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Original Research article

Effective SWCNTs/Nafion Electrochemical Sensor for Detection of Dicapthon Pesticide in Water and Agricultural Food Samples

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ABSTRACT

In this study, we report an effective electrochemical sensor of single-walled carbon nanotubes (SWCNTs)/Nafion glassy carbon electrode (SWCNTs/Nafion/GCE) for determination of dicapthon in water and agricultural food samples. The electroanalytical performance of SWCNTs/Nafion/GCE toward the reduction of dicapthon was analyzed via cyclic and differential pulse voltammetry. The optimum parameters like the effect of pH, concentration of dicapthon solution, scan rate, accumulation potential and accumulation time were thoroughly optimized. At electrochemical optimum conditions, voltammetric reduction peak exhibited a linear with the concentration of dicapthon from 0.2–60.0 μgmL^{-1}, with a detection limit of 0.036 μgmL^{-1}. The modified electrochemical sensor showed good stability and reproducibility. The determination of dicapthon was examined with SWCNTs/Nafion/GCE in water and agricultural food samples.

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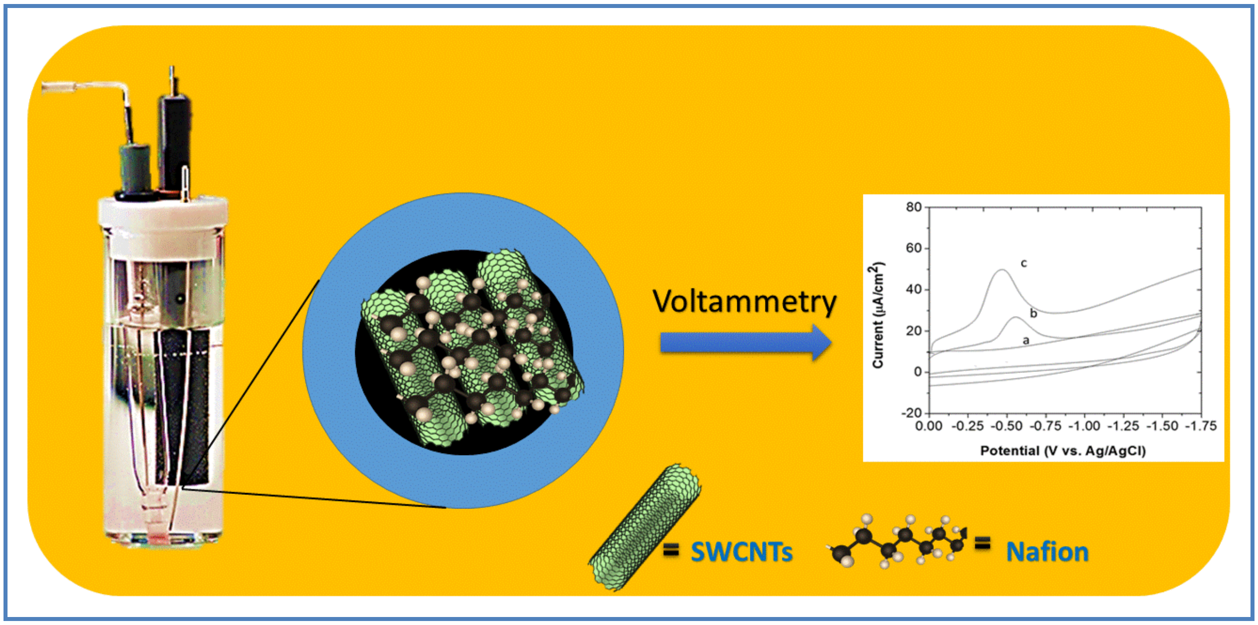
Graphical Abstract



Introduction

Pesticides are generally used to control a broad range of insects on fruits, vegetables and commercial crops and chemical warfare agents [1-3]. Numerous pesticides have been associated with health and environmental issues [2], and the agricultural use of certain pesticides has been abandoned [2]. Pesticides exposure can be in contact with the skin, ingestion, or inhalation. Consequently, the existence of pest residues and metabolites in agricultural food, water, soil are one of the major concerns for environmental chemistry [4]. Dicapthon (*O*-2-chloro-4-nitrophenyl *O,O*-dimethyl phosphorothioate; Molecular Formula: $C_8H_9ClNO_5PS$) is a contact and non-persistent organophosphate pesticide (Figure 1) used in insecticide and mutacide [6-9]. Overview of the organophosphorus pesticides to the market in the 1970s and increasing concerns about health and their potential environmental impact, many analytical methods such as gas chromatography [10], paper bio-chromatographic method [11], spectrophotometric [12], solid-phase extraction followed by gas chromatography/mass spectrometry method [13-15] and high performance liquid chromatography [10, 16, 17] were developed to detect these compounds. Thus, the above techniques involve complex separation processes in sample pretreatment process and exclusive equipments and toxic solvents. Additionally, it is time-consuming, complex and requires skilled persons. Due to high sensitivity, good stability and cost-effectiveness, electrochemical methods are more advantageous [18]. Glassy carbon electrodes (GCE) were used extensively in electroanalytical chemistry and also as the base for surface modified electrodes [19]. However, bare electrodes have limited electrochemical applications because of poor sensitivity and reproducibility, slow electron transfer reaction, low stability over a wide range of solution composition and high potential. Thus, surface modified electrodes enhance the sensitivity and selectivity of electrochemical sensors and prevent surface fouling [20, 21]. Different materials were used for modification of electrode surfaces; such as carbon nanotubes, metal oxides, conductive polymers, and inorganic catalysts [22].

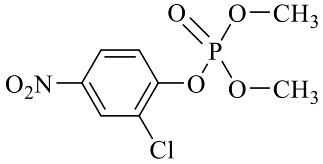


Figure 1. Chemical structure of dicapthon

Carbon nanotubes (CNTs) having two distinct types of structures, namely single-walled and multi-walled [23], are important classes of nanomaterials [24] used for modifying bare electrodes. Due to high mechanical strength, high electrical conductivity, high surface area, good chemical stability in both aqueous and non-aqueous solutions, relative chemical inertness in most electrolyte solutions and a wide potential window [25-27], the use of single-walled carbon nanotubes as a modifier has recently received much attention [28-31]. However, the Nafion modified single-walled carbon nanotubes interfacial interaction, chemical inertness, mechanical strength, ion exchange capacity and hydrophilic nature can be improved [22]. In this study, determination of dicapthon using bare GCE, SWCNT/GCE and SWCNT/Nafion/GCE is described. SWCNT/Nafion/GCE exhibits good electrocatalytic activity towards dicapthon with high sensitivity, selectivity, and reproducibility. Furthermore, the proposed method was successfully applied for the quantitative determination of dicapthon pesticide in water and agricultural food samples.

Experimental

Apparatus and Reagents

Electrochemical studies were carried out by Autolab PG STAT 101 supplied by Metrohm Autolab B.V., The Netherlands. A three electrode system is comprised of a modified glassy carbon electrode (GCE) namely as working electrode, Ag/AgCl/KCl as a reference electrode and Pt wire as a counter electrode. Solutions were deoxygenated with high purity nitrogen for 2-5 min prior to each experiment. An Elico LI-610 digital pH meter supplied by Hanna instruments was used to measure the pH of the solutions.

Single-walled carbon nanotubes (SWCNTs), Nafion (5%), trisodium orthophosphate, boric acid, and citric acid were purchased from Fisher Scientific. Acetone, *N,N*-Dimethylformamide, HNO_3, methanol and ethanol were procured from S. D. Fine Chem Ltd. BR buffers of pH range 2.0 to 10.0 are used as supporting electrolytes and are prepared using 0.2 M boric acid, 0.05 M citric acid and 0.1 M trisodium orthophosphate. The purity of the pesticide samples, which were obtained from Rankem Fine Chemicals Ltd., was tested by thin layer chromatography and also melting point determinations. Stock solution (1000 μgmL^{-1}) was prepared by dissolving dicapthon in acetone. All required experimental solutions were freshly prepared every day from the stock solution. Solutions were deoxygenated with high purity nitrogen for 5 min prior to each experiment. All reagents which were used for the overall process were analytically graded.

Preparation of modified electrode

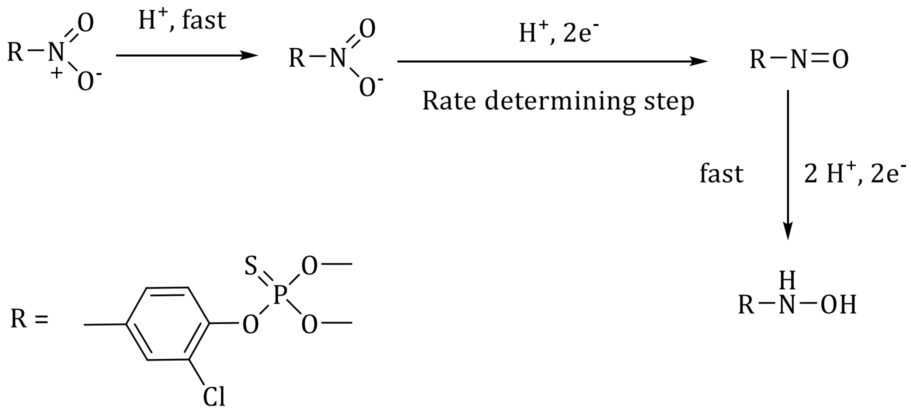
Firstly, the glassy carbon electrode was polished with 0.05 μm alumina slurry, rinsed thoroughly with distilled water and properly cleaned in a sonicator for 5 min to eliminate any remaining alumina particles. 2 mg of SWCNTs was dispersed in 10 mL of Nafion (5%) and also in 1 mL ethanol by ultrasonication for 30 min in order to give homogeneous Nafion/SWCNTs. Then, GCE surface was coated with 10 μl of Nafion/SWCNTs suspension and allowed to evaporate ethanol. Correspondingly, the Nafion modified GCE was prepared as above but without SWCNTs.

Voltammetric procedure

The modified electrode was immersed in 10 ml of 0.01 mol L^{-1} BR buffer solution containing the required amount of pesticide which was deaerated with nitrogen gas for 5 min. The differential scanning was carried out at –0.25 to –1.75 V at scan rate 40 mV/s and after electrode was rinsed for 2 min it was prepared for the next analysis. The addition method was applied for the measurement of water and agricultural samples.

Results and discussion

Electrochemical behaviours of dicapthon at a bare GCE, SWCNTs/GCE and SWCNTs/Nafion coated GCE have been examined by cyclic voltammetry in pH 5.0 (0.01 mol L^{-1}) BR buffer solution in the presence of 3.0 μgmL^{-1} dicapthon. Dicapthon exhibits a single, well-defined 4e^{-} reduction peak in cyclic voltammogram which is attributed to the reduction of $-NO_2$ group to the corresponding saturated product at pH 5.0 (Figure 2). The cyclic voltammogram of the bare GCE has no distinguishing peak observed in the potential range of –0.25 to –1.75 V (Figure 2a), and correspondingly the SWCNTs modified GCE (Figure 2b) shows the weak corresponding reduction peak at -0.46 V due to free electron mobility on the electrochemical system. However, the strong cathodic peak at -0.485 V was observed at the SWCNTs/Nafion coated GCE (Figure 2c), which is more projecting than those obtained at the bare GCE and SWCNT/GCE. In this connection, the accumulation of Nafion into SWCNTs hybrid composite possesses most prominent peak indication that the use of SWCNTs can significantly enhance the electron transfer between SWCNTs/Nafion and the electrode. At reverse scan, no analogous reduction peak was observed, revealing that the electrode reaction of dicapthon is completely irreversible. According to an accepted mechanism for the electrochemical reduction of aromatic nitro group containing pesticides, voltammetric peak was attributed to $4e^-$ reduction process. This phenomenon may be caused by the fact that the adsorption of dicapthon, or its reductive product, occurs at the electrode surface, and hence inactivates the electrode surface. The technique of millicoulometry has been employed in the present investigation to evaluate the number of electrons involved in the reduction process. From the comparison of the observed wave heights, the number of electrons consumed in the overall reduction process of dicapthon is found to be $4H^+$, $4e^-$ at pH 5.0 as a BR buffer system shown in Scheme 1.



Scheme 1. Electrochemical reduction mechanism of dicapthon

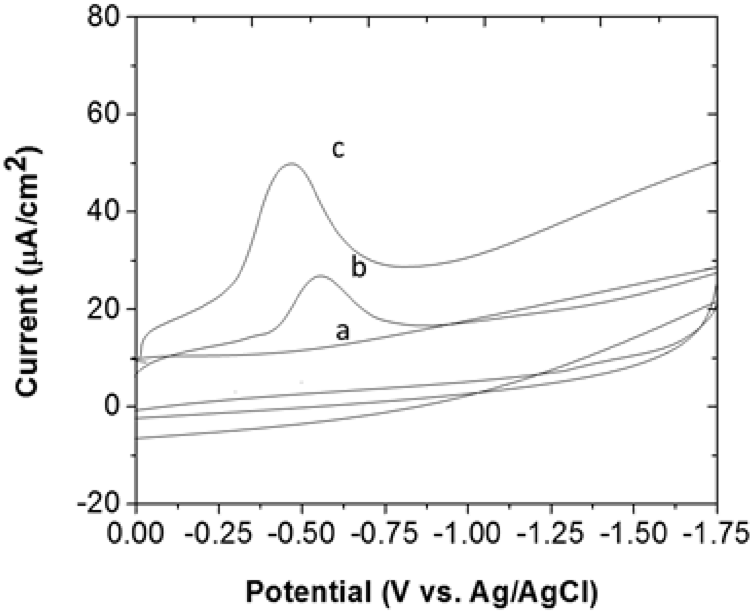


Figure 2. Typical cyclic voltammogram of dicapthon at (a) bare GCE; (b) SWCNTs/GCE; (c) SWCNTs/Nafion/GCE; pH 5.0 (BR buffer); concentration: 3.0 µg mL^{-1}; accumulation potential: -0.40 V; accumulation time: 50 *s*; scan rate: 40 mVs$^{-1;}$ pulse amplitude: 30 mV.

To isolate the reduction product, approximately 30 mg of the substance under investigation is dissolved in minimum amount of solvent acetone and the quantity of supporting electrolyte (pH 5.0) was added and placed in the cell. The applied potential was set at -0.485 V vs. SCE for dicapthon. During the electrolysis, nitrogen gas was kept bubbling through the solution. When the current was lower than 1 µA, the electrolysis was stopped and then 10 ml of water was added to the solution and extracted three times with 100 ml of ether. The ethereal extracts were dried over magnesium sulphate and evaporated. Electrolysis of the electroactive substance has been carried out at −0.485 V vs SCE and the product was formed after the controlled potential electrolysis had been identified and confirmed as the saturated product of the corresponding electroactive species by FTIR spectral data as an absence of -NO_2 stretch at 1550–1290 cm^{-1}.

The voltammetric response of 3.0 µgmL^{-1} dicapthon at bare GCE, SWCNTs/GCE, and Nafion/SWCNTs modified GCE was studied by differential pulse voltammetry (Figure 3). In a pH 5.0 BR buffer and after 50 s of open-circuit accumulation, weak reduction peak appeared on −0.485 V at the bare GCE (Figure 3a) and SWCNTs/GCE (Figure 3b). However, it significantly increased differential pulse peak at the SWCNTs/Nafion coated GCE (Figure 3c). The voltammetric peak current increase may have been caused by the fact that the SWCNTs/Nafion forms a perfect hybrid composite on the GCE surface, and thus enhance electron mobility. Compared to bare GCE and SWCNTs coated GCE working electrodes the SWCNTs/Nafion coated GCE electrochemical sensor shows the voltammetric reduction peak increase significantly due to the extraordinary properties of SWCNTs and Nafion such as restrained electronic properties, good aspect ratio and strong absorptive ability.

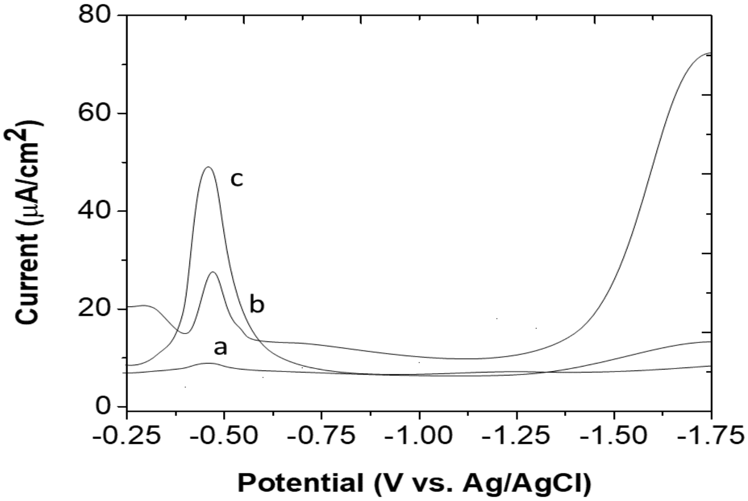


Figure 3. Typical differential pulse voltammogram of dicapthon at (a) bare GCE; (b) SWCNTs/GCE; (c) SWCNTs/Nafion/GCE; concentration: 3.0 μgmL^{-1}; pH of 5.0 (BR buffer); accumulation potential: -0.40 V; accumulation time: 50 s; scan rate: 40 mVs^{-1}; pulse amplitude: 30 mV.

Optimum parameters

The influence of pH was one of the most important parameters for the study of dicapthon peak potential (E_p) and current intensity (i_p) using differential pulse voltammetry. The electrochemical behavior of dicapthon was examined over the pH range 2.0-10.0. The maximum peak current of dicapthon was obtained at pH 5.0 BR buffer system (Figure 4). Once the pH has been increased from 2.0 to 5.0, the peak potentials have been shifted towards more negative values, indicating proton participation in the reduction process.

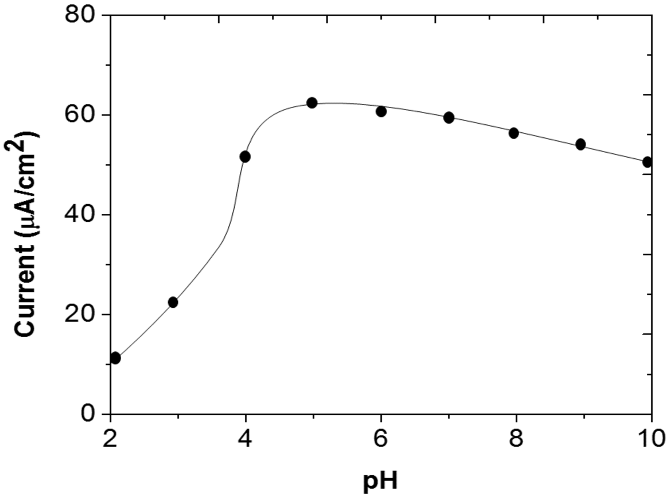


Figure 4. Effect of pH on dicapthon at SWCNTs/Nafion/GCE; concentration: 3.0 µgmL^{-1}; accumulation potential: -0.40 V; accumulation time: 50 *s*; scan rate: 40 mVs^{-1}; pulse amplitude: 30 mV.

The dependence of the differential pulse voltammetric peak current on the accumulation potential was examined over the potential range of -0.25 V to -1.75 V. It was found that the maximum response for dicapthon occurs with potentials equal to or more negative than -0.48 V (Figure 5). Therefore, -0.40 V was chosen as better accumulation potential for rest of the study. However, the dependence of the peak current on the accumulation time was studied at a concentration of 3.0 µgmL^{-1} for dicapthon. Sharp increasing peak currents were obtained up to 50 *s* for further analytical studies in an accumulation time of 50 *s* (Figure 6) which was chosen at SWCNTs/Nafion/GCE.

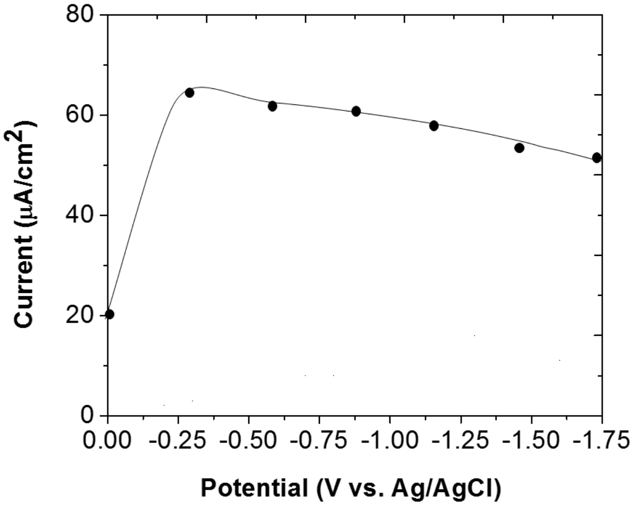
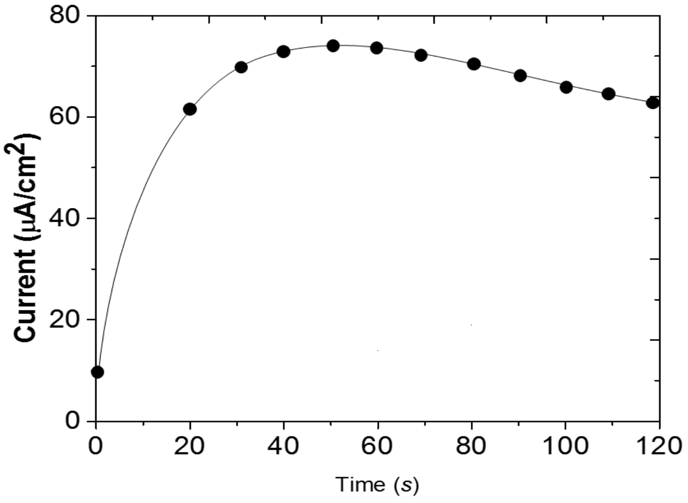


Figure 5. Effect of accumulation potential on the DPV response of dicapthon at SWCNTs/Nafion/GCE; pH 5.0 (BR buffer); concentration: 3.0 µgmL^{-1}; accumulation time: 50 *s*; scan rate: 40 mVs^{-1}; pulse amplitude: 30 mV.



Figore 6. Effect of accumulation time on the DPV response of dicapthon at SWCNTs/Nafion/GCE; pH=5.0 (BR buffer); concentration: 3.0 μgmL^{-1}; accumulation potential: -0.40 V; scan rate: 40 mVs^{-1}; pulse amplitude: 30 mV.

The influence of the pulse amplitude and scan rate was also studied. Thus, the results suggested that differential pulse voltammetric peak current reached the maximum value when the pulse amplitude was 40 mV. As for the scan rate; the current response with increasing the scan rate of 40 mVs^{-1} gave the maximum response. Accordingly, the optimum conditions for recording a maximum development and sharper differential pulse voltammetric peak for 3.0 μgmL^{-1} dicapthon are t_{acc}: 50 s, E_{acc}: -0.40 V, scan rate: 40 mVs^{-1} and pulse amplitude: 30 mV, optimum temperature: 25 °C.

The proposed method was free from interferences in dicapthon and also other constituents present in water and agricultural food samples. Several organic and inorganic species in the environmental samples can potentially contribute to the interference with the dicapthon sensor detection scheme. The selectivity of the sensor is determined by measuring the change in the sensor response in the presence of foreign compounds. The experimental results show that a 100-fold concentration of Pb^{2+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, ascorbic acid, and dopamine which has no interference can be observed at 3.0 μg L^{-1} dicapthon. Therefore, the proposed method does not involve the elaborate cleanup procedures with the other methods.

In order to show the validation of the proposed method, the analytical features of the method such as linear range of the calibration curve, LOD, LOQ, accuracy and precision were examined. Figure 7 shows the differential pulse voltammograms of dicapthon in the concentration range of 0.2–60.0 μgmL^{-1}. Under the optimum conditions, the calibration graph was constructed for the determination of dicapthon and the linear regression equation is Ip (10 μA)=0.8535x + 6.3999 (μg L^{-1}), which was obtained with a correlation coefficient of 0.9916 (Figure 8). The limit of detection (3

S_b/S, where S_b is the standard deviation of dicapthon (n=6) and S is the slope of the calibration curve) and limit of quantification were (10Sb/S) to be 0.036 μg L^{-1}, 0.054 μg L^{-1} respectively. The relative standard deviation (RSD) of 3.2% for dicapthon (*n*=6) implies good repeatability.

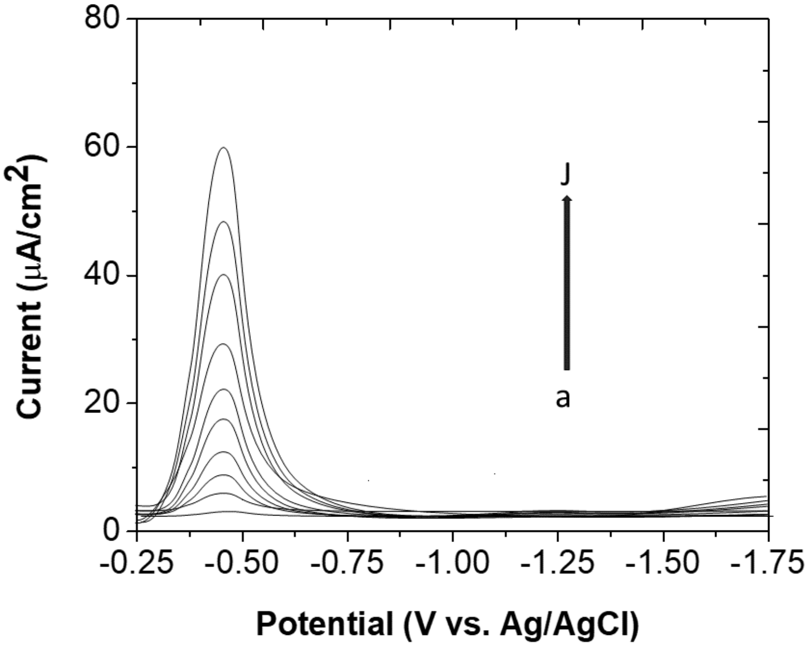


Figure 7. Differential pulse voltammogram of the SWCNTs/Nafion/GCE by (a) 0.4, (b) 5.0 (c) 7.0 (d) 10.0 (e) 15 (f) 20 (g) 30, (h) 40 (i) 50 (j) 60 μgmL⁻¹ dicapthon; accumulation time of 50 *s*, scan rate: 40 mVs⁻¹; pH: 5.0 (BR buffer); pulse amplitude: 30 mV.

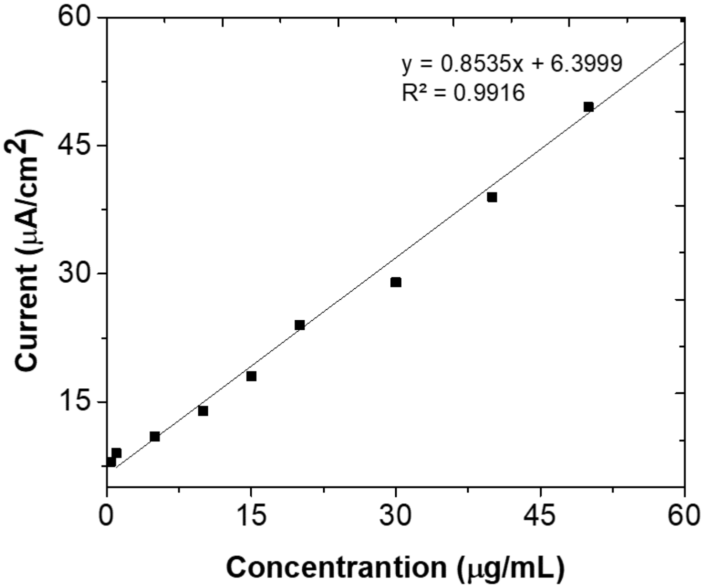


Figure 8. Linear plot of dicapthon at pH=5.0 (BR buffer); accumulation potential: -0.40 V; scan rate: 40 mVs⁻¹; pulse amplitude: 30 mV.

Applications

The water samples were evaluated by analyzing tap and well water samples collected around from Pakala village, Chittoor district, A. P., India. The collected water samples were stored in glass bottles during the season and kept under refrigeration (4 ^{o}C) for no longer than one to two weeks. These samples were filtered through a Whatman No.41 filter paper for removing the bulk molecules. Aliquots of water samples were taken in a 25 mL graduated tube; to its buffer solution which was added and analyzed as described in the voltammetric procedure. The recoveries of dicapthon in water samples ranged from 96.70 to 99.80% and the results are summarized in Table 1.

Table 1. The determination of dicapthon in water samples by differential pulse voltammetry; Conditions: pH of 5.0; accumulation potential: -0.40 V; accumulation time: 50 s; scan rate: 40 mVs^{-1}.

Sample	Amount added(μg mL^{-1})	Amount found(μg mL^{-1})	*Recover(%)	RSD (%)
Tap water	10.0	09.67	96.70	1.48
	20.0	19.75	98.75	0.78
	40.0	38.90	97.25	1.02
Well water	10.0	09.98	99.80	0.84
	20.0	19.90	99.50	0.98
	40.0	39.20	98.00	1.67

*Each value is the average of six determinations

Agricultural food samples were collected from the agricultural field and spiked with different amount of dicapthon pesticide. The samples were macerated with two 20 mL portions of ethanol-demineralized water (1+1), filtered through a Whatman filter paper No.41 and the filtrate was centrifuged at 2500 rpm for 20 min. In the filtrate, it was quantitatively transferred into a 50 mL calibrated flask and made up to the mark with 50% ethanol. Washings were collected in a 25 mL calibrated flask and aliquots were analyzed as recommended by the procedure. The obtained results for the determination of the dicapthon in vegetable samples are presented in Table 2. Recoveries of amitraz ranged from 98.00 to 99.50%, indicating the accuracy and reproducibility of the proposed differential pulse voltammetric method.

Table 2. The determination of dicapthon in agricultural food samples**;** Conditions: pH of 5.0; accumulation potential: -0.40 V; accumulation time: 50 s; scan rate: 40 mVs^{-1}.

Sample	Amount added(μg mL^{-1})	Amount found(μg mL^{-1})	*Recovery(%)	RSD(%)
Rice	10.0	09.80	98.00	1.24
	20.0	19.80	99.00	0.68
	40.0	39.70	99.25	1.08
Corn	10.0	09.90	99.00	1.22
	20.0	19.70	98.50	1.15
	40.0	38.60	99.50	0.42

*each value is the average of six determinations

Conclusion

The electrochemical study of dicapthon was successfully examined by cyclic and differential pulse voltammetry using SWCNTs/Nafion/GCE. In the analytical application, differential pulse voltammetry showed to be a very rapid and sensitive technique that allowed reaching detection limits in the range of trace analysis of dicapthon tap, well and agricultural food samples applied to the agricultural sample formulations. The acquired results clearly show that the significance of SWCNTs based on the prepared modified SWCNT/Nafion can be used for the trace dicapthon determination in various samples.

Conflict of Interest

The all authors declare that there is no conflict of interests about the publication.

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