seeks in some hopefully rational fashion to immobilize a chemical on an electrode surface so that the electrode thereafter, displays the chemical, electrochemical, optical and other properties of the immobilized molecule(s). The connotation following from this statement is that one selects immobilized chemicals on the basis of known and desired properties, to be, for instances, fast outer-sphere electron transfer mediator-catalysts for a valuable substrate reaction, functionalities which scavenge trace molecules from or ions from solutions for analysis in preconcentrated form, photosensitizers for a semiconductor electrode, corrosion inhibitors, and so on. That is the electrode can be tailor-made to exhibit these properties.

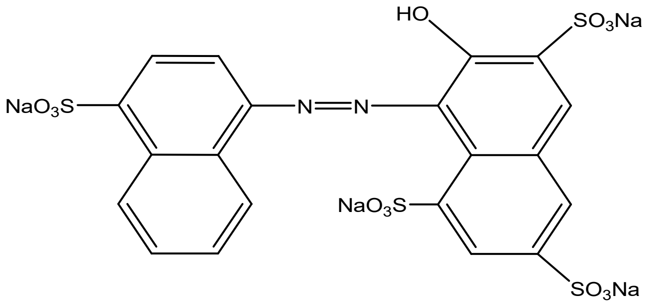
The electrochemical reactions of immobilized chemicals are also special; since these species are confined to the electrode surface, they provide an opportunity to study the basics of electrochemical reactions. These are the ideas and motivations associated with much of the recent and current research on electrode bearing immobilized chemicals. They are dubbed variously chemically modified, dervatized, functionalized, electrostatically trapped and polymer coated.

The most interesting and most studied immobilized chemicals are those, which are electrochemically reactive. If the molecular attachment scheme is such that the immobilized substance (directly or indirectly) exchanges electrons with the electrode surface, the electrode displays electrochemical responses for oxidation or reduction of the substance.

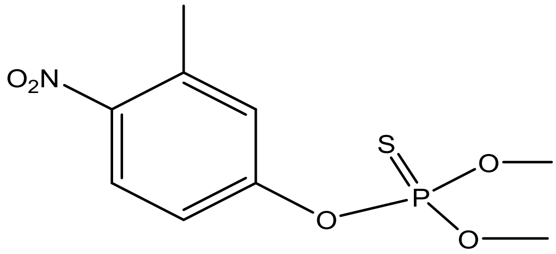
In recent years, polymer modified electrodes have attracted a deal of attraction, as polymeric film exhibits good stability and reproducibility. Especially organic dye (such as neutral red and methylene blue) polymer modified electrodes have been applied widely for the determination of organic compounds. Carmine exhibits a similar property to those of other dyes, which are able to play a redox mediator role in their direct determination.

In general, the derivatives of dyes covalently bonded to an aromatic ring could decrease their proton-doner ability, resulting in improved catalytic activity. Polymerization of dyes could form a cross linked oligomer which leads to the enhancement of its electrocatalytic ability. However, carmine polymer has rarely been used as a mediator to facilitate the electrochemical reaction of any compound.

Previously the electropolymerization of carmine on glassy carbon electrode is investigated and used as a sensor for the determination of parathion. And also, the poly (carmine) modified glassy carbon (GC) electrode is used for the determination of 4-Nitrophenol in another reported paper. The importance of 4-Nitrophenol determination was related to the degradation pathway of several organophospheres pesticides such as fenitrothion, methyl-parathion, ethyl parathion, etc. They were decomposed in soils and water, producing 4-nitrophenol as an intermediate or final product of the reaction.



(a)



(b)

Fig. 2. The molecular structure of carmine (a) and fenitrothion (b)

2.7 Pesticides (12-14)

The term pesticides relates to compounds used for the control of pests of all descriptions - including those directly hazardous to the health of man and animals. Notable among insect pests that act as vectors of Filariasis, yellow fever, meningitis, and ochocerciasis. The term pesticide also embraces compounds for the control of rodents, slugs, snails and household and stored - product pests.

The use of pesticides for different purposes such as forestry management, protection against infections with parasites transmitted to humans by insects, and against insects and weeds in agriculture, is very common all over the world today. Unfortunately, these chemicals are potential pollutants having deleterious effects on human health and environment when their concentration is higher than certain limits. The residues of the pesticides in the environmental samples and their degradation products produced by a combination of hydrolytic, photochemical and microbial process are found in various complex matrices at very low concentration level. There are different types of pesticides:

- Insecticides for the control of insects - these can be Ovicides, Larvicides or Adulticides
- Herbicides for the control of weeds
- Fungicides for the control of fungi and oomycetes
- Bactericides for the control of bacteria
- Miticides for the control of mites
- Molluscicides for the control of slugs and snails
- Nematicides for the control of nematodes
- Rodenticides for the control of rodents
- Virucides for the control of viruses

2.7.1 Insecticides

Insecticides include natural product insecticides, Pyrethrins, Pyrethroids, insecticidal chlorohydrocarbons and organophosphate insecticides. Insecticidal chlorohydrocarbons have played on important role in the history of chemical crop protection. DDT, probably the most well-known of all insecticides, was for many years the no. 1 pecticidal agent. The following factors are chiefly responsible for its phenomenal success in the years subsequent to its synthesis and the discovery of its insecticidal activity.

1. High insecticidal activity

2. Low acute mammalian toxicity
3. Simple manufacture and handling
4. Low price
5. Long duration of activity

With certain qualifications these factors are valid for most other insecticidal chlorohydrocarbons. The past and present importance of DDT lies in its suitability for the control of disease-carrying pests, for example, for malaria control. The heavy criticism leveled at DDT, and increasingly at most other chlorohydrocarbon insecticides, was sparked off by the behavior of residues from these agents. Their high persistence usually a desirable property in relation to long duration of activity-led to a demonstrable accumulation in the environment and a concentration in food chains. Some example of insecticidal chlorohydrocarbons are shown in figure 3.

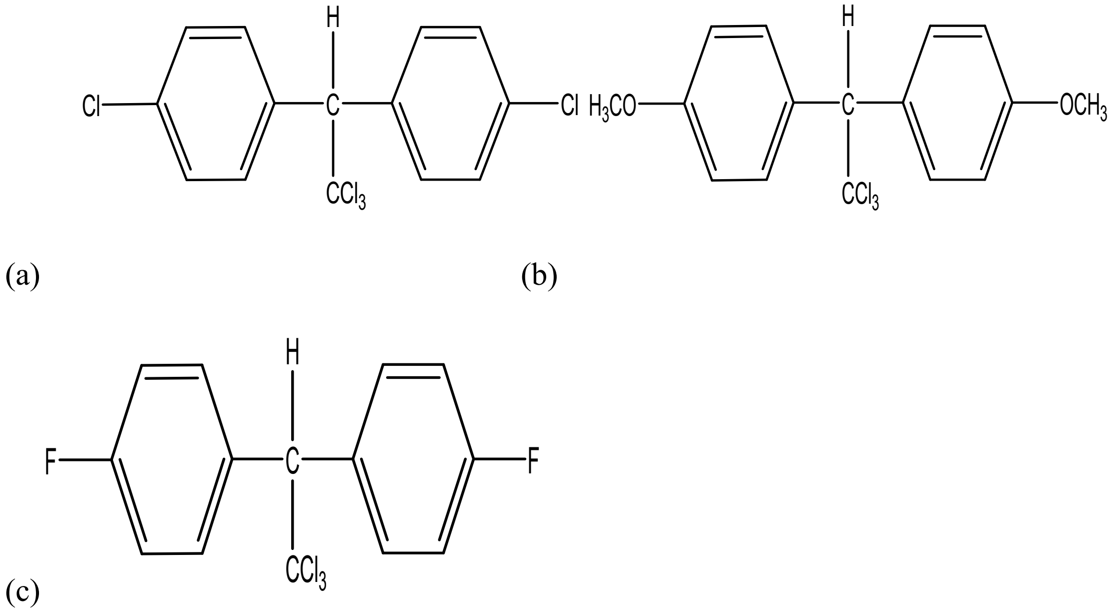
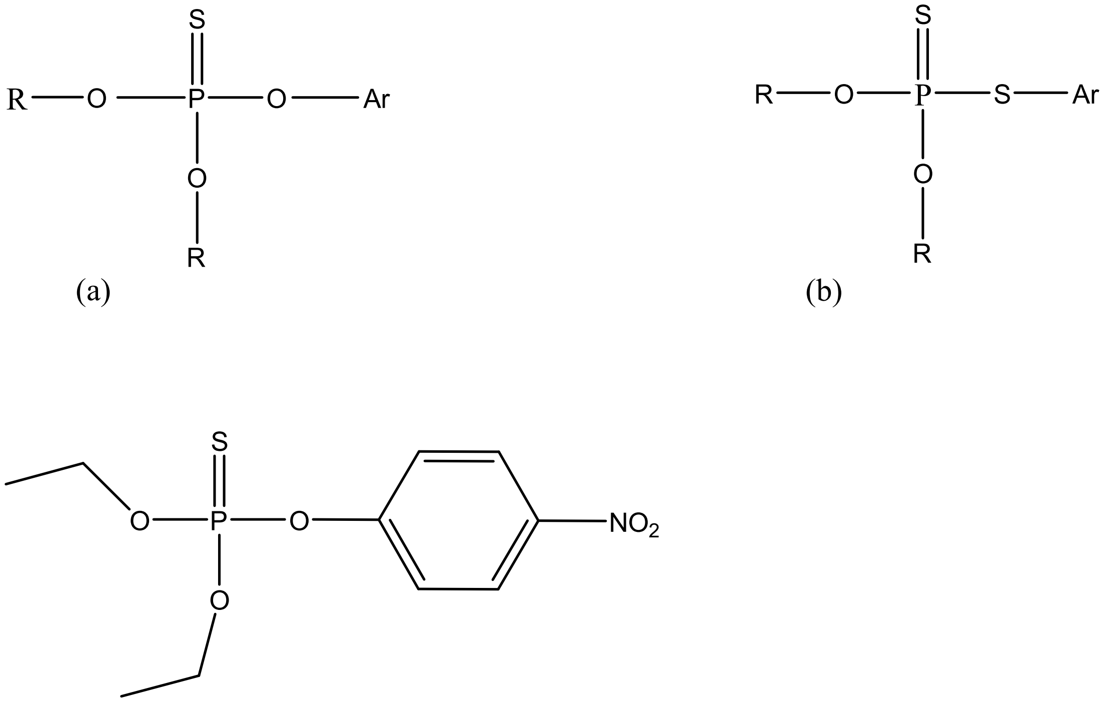


Fig. 3.The structure of (a) DDT (1.1- (2.2.2 - Trichloroethylidene) bis (4-chlorobenzene) (b) Methoxychlor (1.1- (2.2.2- Trichloroethylidene) bis (4-methoxybenzene) and (c) DFDT (1.1- (2.2.2- Trichloroethylidene) bis (4-flourobenzene)

2.7.1.1 Organophosphorus Insecticides

Owing to their ester nature, the organophosphates offer fundamental advantages in this respect. Normally they can be easily degraded hydrolytically, enzymatically or biologically. A further advantage lies in the very low application quantities necessary for the desired insecticidal activity in the field. As a rule, only a row hundred grams per hectare and per application are recommended, which their considerably reduces the danger of undesirable residues in the harvested product. From chemist's view point, the most valuable property of the organophosphates is the sheer diversity of the combinations of substituents possible at the central phosphorus atom. This permits precise variation of the biological activity and toxicological, physical, and chemical properties within certain limits. Some examples of organophosphrus insecticides are parathion, parathion-methyl and fenitorthion. The introduction of a methyl group in to the phenyl ring of parathion reduces the toxicity without fundamentally changing the activity.

Because esters containing the P=S (thione) are resistant to non enzymatic hydrolysis and are not as effective as P=O compounds in inhibiting acetylcholinesterase, they exhibit higher insect mammal toxicity ratios than their nonsulfer analogs. Therefore phosphorthionate and phosphordithionate easters (fig. 4) have been widely used as insecticides. The insecticidal activity of these compounds require metabolic conversion of P=S group to P=O (oxidative desulfuration). Environmentally, organophosphate insecticides are superior to many of the organochloride insecticides because the organophosphates readily undergo biodegradation and do not bioaccumulate.



(a)

(b)

(c)

Fig.4. General formula of phosphorothionates (a), general formula of phsphorodithionates (b) and the structure of parathion (c).

The first commercially successful phsphorthionate/posphorodithionate easters insecticide was parathion, O, O-diethyl-O-P-nitrophenylphosphorothionate, first licensed for use in 1944. This insecticide which inhibits acetylcholinesterase is a super toxic. Since its use began, several hundred people have been killed by parathion. As little as120 mg of parathion has been known to kill an adult human, and a dose of 2 mg has been fatal to a child. Most accidental poisonings has occurred by absorption through the skin. Methyl parathion (a closely related compound with methyl group instead of ethyl group) is regarded as extremely toxic. In order for parathion to have a toxic effect, it must be converted metabolically to paraoxon, which is a potent inhibitor of acetylcholinesterase. Because of the time required for their conversion, symptoms develop several hours after exposure.

The active ingredient fenitrothion is found in a variety of commercial insecticides. Fenitrothion is a general use pesticide as a contact insecticide and selective acaricide of low ovicidal properties. It belongs to the organophosphate family of insecticides. It is considered a cholinesterase inhibitor. Fenitrothion is effective against a wide range of pests, i.e. penetrating, chewing and sucking insect pests (coffee leafminers, locusts, rice stem borers, wheat bugs, flour beetles, grain beetles, grain weevils) on cereals, cotton, orchard fruits, rice, vegetables, and forests. It may also be used as a fly, mosquito, and cockroach residual contact spray for farms and public health programs. Fenitrothion is also effective against household insects. Its effectiveness as a vector control agent for malaria is confirmed by the World Health Organization. Fenitrothion is non-systemic, and non-persistent. Fenitrothion is far less toxic than parathion with a range of insecticidal activity that is very similar and is similar enough in structure to be produced in the same factories. The difference in precursor chemicals might make it somewhat more expensive, but it is heavily used in other countries, including Japan, where parathion has been banned. It is compatible with other neutral insecticides. The acute toxicity of fenitrothion to mammals is considered to be low. Typical symptoms of acute poisoning are observed in rats at doses considerably higher than those applied for parathion-methyl, a structural analogue of this substance.

2.7.2 Herbicides

A herbicide, in the broadest sense of the word, is any compound that is capable of either killing or severely injuring plants and may thus be used for elimination of plant growth or the killing of a plant parts. The designation wood covers a variety of meanings according to the particular situation. According to the general definition a weed is any plant either a wild or cultivated variety that is undesired in that particular place. Weed control by chemical means her undergone rapid expansion since the introduction of the selective organic herbicides. Herbicidal agents are inorganic herbicides and organic herbicides.

2.7.3 Fungicides

Fungicides are widely applied to cereal and food crops to prevent fungal infections of these crops. Because of this, fungicides have the potential to contaminate water. There are different fungicidal agents, which are, inorganic fungicides, organic fungicides, organophosphorus fungicides, antibiotics, phytofungicides, and synthetic organic dungicides.

2.8 Activated glassy carbon electrode (15-23)

The low coast broad applicability of carbon electrodes, particularly in electroanalysis and electrosynthesis, has driven investigators to find the relationship between surface structure and electrochemical phenomena. The process of relating carbon surface structure to electrochemical reactivity is hindered by the formidable barriers. First, the carbon surface varies greatly with origin and pretreatment and is often difficult to characterize structurally. Thus the surface structure is often unknown and can vary from laboratory to laboratory or day today. Second, redox systems vary greatly in there sensitivity to surface structure and therefore to surface history.

The ease with which carbon combines with other elements makes carbon materials reach in surface chemistry, leading to a variety of modifications. On the other hand, because of their richness in surface chemistry the final properties of sold carbons are invariably difficult to predict, to evaluate, and often to reproduce.

Surface treatments have been used extensively to improve the electrochemical performance of several types of carbon electrodes: vitreous (glassy) carbon, pyrolytic graphite, carbon paste, and carbon fibers. Surface activation has been accomplished by chemical oxidation with Chromic acid, heat treatment, exposure to strong laser light pulses, and electrochemical anodization. Studies have been undertaken to obtain additional information about the nature of the surface changes that occur upon anodic activation of carbon.

Electrochemical pretreatment is quite effective towards improving electrode activity. The variables in electrochemical pretreatment of GC electrode include electrolyte composition, applied potential waveform and magnitude of applied potential. As with polishing procedures, there is no consensus on the most effective electrochemical pretreatment procedure to suit the intended use of the electrode. Several laboratories have reported on the effects of this pretreatment or minor variant on electron transfer kinetics and surface structure.

Electrochemical pretreatment may be used to renew GC electrodes, resulting in useful electroanalytical procedures. The adsorption properties of the oxide film formed by electrochemical pretreatment is unusual, GC surface adsorbs ions following electrochemical pretreatment and can undergo ion exchange of cations.

Evidence for increased surface oxygen upon activation has promoted investigators to propose that activation results from electron transfer mediation by oxygen containing groups such as phenolic, quinodal and carboxyl functionalities. Surface waves in current-potential curves with graphite oxides have been attributed to the oxidation/reduction of hydroquinone/quinonelike surface groups, and similar waves for glassy carbon were attributed to a surface group and chemisorbed oxygen. Other evidence indicates the removal of surface impurities can be important. The large increase in double-layer charging that occur with activation f the GC surface was not attributed to an increase in macroscopic surface area, although an increased microscopic surface area or heavy functionalization of the surface on activation is possible.

There is some evidence, however, that dose not support the theory of mediation by oxygen functionalities, especially for GC. The results show that a dominant process during electrochemical activation of the GC surface is the formation of a nearly transparent homogeneous graphitic oxide phase.

The electrochemical activation of GC electrode takes place in different ways in different papers. By continuously cycling the potential between 0.0 and 2.0V at 200mVs^{-1} in 0.1M H_2SO_4 solution, oxidative activation in nondegassed 0.1M H_2SO_4 for various times at an applied potential of +1.8V (when the reductive step is indicated, the electrode were held at an applied potential of –0.20V) and by continuously cycling between potentials of +1.95 and +2.5V in 2M H_2SO_4 solution. Appling potential of +1.8V and above at glassy carbon electrode leads to the activation of the electrode surface.

By assuming that the anodic layer is responsible for activation of the surface, one can account for the physical and chemical changes that cause activation of GC electrodes. This is a reasonable assumption, because activation of the surface combined with growth of the layer and its optical properties over time correlated with changes in the activity of the electrode. The layer grows with uniform composition and that the bulk sample is representative of the phase responsible for activation of the electrode.

Activation of the surface involves a combination of surface roughening, the formation of graphite oxide, intercalation and adsorption of the redox couple, and reduction of the anodic layer to form a porous, hydrated and partially conductive structure. These processes result in both chemical and physical changes.

The capacitance of the electrochemically treated carbon materials is indicative of the substantial changes in the surface properties that result from this treatment. Electrochemical treatment increases the capacitance five fold based on the geometric area. The "excess" capacitance correlates with the increased microscopic surface area of the carbon material caused by surface cracking during oxidation.

3. ELECTROCHEMICAL STUDIES (CYCLIC VOLTAMMETRY (CV) AND LINEAR SWEEP VOLTAMMETRY (LSV)) (4,5)

3.1 Basic principles

The most common experimental configuration for recording cyclic voltammograms consists of an electrochemical cell that has three electrodes, i.e., counter or auxiliary electrode (C), reference electrode (R), and working electrode (W), all immersed in a liquid and connected to a potentiostat. The potentiostat allows the potential difference between the reference and working electrode and the working electrode to be controlled with minimal interference from IR (ohmic) drop. In this configuration, the current flowing through the reference electrode also can be minimized thereby avoiding polarization of the reference electrode and hence keeping the applied potential distribution between the working and reference electrode stable.

Positioning the reference electrode close to the working electrode further helps to minimize the IR drop between the reference and working electrode due to the reversibility of the solution phase. Instrumental methods, based on positive feedback or other circuitry, for compensation of uncompensated resistance are also available. The eleeectrode commonly used for cyclic voltammetry experiments are:

(i) Reference electrode: commonly used are aqueous Ag/AgCl or calomel half cell which can be obtained commercially or easily proposed in the laboratory. Sometimes, when a suitable conventional reference electrode is not available (e.g. for some organic solvents) or introduce problems with salt leakage or junction potentials, pseudo-reference electrode such as a simple silver or platinum wire are used.

(ii) Counter electrode: non-reactive high surface area electrode, commonly a platinum gauze or a titanium wire.

(iii) Working electrode: most commonly used are inlaid disc electrodes (Pt, Au, graphite, glassy carbon, etc.) employed beneficially in appropriate circumstances (dropping or hanging mercury hemisphere) with the appropriate modification to the data analysis.

The simplest of these techniques is linear sweep voltammetry (LSV), and this involves sweeping the electrode potential between limits E_1 and E_2 at a known sweep rate, υ, before halting the potential sweep. A generally more useful (and consequently more widely applied) technique is cyclic voltammetry (CV). In this case the waveform is initially the same as in LSV, but on reaching the potential E2 the sweep is reversed (usually at the same scan rate) rather than terminated. On again reaching the initial potential, E_1, there are several possibilities. The potential sweep may be halted, again reversed, or alternatively continued further to a value E_3. In both LSV and CV experiments the cell current is recorded as a function of the applied potential (it should be noted, however, that the potential axis is also a time axis). The sweep rates used in conventional experiments range from a few mV s^{-1} up to a few hundred V s^{-1}. Rates up to several thousand V s^{-1} have been used, but such high values introduce considerable experimental difficulties (e.g. double layer charging and iR_u drop effects can both be very large) which generally restricts their application.

One of the electrochemical techniques that is often used to study the electrochemical properties of conjugated polymers is cyclic volotammetry. It represents the principal source of experimental information on the charging and discharging processes of conducting polymers. The charging is shown as a steep anodic wave followed by a broad flat plateau as the potential increases. It has been suggested that the plateau is related to capacitive charging of double layers of the system.

4. EXPERIMENTAL SECTION

4.1 **Chemicals and Solution**

0.5M H_2SO_4 solution was used for the electrochemical pretreatment of the GC electrode and electrochemical polymerization of carmine on GC electrode. A mixture of disodium orthophosphate ($Na_2HPO_4.12H_2O$) and dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$) is used to prepare pH 6.0 buffer. And the buffer is used as a bulk sample in the electrochemical pretreatment of GC electrode, for the preparation of 2mM carmine solution and for the preparation of different concentrations of the analyte (Fenitrothion).

4.3 Experimental setups

All the electrochemical polymerization and electrochemical characterization were carried out in a three-electrode one-compartment electrochemical cell. An electrochemical analyzer (Bass CV-50W) was used to run all electrochemical experiments. All potentials are reported versus Ag/AgCl reference electrode. And platinium wire has been used as a counter electrode.

4.2 Preparation of modified glassy carbon electrode

Electropolymerization of carmine by using cyclic voltammetric method between -1.0 and 2.0 V potential versus Ag/AgCl reference electrode has been used to prepare poly (carmine) modified glassy carbon electrode, platinum wire is used as counter electrode. Electrochemical pretreatment of glassy carbon electrode is under taken with the same condition in 0.5 M H_2SO_4 and 1.0 M (pH 6.0) phosphate buffer solution.

Working potential window for the electropolymerization of carmine was selected from previously reported paper and electrochemical pretreatment was undertaken in this same potential window. Then electrochemical behavior of the monomer, homopolymer and electrochemically pretreated GC electrode were studied. For the electrochemical characterization the appropriate working potential window was selected using the supporting electrolyte. Finally the electrocatalytic behavior of the polymer and electrochemically pretreated GC electrode were studied on a selected pesticide (fenitrothion).

5. OBJECTIVE OF THE STUDY

Comparison of poly (carmine) modified and electrochemically pretreated (EPT) glassy carbon electrode under similar condition and comparison of both poly (carmine) modified and EPT glassy carbon electrode for the voltammetric study of fenitrothion.

6. RESULTS AND DISCUSSION

From Previously reported paper, electropolymerization of carmine on the glassy carbon electrode is accomplished with cyclic voltammetry in pH 6.0 phosphate buffer solution containing 2.0 x 10^{-3} mol L^{-1} carmine. A poly (carmine) film formed on the electrode surface upon sweeps between -1.0 V and +2.0 V for ten cycles (10). The cyclic voltammetric response for the electropolymerization of carmine is recorded and compared with the 10 cycle cyclic voltammetric response of electrochemical pretreatment of glassy carbon electrode in 0.1 M (pH 6.0) phosphate buffer solution between -1.0 and 2.0 V potential. The result shows that the cyclic voltammetric response of carmine electropolymerization and electrochemical pretreatment of GC electrode is similar with the same film growth progress on the electrode.

The voltammetric behavior of glassy carbon electrode is drastically altered by electrochemical treatment. As with other methods for the activation of carbon, the apparent electron-transfer rates for many compounds are accelerated. However, several distinct features are immediately apparent from a voltammetric curves. Because the electropolymerization of carmine is carried out in a high potential sweep of +2.0V, both the –N=N- and –OH groups can be oxidized to give free-radicals to form polymer. Thus, the structural formula for the polymer of carmine is difficult to be confirmed. In addition, this high potential sweep (i.e. +2.0V) will also activate the glassy carbon surface oxidatively.

The voltammetric results for the electropolymerization of carmine and electrochemical pretreatment of glassy carbon electrode surface suggests that the same kind of electrochemical process is taking place inside the cell. That is more likely the activation of glassy carbon electrode surface. These features are a direct result of the electrochemical pretreatment and can be correlated with the known physical and chemical properties of activated glassy carbon electrode. To say that the electropolymerizatioon of carmine doesn’t happen but electrochemical activation of glassy carbon electrode surface additional supporting evidences are necessary.

Surface treatment has been used extensively to improve the electrochemical performance of glassy carbon electrode. Surface activation has been accomplished by electrochemical anodization (16,17). Electrochemical activation of glassy carbon electrode takes place by continuously cycling the potential between 0.0 and 1.8 V in 0.1 M H_2SO_4 solution (16). And it is reported that the electropolymerization of carmine on glassy carbon electrode to use as parathion sensor can be done by recording continuous ten cycle cyclic voltammogram between a potential of -0.1 and 2.0 V in phosphate buffer solution (10).

6.1 Electrochemical pretreatment of glassy carbon electrode in sulfuric acid

Figure 5 shows the cyclic voltammetric response of the electrochemical pretreatment of glassy carbon electrode in 0.5 M H_2SO_4. The electrochemical pretreatment has been done using cyclic voltammetry for ten cycles. The Ten cycle cyclic voltammetric response have reductive peak at -0.55 V potential that increases. And another peak at potential of around 1.5 V which is not increasing but shifting to smaller potential in every cycle shows the activation of the electrode surface. This cyclic voltammetric response is comparable with the electrochemical pretreatment of glassy carbon electrode in pH 6.0 phosphate buffer solution.

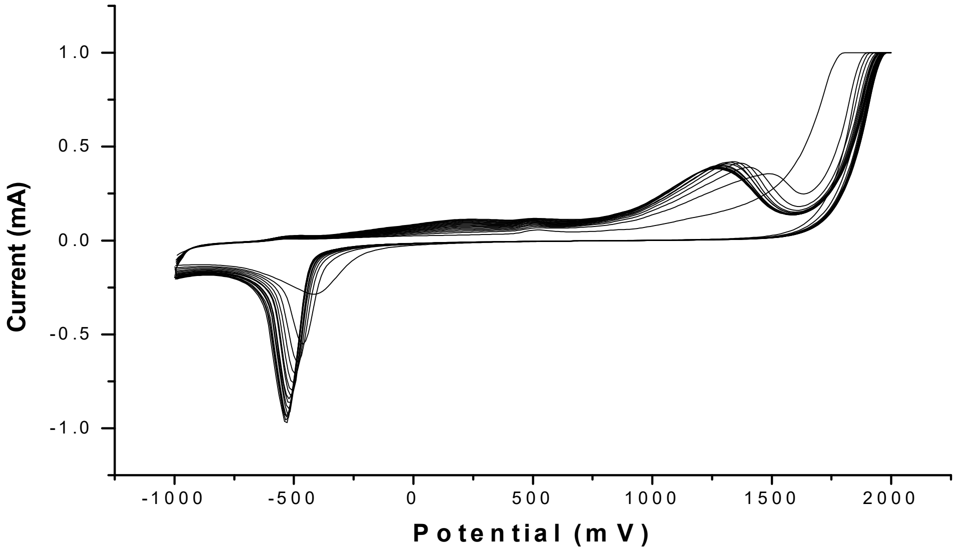


Fig.5. Ten cycle cyclic voltammogram of GC electrode in 0.5M H_2SO_4. Scan rate $50mVs^{-1}$

6.2 Electropolymerization of carmine and electrochemical pretreatment in phosphate buffer

Since, it has been reported somewhere that the poly (carmine)-modified glassy carbon electrode is prepared by electropolymerization of carmine in 0.1 M (pH 6.0) phosphate buffer solution between a potential of -0.1 and 2.0 V (10). Ten cycle cyclic voltammetric response of the glassy carbon electrode in the proposed potential window is recorded in 0.2 M carmine prepared in 0.1 M (pH 6.0) phosphate buffer solution and EPT of the glassy carbon electrode in 0.1 M (pH 6.0) phosphate buffer solution. This resulted in a similar voltammetric response for the electropolymerization of carmine and EPT of glassy carbon electrode. Figure 6 shows the voltammetric response of carmine electropolymerization which has similar reductive peak as the voltammetric response of EPT glassy carbon electrode in sulfuric acid solution. And figure 7 shows the EPT of glassy carbon electrode in phosphate buffer solution wich is exactly the same as the voltammetric response of carmine electropolymerization. Figure 8 shows the voltammetric response of carmine electropolymeriztion and EPT of glassy carbon electrode which suggested that electropolymeriztion of carmine did not happen. The glassy carbon electrode surface it self is oxidatively activated more likely forming graphitic oxide phase on its surface, since scanning the potential up to +2.0 V oxidize the glassy carbon electrode. In order for the formation of the polymer film the electrode should not be oxidized concurrently with the polymer.

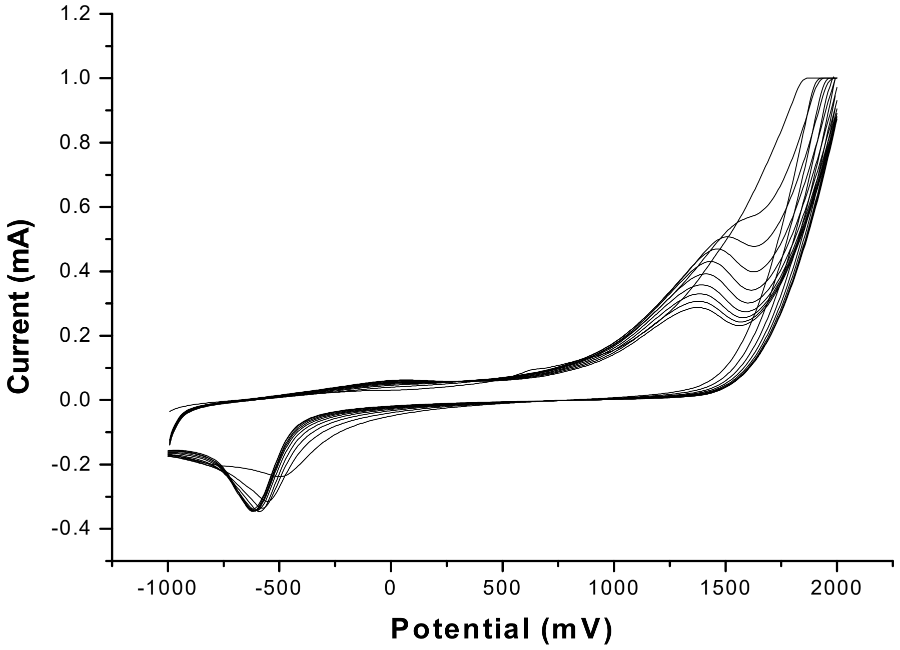


Fig.6. Cyclic voltammogram for the electropolymerization of carmine in 0.1M (pH 6.0) phosphate buffer solution. Scan rate, 50mVs^{-1}

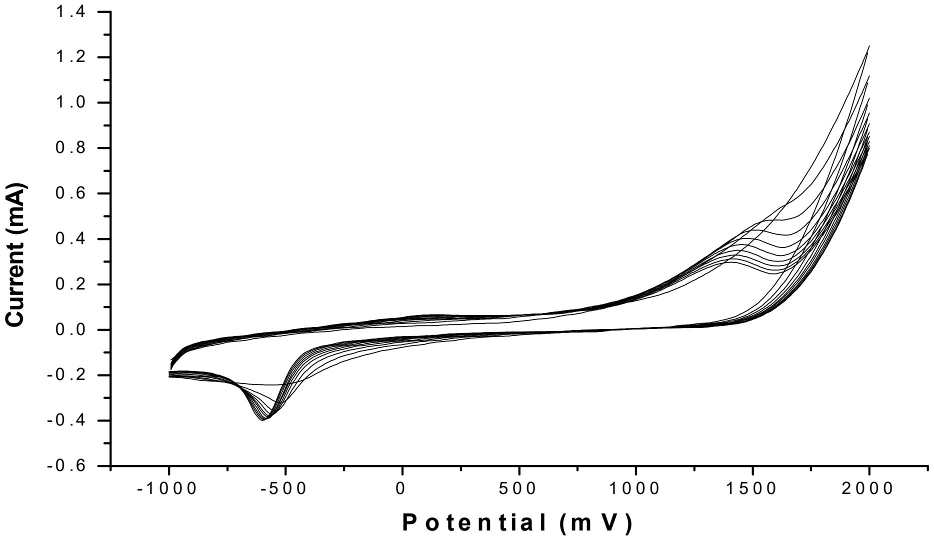


Fig.7. Ten cycle cyclic voltammogram of Glassy carbon electrode in P^H 6, 0.1 M phosphate buffer. Scan rate, 50mV s^{-1}

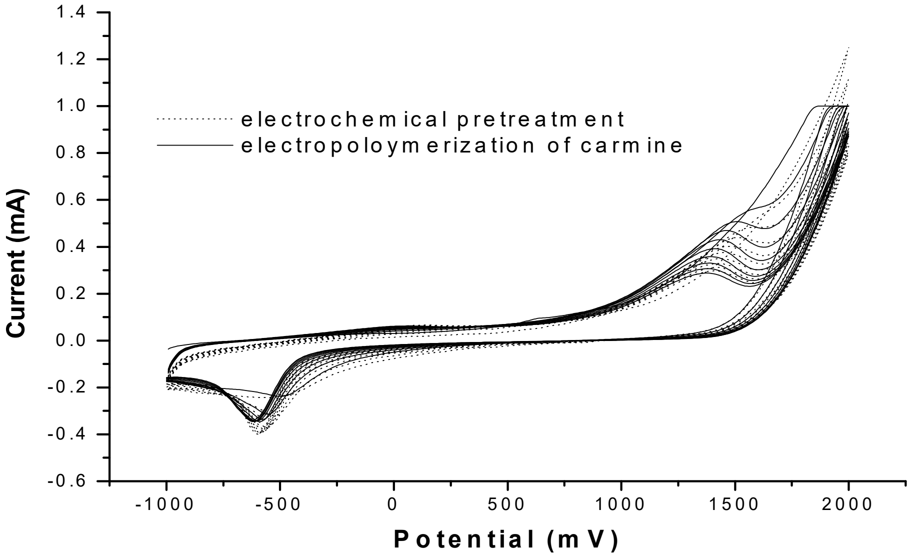


Fig.8. Cyclic voltammogram of carmine electropolymerization and electrochemical pretreatment of GC electrode in 0.1 M (pH 6.0) phosphate buffer solution. Scan rate 50mVs^{-1}

As the electrochemical pretreatment of the glassy carbon electrode in sulfuric acid solution showed increasing reductive peak at around -0.55 V potential, the same thing happened for the electropolymerization of carmine as well as EPT of glassy carbon electrode in phosphate buffer solution.

By assuming that the anodic layer is responsible for activation of the surface one can account for the physical and chemical changes that cause activation of the glassy carbon electrodes. This is reasonable assumption, because activation of the surface with growth of the layer correlated with changes in the activity of the electrode. The layer grows with uniform composition and that the bulk sample is representative of the phase responsible for activation of the electrode.

Figure 9 shows the cyclic voltammetric response of the bare glassy carbon electrode, monomer free of the poly (carmine) modified glassy carbon electrode and the response of electrochemically pretreated glassy carbon electrode. From the similarity of the responses for the electropolymerization of carmine and electrochemical pretreatment of glassy carbon electrode in phosphate buffer one can say that the electrochemical pretreatment of glassy carbon electrode in different bulk samples. This shows the change in the activity of the electrode and responsibility of the bulk sample for the composition of the phase responsible for the activation of the electrode.

As it is reported elsewhere oxidative activation of the glassy carbon electrode between 0.0 and 1.8 V potential involves a combination of surface roughening, the formation of graphite oxide, and adsorption of the redox couple, and reduction of the anodic layer to form a porous, hydrated, and partially conductive structure (16). In our case oxidative activation and reduction of the phase is a side by side process, which take place in every cycle continuously. The reductive peak of electrochemically activated glassy carbon electrode without the presence of carmine in the bulk sample is shifted positively from the reductive peak of the activation in the presence of carmine in the bulk sample. This shows the graphitic oxide formed on the electrochemically pretreated glassy carbon electrode is reduced faster than a phase that is formed on the glassy carbon electrode surface in the presence of carmine in the bulk sample.

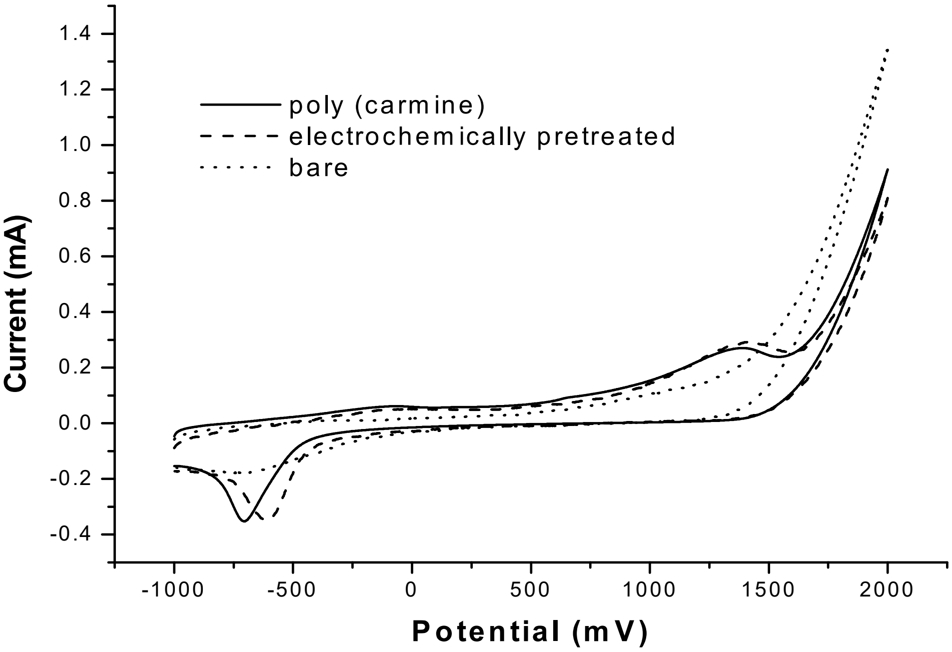


Fig.9. Cyclic voltammetric response of electrochemically pretreated GC electrode, poly (carmine) modified GC electrode and bare GC electrode in pH 6.0 phosphate buffer solution,

6.3 Electrochemical behavior of a Fenitrothion sensor

The mechanism of the fenitrothion redox process is the same as parathion since the cyclic voltammetric response of fenitrothion is similar with that of parathion (10). And the introduction of a methyl group in to the phenyl ring of parathion reduces the toxicity without fundamentally changing the activity (14).

The reduction of fenitrothion is a complex processes in which the nitro group can receive up to six electrons until complete reduction occurs to the corresponding amine. The formation of the nitro derivatives (ø-NO) and hydroxylamine (ø-NHOH) requires a total of four electrons and four protons. In the reaction of the protonated form, the reduction of the hydroxylamine to the corresponding amine requires two electrons.

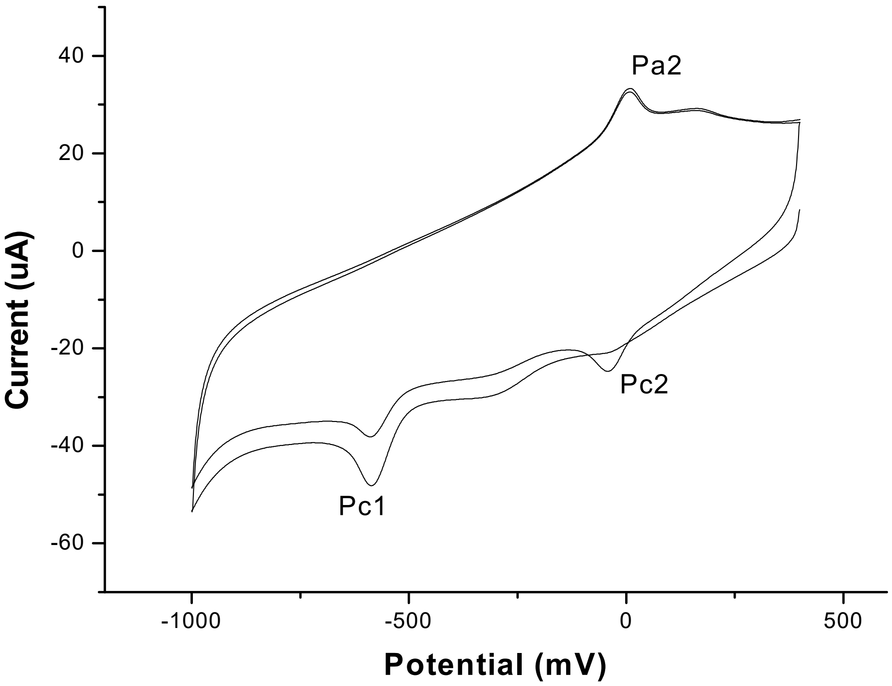
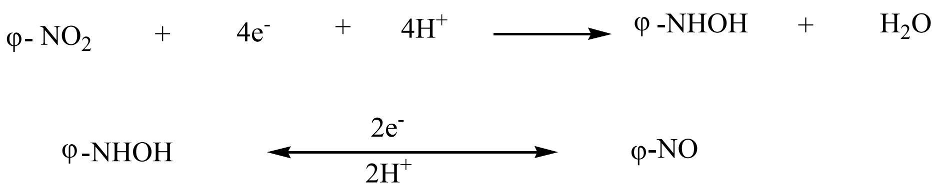


Fig. 10. Cyclic voltammogram of 1.0 x 10^{-4} mol L^{-1} Fenitrothion in 0.1 M (pH 6.0) phosphate buffer solution at the poly (carmine) modified glassy carbon electrode. Scan rate: 50 mV s^{-1}

Figure. 10 shows voltammograms of 1.0 x 10^{-4} mol L^{-1} Fenitrothion on the poly (carmine) modified glassy carbon electrode in pH 6.0 phosphate buffer solution. In the first cycle, one peak appears at -0.598 V (Pc1) during the cathodic sweep, and another one (Pa2) appears at -0.012V during the anodic sweep. In the successive cycles, one new reductive peak (Pc2) appears at -0.04 V during the cathodic sweep. Thus a couple of well-defined redox peaks is observed, and the anodic peak potential (Epa2) and the cathodic peak potential (Epc2) are located at -0.012 V and -0.04 V, respectively. The peak-to-peak potential separation (ΔEp) is about 28 mV, indicating that the fenitrothion electroreduction is reversible. Its voltammetric behavior is consistent with the electrochemical characteristics of parathion reported elsewhere (10). Nevertheless, it is believed that the same electron transfer mechanism can be applied in this study:



$$\varphi\text{-}NO_2 + 4e^- + 4H^+ \longrightarrow \varphi\text{-NHOH} + H_2O$$

$$\varphi\text{-NHOH} \xleftrightarrow[2H^+]{2e^-} \varphi\text{-NO}$$

Fig. 11. Scheme of electron transfer mechanism of fenitrothion.

Typical cyclic voltammograms of fenitrothion at a bare glassy carbon electrode, EPT glassy carbon electrode and poly (carmine) modified glassy carbon electrode are shown in figure 12. It can be seen that 1.0 x 10^{-4} mol L^{-1} fenitrothion has smaller redox signals at the bare glassy carbon electrode. However, under the same condition, fenitrothion yields a sensitive oxidative and reductive peak with a peak potential or -0.012 V and -0.04 V respectively at the poly (carmine) film modiried glassy carbon electrode and EPT glassy carbon electrode with almost equal sensitivity. With regard to sensitivity for fenitrothion determination, the oxidative peak (Pa2) is selected for comparison using linear sweep voltammetry.

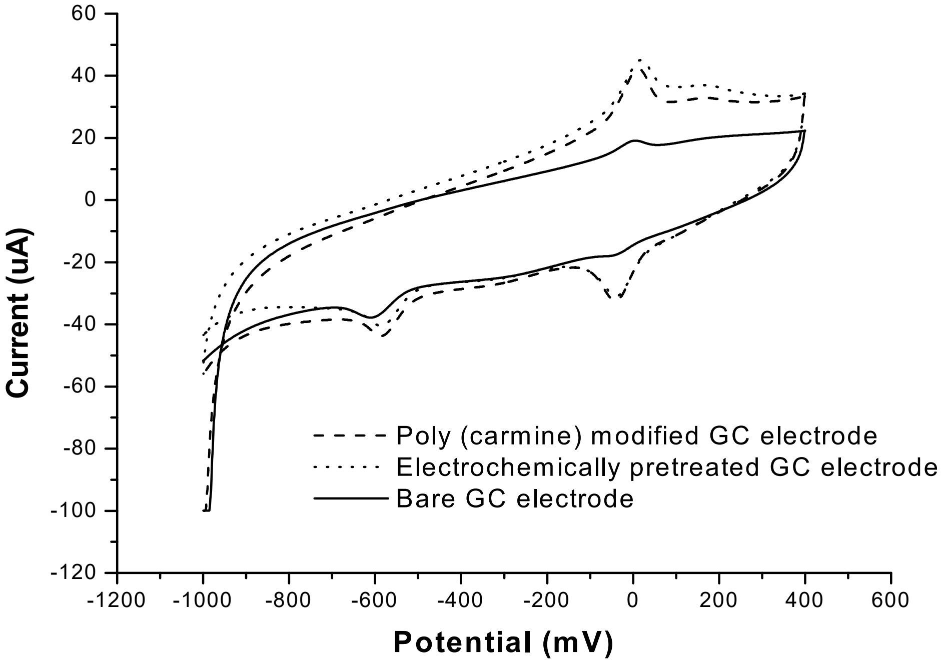


Fig. 12. Cyclic voltammogrames of 1.0 x 10^{-4} mol L^{-1} Fenitrothion at poly (carmine) modified GC electrode, electrochemically pretreated GC electrode and bare GC electrode. Scan rate, 50 mV s^{-1}

Figure 13 shows linear scan voltammograms of 1.0 x 10^{-4} mol L^{-1} fenitrothion in pH 6.0 phosphate buffer solution at a bare glassy carbon electrode, the electrochemically pretreated glassy carbon electrode and poly(carmine) modified glassy carbon electrode. A very low oxidation peak at -0.012 V can be seen at the bare glassy carbon electrode (curve a). However, the oxidation peak of fenitrothion increased significantly when the poly (carmine) modified glassy carbon electrode (curve b) and EPT glassy carbon electrode (curve c) is employed. This result shows that the sensitivity of the oxidation peak of fenitrothion in both poly (carmine) modified and EPT glassy carbon electrode has no much difference. So that, a poly (carmine) is not formed on the glassy carbon surface due to the concurrent oxidation of the electrode surface with the high potential scanning of +2.0 V. The EPT glassy carbon electrode has relatively larger background current due to its high capacitive current produced during activation.

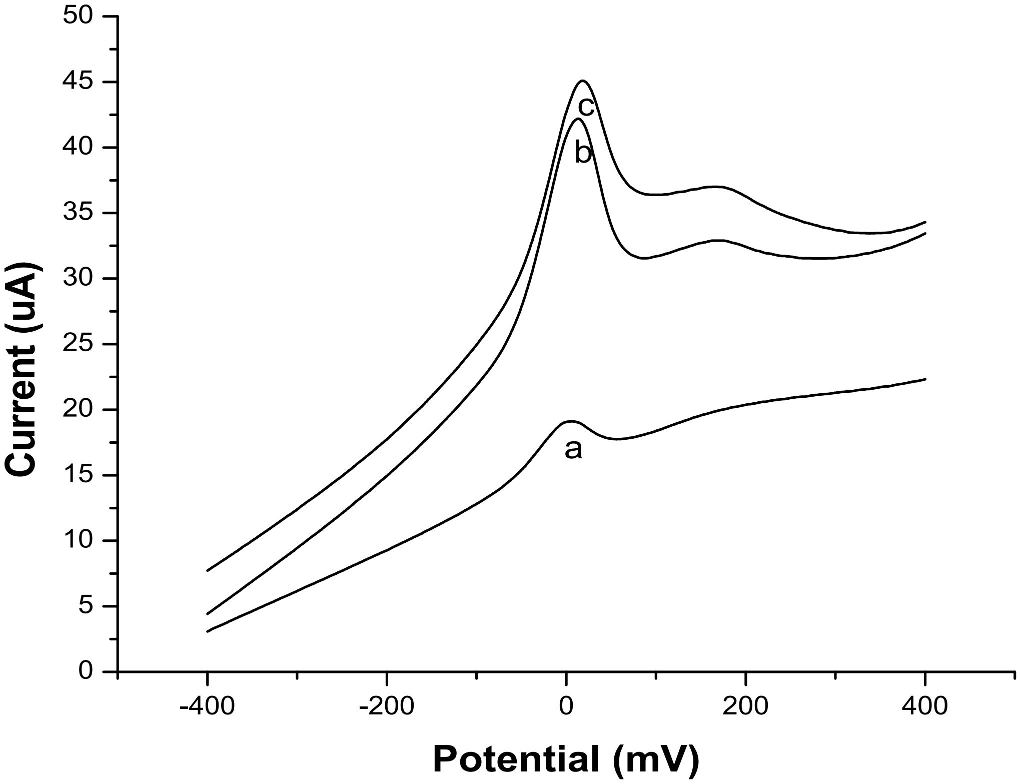


Fig. 13. Linear scan voltammogram of 1.0 x 10^{-4} mol L^{-1} Fenitrothion at the (a) bare GC electrode (b) poly (carmine) modified GC electrode (c) electrochemically pretreated GC electrode in 0.1M (pH 6.0) phosphate buffer solution.

Figure 14 shows the linear sweep voltammogram of fenitrothion oxidation at the poly (carmine) modified glassy carbon electrode by changing its concentration from 5.0 x 10^{-6} – 1.2 x 10^{-4} mol L^{-1}. It is increasing linearly up to 1.2 x 10^{-4} mol L^{-1}. Figure 15 shows the calibration curve of the poly (carmine) modified glassy carbon electrode prepared for the determination of fenitrothion. Calibration of the electrode is carried out using the established current response.

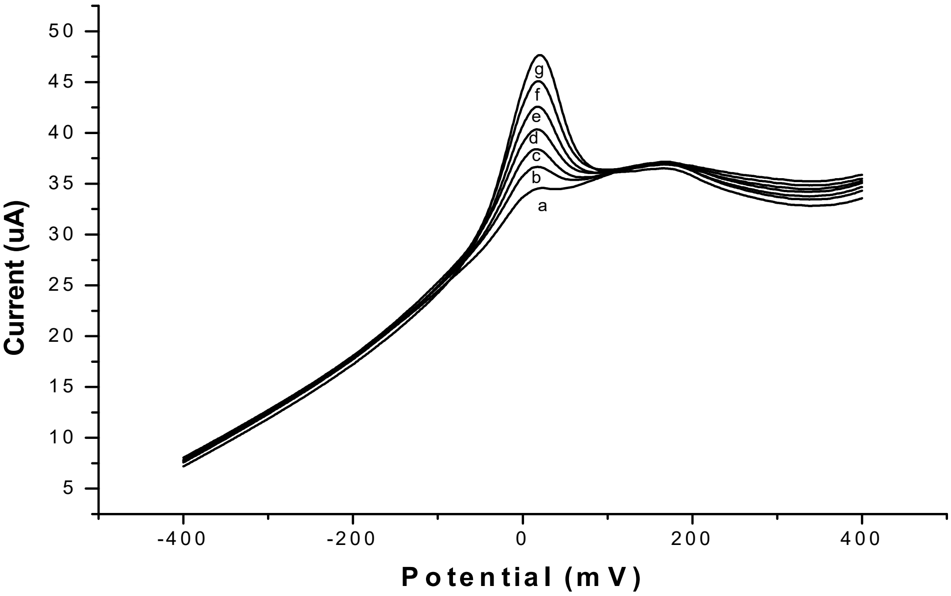


Fig. 14. Linear sweep voltammogram of the oxidation peak of fenitrothion in (a) 5uM, (b) 20uM, (c) 40uM, (d) 60uM, (e) 80uM, (f) 110uM and (g) 120uM fenitrothion using poly (carmine) modified GC electrode.

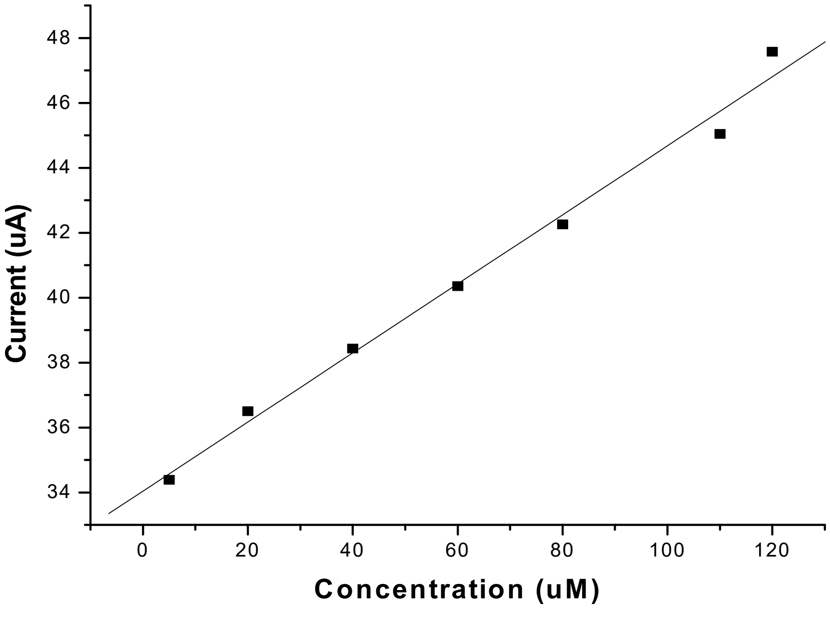


Fig. 15. Calibration curve for the determination of fenitrothion at poly (carmine) modified GC electrode.

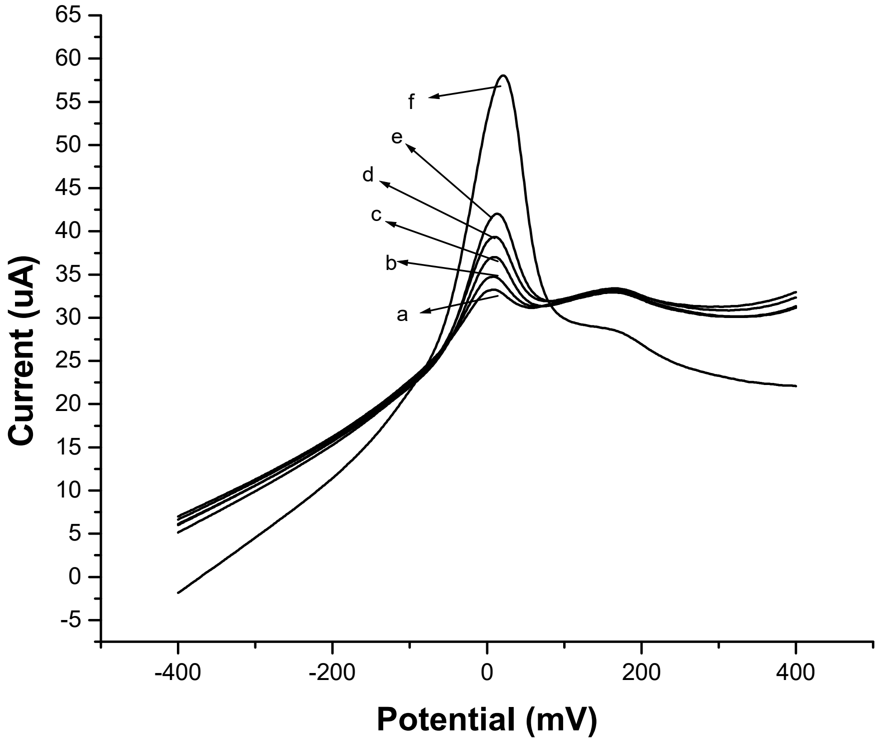


Fig. 16 Linear sweep voltammogram of the oxidation peak of fenitrothion in (a) 5uM, (b) 20uM, (c) 50uM, (d) 80uM, (e) 100uM and (f) 120uM fenitrothion using electrochemically pretreated GC electrode.

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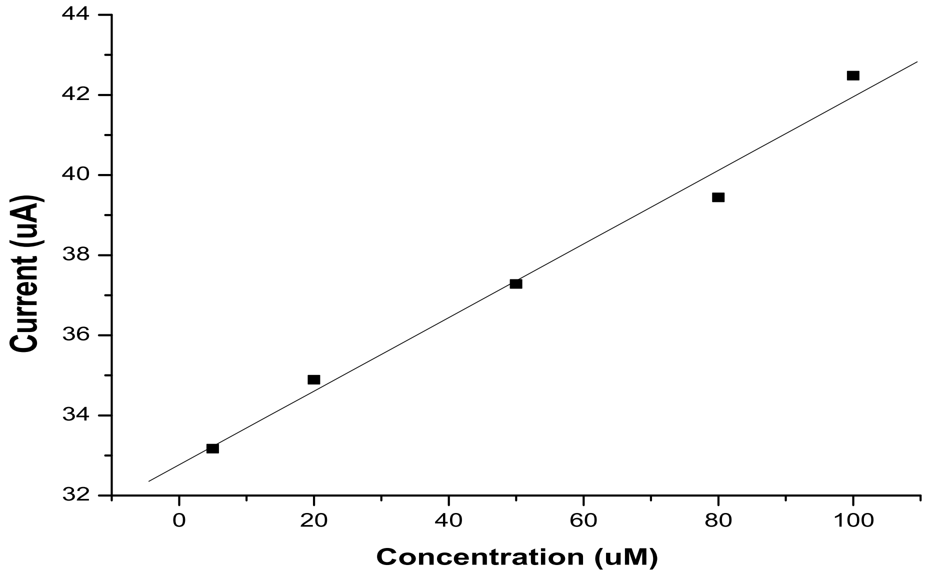

Fig. 17.Calibration curve for the determination of fenitrothion at electrochemically pretreated GC electrode.

Figure 16 shows the linear sweep voltammogram of fenitrothion oxidation at the EPT glassy carbon electrode by changing its concentration from 5.0 x 10^{-6} – 1.2 x 10^{-4} mol L^{-1}. It is increasing linearly up to 1.0 x 10^{-4} mol L^{-1}. Figure 17 shows the calibration curve of the EPT glassy carbon electrode prepared for the determination of fenitrothion. Calibration of the electrode is carried out using the established current response.

Under optimum condition, the poly (carmine) film glassy carbon electrode exhibit a linear relationship between the peak current and the concentration of fenitrothion as shown in figure 15 with a linear range from 5.0 x 10^{-6}-1.2 x 10^{-4} mol L^{-1}. The linear regression equation is ip = 32.76 x 0.09 C (mol L^{-1}), with a correlation coefficient of 0.9923. And under the same condition the electrochemically pretreated glassy carbon electrode exhibit a linear relationship between the peak current and the concentration of fenitrothion as shown in figure 17 with a linear range from 5.0 x 10^{-6}-1.0 x 10^{-4} mol L^{-1}. The linear regression equation is ip = 34.01 x 0.11 C (mol L^{-1}), with a correlation coefficient of 0.9962.

7. Conclusion

An electrochemical sensor for the determination of fenitrothion has been developed based on the electropolymerization of carmine on a glassy carbon electrode. The electropolymerization of carmine by scanning up to high positive potential (i.e. +2.0V) can oxidize the glassy carbon electrode surface itself resulting in activation of the electrode. As a result, the current response of the poly (carmine) modified glassy carbon electrode and electrochemically pretreated glassy carbon electrode is comparable. The linear range of fenitrothion using poly (carmine) modified glassy carbon electrode is 5.0 x 10^{-6}-1.2 x 10^{-4} mol L^{-1} and the linear range of fenitrothion using electrochemically pretreated glassy carbon electrode is 5.0 x 10^{-6}-1.0 x10^{-4} mol L^{-1}.

REFERENCES

1. H. Lund, O. Hammerich, *Organic Electrochemistry*, 4th edition, Marcel Dekker, New York, **2001**
2. A. J. Bard, *Electroanalytical Chemistry*, Vol. 13, Marcel Dekker, New York, **1984**
3. R. E. White, J. M. Bockris, B. E. Conway, *Modern aspects of Electrochemistry,* No. 33, Kluwer Academic, New York, **1999**
4. A. J. Bard, L. R. Fauckner, *Electrochemical methods fundamentals and applications*, John Wily and Sons, Texas, **2001**
5. T. A. Skotheim, R. L. Elsenbaumer, J. R. Keynolds, *Handbook of Conducting Polymers*, 2nd edition, Marcel Dekker, New York, **1998**
6. J. M. Andre, J. Delhalle, J. L. Breder, *An introduction to the Quantum chemistry of polymers and its application,* Vol.2, world scientific publishing, Singapor, **1991**
7. C. D. Craver, C. E. Carraher, *Applied Polymer Science 21st Century*, Elsevier, Netherlands, **2000**
8. I. Rubinstein, *Physical Electrochemistry Principles, Methods and Application*, Marcel Dekker, New York, **1995**
9. J. F. Rubinson, H. B. Mark, *Conducting Polymers and Electrolytes*, American Chemical Society, Washington DC, **2003**
10. X. Y. Liu, C. Y. Li, S. Hu, *Microchim Acta* 154, 275-280, **2006**
11. C. Li, *J. Appli. Polymer Science* 103, 3271-3277, **2007**
12. S. E. Manhan *Environmental chemistry*, 8th edition, CRC press, Boca Raton, **2005**

13. M. Negussie, *Trace enrichment of triazine Herbicides using the supported Liquid membrane extraction technique: Application to the study of waters in Ethiopia lakes*, Ph. D Dissertation, Department of Chemistry, Addis Ababa University, **2000**
14. K. H. Buchel, *Chemistry of Pesticides*, John Wily and Sons, New York, **1977**
15. A. J. Bard, *Elctroanalytical Chemistry*, Vol. 17, Marcel Dekker, New York, **1991**
16. L. J. Kepley, A. J. Bard, *Anal. Chem*. 60, 1459-1467, **1988**
17. G. E. Cabaniss, A. A. Diamantis, W. R. Murphy, J. R. W. Linton, T. J. Meyer, *J. Am. Chem. Soc* 107, 1845-1853, **1985**
18. P. Chen, R. L. Mccreery, *Anal. Chem*. 68, 3958-3965, **1996**
19. S. Panero, P. Prosperi, B. Scrosati, *Electrochemica Acta* 32, 1451-1464, **1987**
20. J. F. Evans, T. Kuwana, *Anal. Chem*. 49, 1632-1635, **1977**
21. P. M. Kovach, M. R. Deakin, R. M. Wightman, *J. Phys. Chem*. 90, 4612-4617, **1986**
22. I. F. Hu, D. H. Karweik, T. Kuwana, *J. Electroanal. Chem*. 188, 59-72, **1985**
23. J. M. Zen, J. J. Jou, A. S. Kumar*, Analitica Chemica Acta* 396, 39-44, **1998**