

GLASSY CARBON ELECTRODE MODIFIED WITH COBALT PHTHALOCYANINE AND GRAPHENE COMPOSITES FOR ELECTROANALYSIS OF BROMFENVINFOS AND TETRACHLORVINPHOS

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ABSTRACT

The voltammetric behaviour of two common organophosphorus(OP) pesticides such as bromfenvinfos (BRFV) and tetrachlorvinphos (TCVP) were investigated at glassy carbon electrode (GCE) modified with cobalt phthalocynine (CoPc) and graphene (Gr) composites. The modified electrode film was characterized by scanning electron microscopy (SEM) and cyclic voltammetry (CV). The electro active behaviour of the pesticides was accomplished by the cyclic voltammetry and square wave voltammetric studies. The square wave voltammetric method was used to analyze the above-mentioned pesticides using GCE, CoPc/GCE, and CoPc/Gr/GCE in soil and human urine samples. An irreversible reduction peaks were obtained for BRFV and TCVP on the modified Co/Gr/GC electrode system. The above mentioned pesticides were compared each other on GCE modified system. The results shows that BRFV and TCVP exhibits excellent electrocatalytic motion on modified CoPc/Gr/GCE system in Britten- Robinson buffer solution (BRS) of pH range 2.0–12.0. To carry out the process among the three electrode system and the concentration contains $2.25 \times 10^{-7} \text{M}$ for TCVP and BRFV. The limit of detection (LOD) for TCVP and BRFV are 5.35×10^{-9} and $3.05 \times 10^{-9} \text{M}$ on CoPc/Gr/GCE modified system respectively. A simple, sensitive and rapid square wave voltammetric method was successfully applied for quantitative determination of TCVP and BRVF in soil and human urine samples.

KEYWORDS: Bromfenvinfos, Tetrachlorvinphos, CoPc/Gr/GCE, Cyclic Voltammetry, Square Wave Voltammetry

INTRODUCTION

Graphene, a two-dimensional monolayer of sp^2 -bonded carbon atoms tightly packed into a planar honeycomb lattice and characterized as the thinnest material in our universe, has attracted considerable attention owing to its high surface area, high chemical stability, and unique electronic and mechanical properties [1],[2]. Therefore, it can be applied in numerous areas ranging from in nanoelectronic devices, biosensors, energy storage, optical application, catalysis and super capacitors [3]-[7]. It has ultra large surface area (up to $2600 \text{ cm}^2 \text{ g}^{-1}$) which means it has high capacity for the adsorption of target molecules[8]. Owing to their unique electronic properties and promising applications, a huge number of studies have focused on the processing of graphene nanosheets. Until now, graphene has been successfully used as a matrix for the preparation of graphene based composites, including metal, metal oxide, conducting polymer, carbon materials. It comprises large delocalized π -electron system which can form strong π - π stacking interaction with aromatic rings [9].

Nonetheless, macrocyclic metal complexes such as metalloporphyrins (MPs), metallophthalocyanines (MPcs) and related compounds are drawn in great variety of electrochemical reactions [10]-[12]. The advantage of the MPs and MPcs is adsorb strongly on graphite and carbon-based electrode materials for detection of molecules in biological and environmental aspects [13]-[18]. Analytes such as thiols, oxygen and nitric oxide have been reported to coordinate with the metal centre of the MPc complex, during catalysis [19]. In an effort to improve sensitivity and stability, MPc complexes

have been immobilized together with enzymes for detection of the pesticide [20]-[22]. However the stability of the biosensor remains a problem, to detect dicrotophos in particular, acetylcholinesterase failed whereas the method worked for other organophosphates [23]. Sreedhar et al detected pesticides which yielded good detection limits, however the method was done by polarography [24]. The mode of electrochemical reduction of pesticides like monocrotophos, dichlorovos and dicrotophos, which are similar in structure to bromfenvinfos and tetrachlorvinphos has been reported [25].

One of the most important classes of insecticides are organophosphorus compounds. Bromfenvinfos (EZ)-2-bromo-1-(2,4-dichlorophenyl)vinyl diethyl phosphate) and tetrachlorvinphos ((Z)-2-Chloro-1-(2,4,5-trichlorophenyl)vinyl] dimethoxy phosphate) are systemic and general insecticides, the structures shown in figure 1 [26],[27]. These are effective against a wide range of insects on fruits, vegetables, and commercial crops. At the moment these are widely used because of their low doggedness and high inefficiency. It is found that a number of organophosphorus pesticides have been determined by means of techniques such as gas chromatography, thin-layer chromatography, high performance liquid chromatography as well as spectrophotometry in fruits and vegetables [28]-[30]. Electrochemical techniques have been widely used for the determination of $>C=C<$ containing pesticides [31].

In the present work carried out electroanalysis method to determine the BRFV and TCVP at modified CoPc/Gr/GCE by electro reduction process. The developed modified electrode exhibited excellent performance such as high sensitivity, a low detection limit, short response time, better reproducibility and wide concentration range for the detection of BRFV and TCVP.

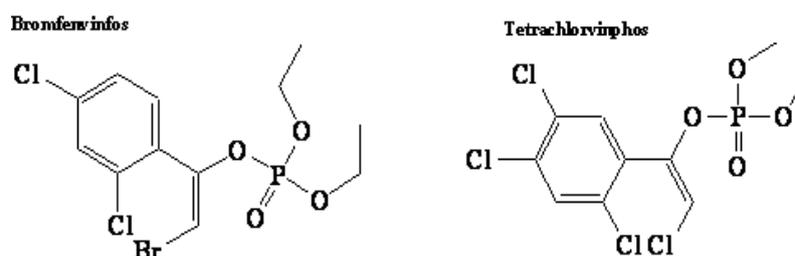


Figure 1: Structures of Bromfenvinfos and Tetrachlorvinphos

EXPERIMENTAL

Apparatus

Electrochemical studies were carried out by Autolab PG STAT101 supplied by Metrohm Autolab B.V., The Netherlands. A three electrode system comprising of a glassy carbon electrode modified with cobalt phthalocynine (CoPc) and graphene (Mpc/GRP/GCE) composites as a working electrode. Glassy carbon electrode (GCE) obtained from Metrohm India Ltd Chennai and graphene powder and cobalt phthalocynine obtained from Aldrich. Saturated Ag/AgCl/KCl as a reference electrode and Pt wire as a counter electrode obtained from local scientific labs. Electrode surface morphology study was carried out by SEM instrument model OXFORD instrument INCA PENTA FETX3 CARL ZEISS from Japan. An Elico LI-120 pH meter supplied by Elico LTD, Hyderabad, India was used to determine the pH of the buffer solution.

Chemicals and Reagents

All reagents were of analytical grade and ultrapure water was used during all the detection proces. Pesticide standards BRFV and TCVP were obtained from local pesticide shop at Tirupati, India. Standard solutions $2.25 \times 10^{-7} M$ of BRFV and TCVP were prepared by dissolving in acetone. These solutions were stored in the dark at $4^\circ C$. Working solutions of lower concentration were freshly obtained by dilution with acetone. Britten- Robinson buffer was prepared from 0.04 mol L^{-1} solutions each of O-phosphoric acid, acetic acid, boric acid and the pH was adjusted using 0.2 mol L^{-1}

NaOH solution. All the chemicals and solvents used were of analytical grade obtained from Merck (Mumbai, India).dissolving these reagents in ultrapure water and adjusting to the desired pH with sodium hydroxide and hydrochloric acid solutions. All solutions were filtered through a 0.45 mm membrane filter, and then degassed by sonication and evacuation.

Preparation of the CoPc/Gr/GCE Modified Electrode

The bare GCE was polished with 0.05 μm alumina powder before it was used, rinsed ultrasonically with 1:1HNO₃, ethanol, and deionised water, respectively, and dried at room temperature. Graphene was dispersed in ethanol (1 mg/mL) with ultrasonication for 30 min. 5 μL of the graphene suspension was cast on the surface of GCE and dried in air. Prior to use, the modified electrode was carefully rinsed with Millipore water and dried in an air stream. And then the CoPc solution was prepared and then by drop-coating 20 μL of the CoPc standby solution on the GCE followed by air-drying for 3–4 h. A smooth, bright and blue thin film appeared on the GC surface. The resulting modified electrode is denoted as CoPc/Gr/GCE. After dried under ambient conditions, the CoPc/Gr/GCE was washed with redistilled deionised water to remove the unimmobilized mixture. All the modified electrodes were stored at 4° C in a refrigerator before use. Figure 2 indicates the modification process of CoPC/Gr/GCE.

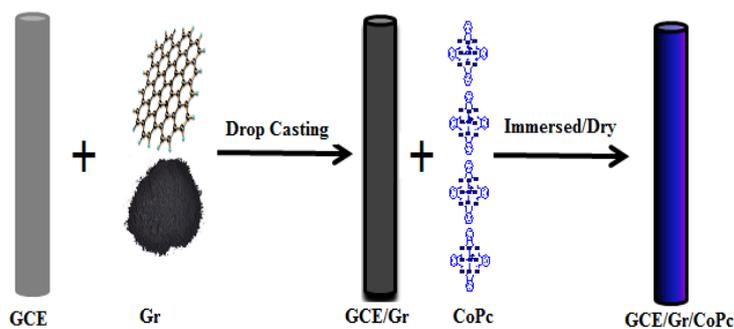


Figure 2(A): Schematic Electrode Modification Process

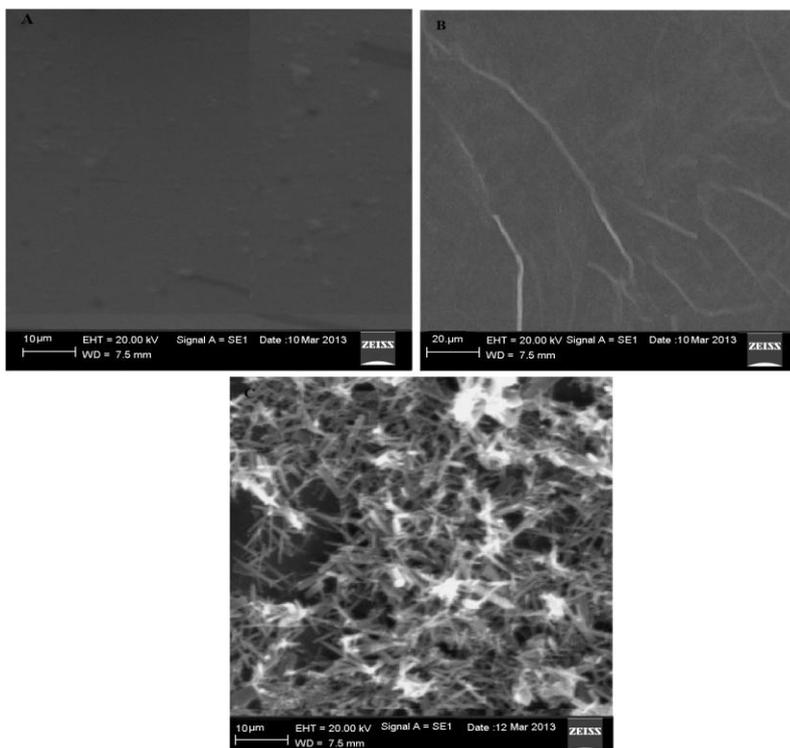


Figure 2(B): SEM Image of CoPc/GCE (A), Gr/GCE (B), and CoPc/Gr/GCE (C)

Analytical Procedure

A stock solution (1.0×10^{-3} M) was prepared by dissolution of the appropriate amount of the electro active species in ethanol. 1 ml of standard solution was transferred into electrolytic cell and diluted with 9 ml of supporting electrolyte and then deoxygenated with nitrogen gas for 10 min. After the voltammogram is recorded, small increments (0.5 ml) of standard solution is added and then voltammogram is recorded after each addition under similar conditions. In present study, the best recovery was obtained at pH 4.0 at potential of -0.90 V, -1.20 V for two compounds respectively. The relative standard deviations and correlation coefficients were found to be 2.6%, 3.5% and 0.9952%, 9862% of the respective compounds. This procedure was successfully used for the determination of these compounds at different pH values.

RESULTS AND DISCUSSIONS

Surface Morphology Study of Modified Electrode

SEM images of CoPc and Gr modified glassy carbon electrode are shown in Figure 2 (A), (B) and (C) CoPc/GCE, Gr/GCE and CoPc/Gr/GCE film with different magnifications respectively. It has shown that the film surface is continuous and graphene powder successfully deposited on GCE surface. The film displayed a relatively high surface roughness, it can be due to the deposition of CoPc nanoparticle, indicates that CoPc were successfully fabricated into the composite film.

Electrochemical Behaviour of Modified Electrode

The electrochemical behaviour of glassy carbon electrode modified with CoPc and Gr composites (CoPc/Gr/GCE) for the determination of BRFV and TCVP in ethanol with Ag/AgCl/KCl as reference electrode by use of cyclic voltammetry. BRFV and TCVP pesticides are obtained well defined reduction peaks in the potential range -0.4 V to -1.6 V. The pH of the electrolysis medium is one of the variables that often severely affect the shape of the voltammogram, the peak potential and peak current, the effect of pH was to examine in detail. A stream of oxygen-free nitrogen gas was passed into the solution for 15 minutes before measuring the voltammetric study and all the measurements were carried out at constant temperature. Figure 3 shows a typical cyclic voltammograms of both BRFV and TCVP shows one peak at potential $E = -0.90$ V and -1.2 V on CoPc/Gr/GCE modified system respectively. This is clearly shows that BRFV and TCVP undergo reduction at the glassy carbon modified electrode surface. Cathodic peak may be due to reduction of carbon-carbon double bond (alkenyl group) involves two protons and two electron transfer reaction shown in scheme 1 [31]. CV is carried out with the potential sweep rate in the range of -25mVs^{-1} to -150mV s^{-1} and well defined cathodic peaks obtained between -0.90 V to -1.3 V of both compounds. As the potential sweep rate is increased, the peak current also increased and peak potential shifted to more negative value and no peak appeared in the reverse sweep, indicating irreversible nature of the reaction process.

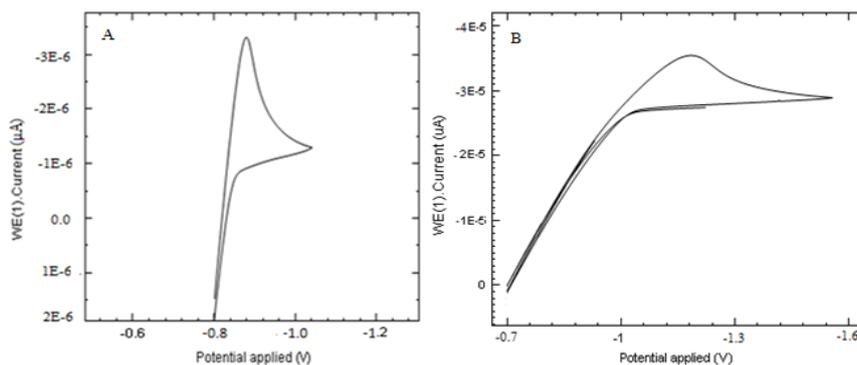
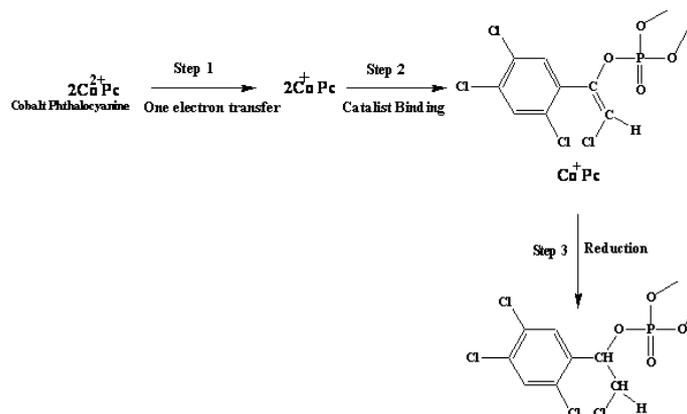
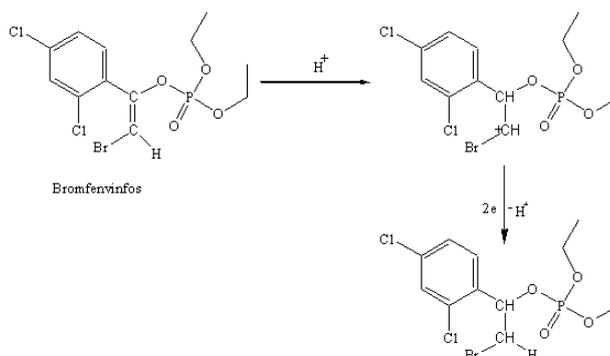


Figure 3: Cyclic Voltammogram of BRFV (A) and TCVP (B)

Schemes



Scheme 1(A): TCVP Reduction Mechanism



Scheme 1(B): BRFV Reduction Mechanism

Cyclic Voltammetric (CV) Studies

Cyclic voltammetric studies of 2.25×10^{-7} M of BRFV and TCVP at 0.70Vs⁻¹ to -1.4Vs⁻¹ revealed the presence of reduction peak at pH4.0 on plain GCE, CoPc/GCE, Gr/GCE but well defined peak was obtained at CoPc/Gr/GCE system only. Peak with lowest potential and negative current was observed only at pH 4.0 for BRFV and TCVP revealing easy reduction due to prior alkenyl group was easily reduced at Cl atoms substrate, which facilitated reduction cleavage. Thus pH 4.0 was selected as the suitable medium for the electrochemical studies of BRFV and TCVP. One well defined reduction peak each at -0.90V and -1.7V for BRFV and TCVP on CoPc/Gr/GCE system in BRS of pH 4.0. There was no anodic response in the reverse scan indicating the irreversible electron transfer process. Figure 3 (A)&(B) showed cyclic voltammograms of BRFV and TCVP on CoPc/Gr/GCE at pH.4.0 correspondingly.

Effect of pH

The effect of pH on the peak current and peak potential of the irreversible reduction peak of BRFV and TCVP at the CoPc/Gr/GCE was investigated of the pH range 2.0–10.0. Figure 4A describes various pH ranges containing 2.25×10^{-7} M BRFV and TCVP at CoPc/Gr/GCE in BRS by cyclic voltammetry. The reductive peak current increased with pH until it reached its maximum at pH 4.0 and then began to decrease slightly. The peak current decreased observed higher than at pH 4.0 could be ascribed to the decreasing proton concentration in the buffer system which is needed for the reduction of the alkenyl group of BRFV and TCVP. Therefore, pH 4.0 was taken as the optimum solution pH for further analyses. The effect of solution pH on the reductive peak potential of BRFV and TCVP was also investigated. A potential shift in the negative direction was observed with increasing pH indicating the participation of protons in the reduction of BRFV and TCVP. Figure 4B depicts a linear relationship between reductive peak potential (E_{pc}) and solution pH with a

slope of 65.32 shows the participation of protons and electrons in a 1:1 ratio [32].

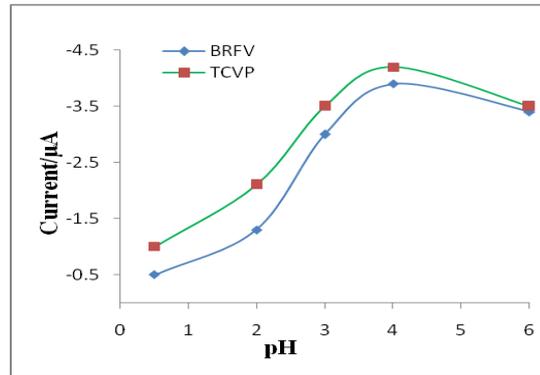


Figure 4(A): Reductive Peak Current versus pH of BRFV and TCVP Concentration 2.25×10^{-7} M at CoPc/Gr/GCE

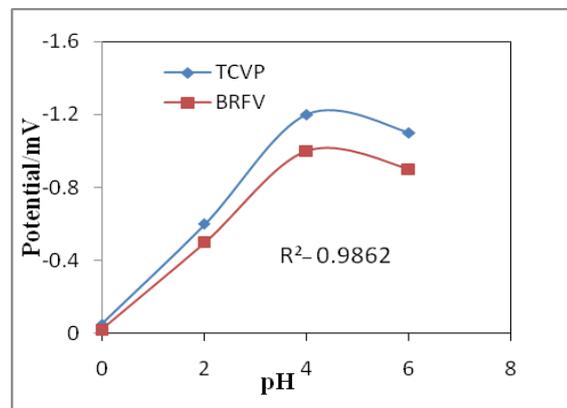


Figure 4(B): Reductive Peak Potential at Different pH Ranges of BRFV and TCVP Concentration 2.25×10^{-7} M at CoPc/Gr/GCE

Effect of Scan Rate

The influence of potential scan rate on the peak current (I_{pc}) and peak potential (E_{pc}) of 2.55×10^{-7} M BRFV and TCVP in BRS of pH 4.0 at CoPc/Gr/GCE modified system was studied in the range 20–300 mV s^{-1} . Figure 5A and 5B represents cyclic voltammograms of BRFV and TCVP at different scan rates. Reductive peak current showed linear dependence on potential scan rate with a better correlation coefficient in contrast to its dependence on the square root of scan rate, Figure 5C indicating that the square root of scan rate versus current plot. Moreover, the peak potential shift observed with increasing scan rate confirmed the irreversibility of the reduction process.

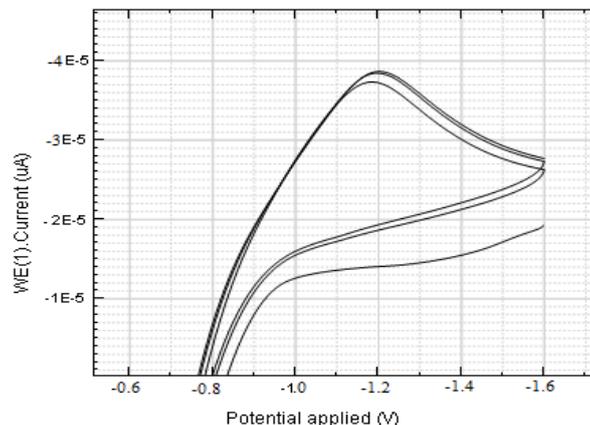


Figure 5(A): Cyclic Voltammogram of TCVP in BRS Containing 2.25×10^{-7} M at Different Scan Rates CoPc/Gr/GCE

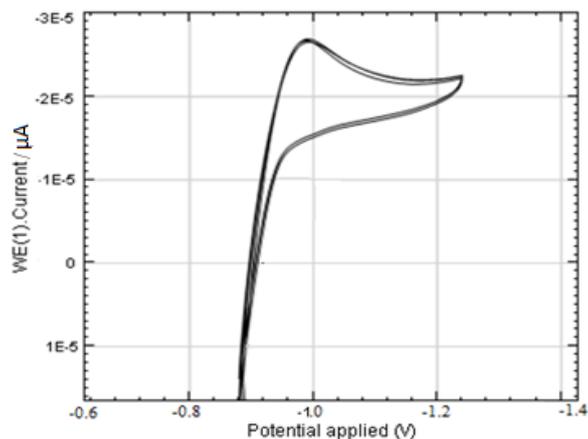


Figure 5(B): Cyclic Voltammogram of BRFV in BRS Containing 2.25×10^{-7} M at Different Scan Rates at CoPc/Gr/GCE

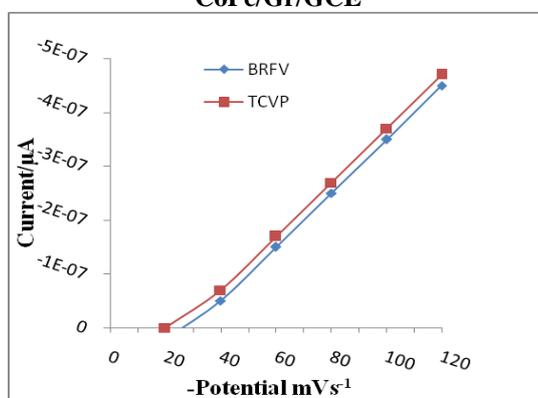


Figure 5(C): Plot of Peak Current versus Potential Scan Rates of 2.25×10^{-7} M BRFV and TCVP in BRS (pH-4.0) at CoPc/Gr/GCE

Square Wave Voltammetry for the Analyses of BRFV and TCVP

In view of the fact that square wave voltammetry (SWV) has sensitivity and better resolution than cyclic voltammetry, the relevance of CoPc/Gr/GCE for the quantitative determination of BRFV and TCVP has been investigated using SWV. Figure 6 describes the square wave voltammograms of BRFV and TCVP containing 2.25×10^{-7} M in BRS at CoPc/Gr/GCE at pH 4.0. The peak current response at CoPc/Gr/GCE curve (b) of BRFV was two-folds when compared to the peak at the CoPc/Gr/GCE curve (a) of TCVP besides the peak potential shift towards negative direction by about 50 mV. The peak current enrichment and peak potential shift are conformations for the electrocatalytic effect of the CoPc/Gr/GCE towards the reduction of BRFV and TCVP. Taking in to account the peak current response and peak shape, SWV parameters such as the step potential, pulse amplitude and frequency were optimized -25 mV, -75 mV and 50Hz, and -35 mV, -85 mV and 50 Hz for BRFV and TCVP respectively.

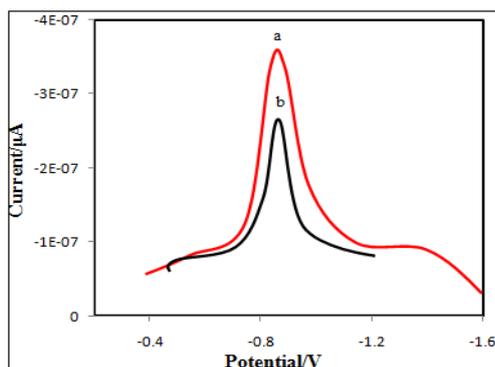


Figure 6: Square Wave Voltammograms of 2.25×10^{-7} M BRFV and TCVP in BRS (pH-4.0) at CoPc/Gr/GCE

Effect of Accumulation Potential and Time

Since the reduction of BRFV and TCVP at the CoPc/Gr/GCE is adsorption-controlled, the effect of accumulation potential (E_{acc}) and time (t_{acc}) were investigated. The dependence of accumulation potential on the peak current response of CoPc/Gr/GCE for BRFV and TCVP at t_{acc} 30s and 40s respectively. The peak current increased with increasing E_{acc} from -0.2 to -1.3 V and then decreased at higher negative potentials showing that -0.90 and -1.2 V is the optimum accumulation potential for BRFV and TCVP. The effect of t_{acc} on the peak current response of CoPc/Gr/GCE for BRFV and TCVP were recorded at E_{acc} -0.90 , 1.2 V respectively. The peak current increased with t_{acc} up to 90 s beyond which is levelled off. This could be due to the saturation level of the active electrode surface. Hence, -0.90 V, 30 s and -1.2 V, 40 s were taken as the optimized E_{acc} and t_{acc} of BRFV, TCVP respectively.

Limit of Detection and Linear Range

Over the optimized solution and method parameters, calibration curve was constructed by recording the SWV peak current responses of CoPc/Gr/GCE for different concentrations of standard BRFV and TCVP. Figure 7(A) & (B) shows the square wave voltammograms of BRFV and TCVP in different concentration ranges from $10\mu\text{M}$ to $60\mu\text{M}$. The peak currents were linearly related to concentration 2.25×10^{-7} M with a regression coefficient and limit of detection (LOD) of 0.9862 , 0.9952 and 1.55×10^{-9} M and 3.55×10^{-9} M for BRFV and TCVP respectively. The observed gradual deviation from linearity of the current response for concentrations higher than 2.25×10^{-7} M could be due to the saturation level of the electrode surface. Figure 7(C) shows the relation between concentration versus current for BRFV and TCVP in BRS of pH 4.0 at CoPc/Gr/GCE modified system.

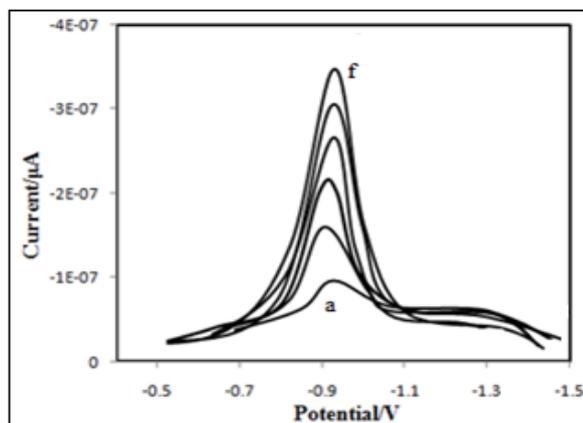


Figure 7(A): SWV of BRFV Containing various Concentrations from $10\mu\text{M}$ to $60\mu\text{M}$ in BRS at CoPc/Gr/GCE

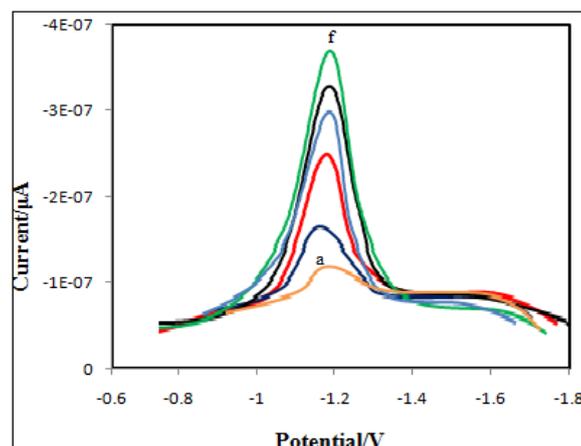


Figure 7(B): SWV of TCVP Containing various Concentrations from $10\mu\text{M}$ to $60\mu\text{M}$ in BRS at CoPc/Gr/GCE

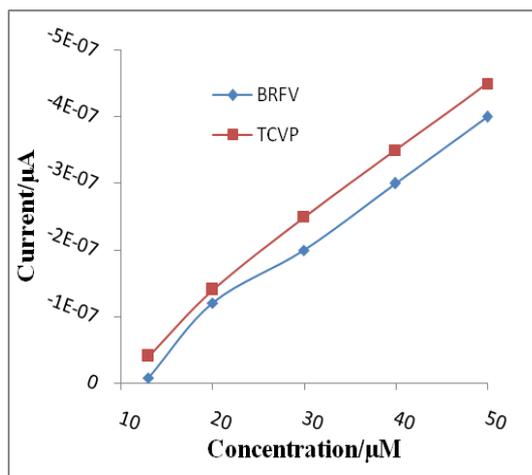


Figure 7(C): Plot of Peak Current Response versus Concentration of BRFV and TCVP in BRS at CoPc/Gr/GCE

Recovery Study of BRFV and TCVP from Soil Samples

Three standard BRFV and TCVP samples (A, B and C) containing $2.25 \times 10^{-7} \text{ M}$ of pH 4.0 in BRS were prepared using soil. Then, the samples (A, B and C) were spiked with 10, 15 and $20 \times 10^{-7} \text{ M}$ standard BRFV and TCVP respectively. The SWV results were recorded under the optimized conditions are summarized in Table 1. Recoveries in the range 97.50–99.50% showed the applicability of the developed method for quantitative determination of BRFV and TCVP in soil samples. Moreover, low RSD (2.15%, 2.60%) values indicate the reproducibility of the measurements.

Reproducibility, Repeatability and Stability

To investigate the reproducibility of the proposed technique, under the same conditions, three electrodes fabricated independently were examined. The results indicated that the CoPc/Gr/GCE showed excellent reproducibility. The relative standard deviation (RSD) was 2.6% shown in table.1.

To investigate the repeatability of the CoPc/Gr/GCE, the experiments were performed in $2.25 \times 10^{-7} \text{ mol L}^{-1}$ of BRFV and TCVP using the same modified electrode. Three electrodes were prepared by using the same modification method about different cycles shown in figure 8 (A). Then, the three electrodes were used to determine the same BRFV and TCVP solution. The calculated RSD was about 3.5% shown in table 2.

The results showed that the proposed modified electrode was good repeatability. We also performed the regeneration experiment of developed sensor. The regeneration procedure was as follows: in the experiment, after the detection, the electrodes were washed by 0.1 mol L^{-1} BRS (pH 4.0) for 5 min to extract the templates. When the oxidation peak currents of these electrodes were the same as Figure 8(A), the regeneration procedure was finished the cyclic voltammogram shown in figure 8 (B).

It revealed that binding of BRFV and TCVP to the hollow space was irreversible. The electrodes were allowed to dry. Then the electrodes were used to detect BRFV and TCVP solution again. Afterwards, the electrodes were washed again and the next detection was processed similarly. The experimental results unproven the CoPc/Gr/GCE could be regenerated very well. The long-term stability of the sensor was also important.

The stability of the sensor has been examined by monitoring the current response for $2.25 \times 10^{-7} \text{ mol L}^{-1}$ BRFV and TCVP at different intervals for a period of two months. After two months the sensor retained 90% of current response. It was suggested that the proposed modified possess acceptable for storage stability.

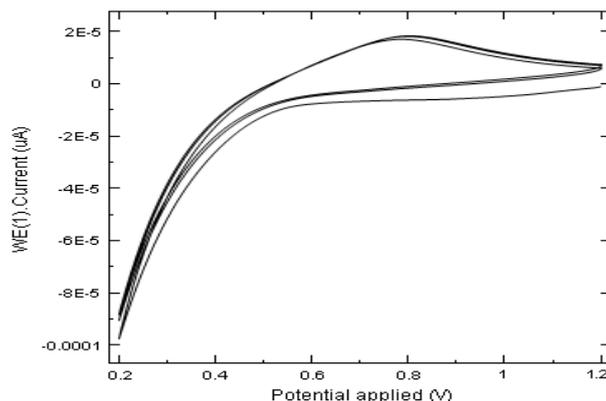


Figure 8(A): The Stability of the Modified Electrode by Cyclic Voltammogram in BRS at pH 4.0 for Different Cycles at Beginning of the Electrode Modification

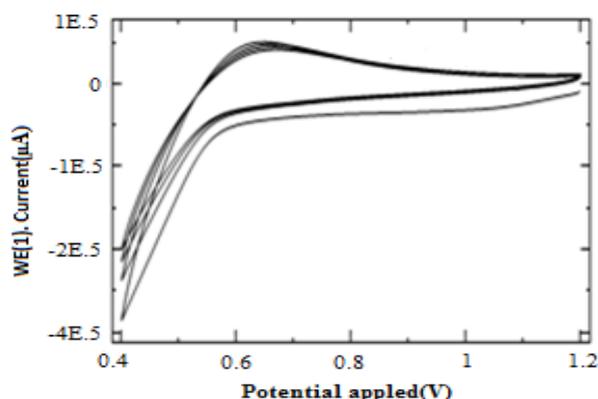


Figure 8(B): The Stability of the Modified Electrode by Cyclic Voltammogram in BRS at pH 4.0 for Different Cycles after Two Months from First Modification of the Electrode

Recovery Study of BRFV and TCVP from Human Urine Samples

Three human urine samples were prepared as described in the experimental part. The three human urine samples were spiked with appropriate amounts of standard BRFV and TCVP until the final concentrations are $10, 15,$ and 20×10^{-7} M, respectively. The recovery of the method developed was investigated by comparing the current response for the three human urine samples against the spiked concentrations of standard BRFV and TCVP in BRS at pH 4.0. Recoveries in the range 96.52-98.25% from human urine shown in Table 1 still indicated the applicability of the method for determination BRFV and TCVP in real samples. Moreover, lower recovery for a lower concentration of BRFV and TCVP signified the influence of urine matrix in the determination of BRFV and TCVP from human urine, at low concentrations. The slight potential shift observed for the SWVs of BRFV and TCVP in human urine, samples could probably be due to the effect of co-adsorption of urine matrix.

Table 1: Recovery Studies of BRFV and TCVP in Soil and Human Urine Samples

Sample	SWV	Initial	Spiked (μM)	Detected ^a (μM)	Recovery ^b (%)	RSD%
Soil (BRFV)	A	10	10	18.89	97.52	1.75
	B	10	15	23.90	97.85	1.85
	C	10	20	29.10	98.50	2.15
Soil (TCVP)	A	10	10	19.92	98.60	2.20
	B	10	15	24.50	99.20	2.50
	C	10	20	29.80	99.50	2.60
Human urine (BRFV)	A	10	10	17.60	96.52	1.35
	B	10	15	22.98	96.85	1.45
	C	10	20	28.20	98.50	2.15

Table 1: Contd.,

Human urine (TCVP)	A	10	10	19.92	97.60	1.75
	B	10	15	24.60	97.70	1.80
	C	10	20	29.20	98.25	2.10

a- Mean of the triplicate measurements

b- Mean recovery of triplicate

Table 2: Recovery Studies of BRFV and TCVP in Soil and Human Urine Samples after Two Months

Sample	SWV	Initial	Spiked (μM)	Detected ^a (μM)	Recovery ^b (%)	RSD%
Soil (BRFV)	A	10	10	16.89	96.45	1.95
	B	10	15	18.90	96.55	2.20
	C	10	20	28.20	97.32	3.15
Soil (TCVP)	A	10	10	17.85	98.20	3.20
	B	10	15	23.55	98.35	3.40
	C	10	20	29.75	98.60	3.50
Human urine (BRFV)	A	10	10	16.25	96.15	1.40
	B	10	15	21.96	96.35	1.52
	C	10	20	27.30	97.25	2.85
Human urine (TCVP)	A	10	10	18.95	97.48	1.80
	B	10	15	23.60	98.22	3.28
	C	10	20	28.84	98.50	3.50

a- Mean of the triplicate measurements

b- Mean recovery of triplicate

CONCLUSIONS

The electrochemical behaviour of BRFV and TCVP both at CoPc/Gr/GCE were studied using cyclic voltammetry. Irreversible reductive peaks were obtained at CoPc/Gr/GCE for above said compounds. In contrast to the CoPc/Gr/GCE showed about 3-folds of peak current enrichment and potential shift to lower values representative its catalytic activity towards BRFV and TCVP. The effects of pH and scan rate on peak current and peak potential for the irreversible reductive peak of BRFV and TCVP were investigated. A reaction mechanism involving 1:1 electron-proton reduction of the alkenyl group of BRFV and TCVP were proposed. The SWV current response of CoPc/Gr/GCE for BRFV and TCVP wide-ranging linearly with the concentration in the range $2.25 \times 10^{-7} \text{M}$ with a linear regression equation, correlation coefficient and limit of detection of $R^2 = 0.9952$, 0.9862 and $1.5 \times 10^{-9} \text{M}$, $3.5 \times 10^{-9} \text{M}$ of BRFV and TCVP respectively. The method exposed recoveries of BRFV and TCVP from spiked human urine and soil samples in the range of 97–98.50% indicating the applicability of the developed method for determination of BRFV and TCVP in real samples.

ACKNOWLEDGEMENTS

I am very much thankful to UGC-BSR for providing financial assistance.

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