ORIGINAL RESEARCH PAPER

Pd@MWCNTs/GCE based voltammetric sensor for butachlor herbicide detection in soil samples

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ABSTRACT

Butachlor is a herbicide that belongs to the acetanilide family. It is widely used as a granule-based post-emergence herbicide on rice in India. As a result of the ongoing usage of these synthetic substances, soil fertility and soil organisms are declining. Differential pulse voltammetry was used to determine butachlor herbicide in soil samples with a modified glassy carbon electrode voltammetric sensor with palladium-supported multiwalled carbon nanotubes (Pd@MWCNTs). Scanning electron microscopy, energy dispersive x-ray spectroscopy, and X-ray diffraction spectroscopy were used to investigate the morphology of Pd@MWCNTs, while cyclic and differential pulse techniques were used to investigate the voltammetric properties. The butachlor herbicide under voltammetric investigation involves irreversible, two-electron reduction based on the protonation of the carbonyl group ($>C=O$). The voltammetric method was developed for the determination of butachlor in phosphate buffer solution at pH 6.0 as a supporting electrolyte. A good linear response to butachlor in the concentration ranging from 0.10 µg·mL^{-1} to 32.0 µg·mL^{-1} was observed, and a limit of detection of 0.044 µg·mL^{-1} was obtained with the calculation based on signal/noise=3. The suggested method was efficaciously applied for the detection of butachlor in soil samples.

Keywords: *Butachlor, Palladium, Voltammetry, Reduction, Soil*

INTRODUCTION

Butachlor (*N*-(butoxy ethyl)-2-chloro-2',6'-diethyl)acetanilide (Fig. 1)) is a chloroacetanilide class of chemistry and is the herbicidal active ingredient in Machete®[1]. Butachlor was used as the pre-emergence herbicide to control undesirable grasses and broadleaf weeds in transplanted, direct-seeded rice, barley, and green vegetable fields [2]. It has anthropoid toxicity following acute oral, dermal, and inhalation exposure [3, 4]. Thus, butachlor has the potential to cause allergic skin reactions following repeated or prolonged exposure. Subchronic and chronic exposure primarily produces liver and kidney toxicity for which large safety margins exist [5, 6]. Many monitoring methods have been reported for the quantitative analysis of various pesticides such as capillary electrophoresis [7-9], spectrophotometry [10], high-performance liquid chromatography (HPLC) [11, 12], liquid chromatography-mass spectrometry (LC-MS) [13,14], ultra-performance liquid chromatography coupled to tandem mass spectrometry [15] and voltammetry [4, 16].

Most of the above methods are time-demanding

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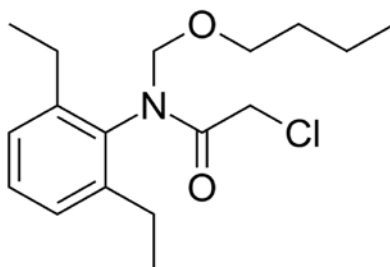   *prprasadchem@gmail.com*

Fig. 1. Chemical structure of butachlor

procedures, expensive, and required more toxic solvents with multiple sample preparation and measurement steps. Electrochemical analysis of pesticides offers simple, rapid, and cost-effective methods with few sample pre-treatment steps. Hence, there are a wide variety of modified electrodes developed for the determination of pesticides viz. Nafion double-layer membrane modified electrode, Au-MWCNTs, polyaniline modified GCE, nano TiO_2 polymer film modified GCE CNTs-encapsulated polypyrrole and polyaniline copolymer modified GCE and nano TiO_2/Nafion composite, etc., [17-24]. Hence, to improve the analytical figures of merit, there exists a need for highly sensitive sensors for early detection and accurate determination of butachlor herbicide in soil matrices. Nevertheless, to the best of our knowledge, there are no electro analytical reports concerning the determination of butachlor herbicide using Pd@MWCNTs modified glassy carbon electrode.

Here, the reliable electrochemical nanosensor based on palladium (Pd) supported multiwalled carbon nanotubes (MWCNTs) is used for the determination of butachlor herbicide in soil samples by differential pulse voltammetry. The electrochemical characteristics of Pd@MWCNTs nanocomposites were systematically examined by cyclic and differential pulse voltammetry. The electrochemical study was based on the fact that palladium-supported MWCNTs can improve the advances in electrochemical properties and lead to enhancements of their electro-catalytic performance.

MATERIALS AND METHODS

Apparatus

Electrochemical studies were carried out by Autolab PG STAT 101 supplied by Metrohm Autolab B. V. Netherlands. A three-electr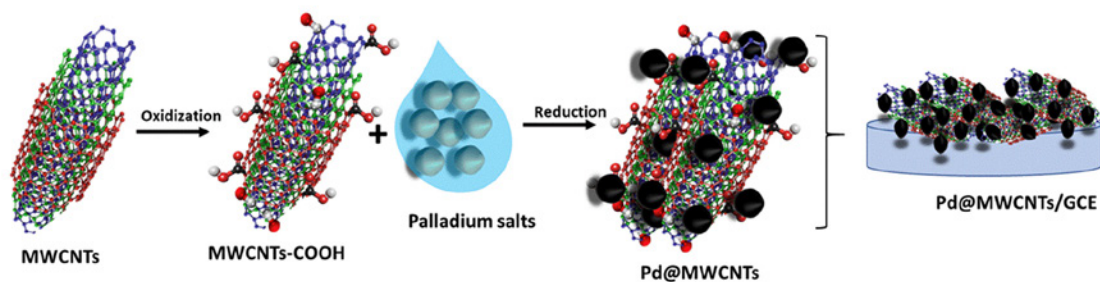ode system comprising a glassy carbon electrode (GCE) modified with Pd@MWCNTs nanocomposites served as the working electrode. Saturated Ag/AgCl/KCl was used as a reference electrode and Pt wire as a counter electrode. The morphology of the electrode surface was carried out using a scanning electron microscope (SEM) of the Ultra 55 Carl Zeiss instrument with an operating voltage of 10 kV. X-ray diffraction (XRD) using CuKα with λ = 1.54 Å, and a lineon X'pert PRO X-ray diffractometer. The pH meter model ELICO LI-120 supplied by ELICO Ltd. Hyderabad, India., was used to determine the pH of the buffer solution.

Materials and reagents

H_2PdCl_4, NaH_2PO_4, $NaBH_4$, and $NaHPO_4$ were attained from Merck Chemicals Ltd. Multiwalled carbon nanotubes (MWCNTs) (with diameters of 6-9 nm×5μm, ≥95% carbon basis) purchased from Sigma Aldrich. Butachlor was procured from Siddarth Inc. in Hyderabad, India. A stock solution of 1000 mg/L butachlor was prepared by dissolving 100 mg butachlor in 100 mL acetone. Phosphate buffer solutions at different pH values (pH 2.0-12.0) were prepared by mixing standard solutions of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 and adjusting the pH with 0.1 M NaOH. Ultrapure water (18.2 MΩ.cm) was used in all experiments. All other chemicals and solvents were of analytical reagent grade.

Preparation of Pd@MWCNTs and Pd@MWCNTs/ GCE

Production of Pd@MWCNTs electrochemical sensor, initially the MWCNTs were oxidized by adding a 40 mL acidic mixture of H_2SO_4/HNO_3 (3:1 ratio) and ultra-sonicated for 5 hours. The oxidized MWCNTs were then vacuum filtered, washed with ultra-pure water several times to remove the acidic contents, and dried overnight in an oven at 60 °C. Then, 5 mg of the dried oxidized MWCNTs were dispersed in 2 mL of ultra-pure water to form

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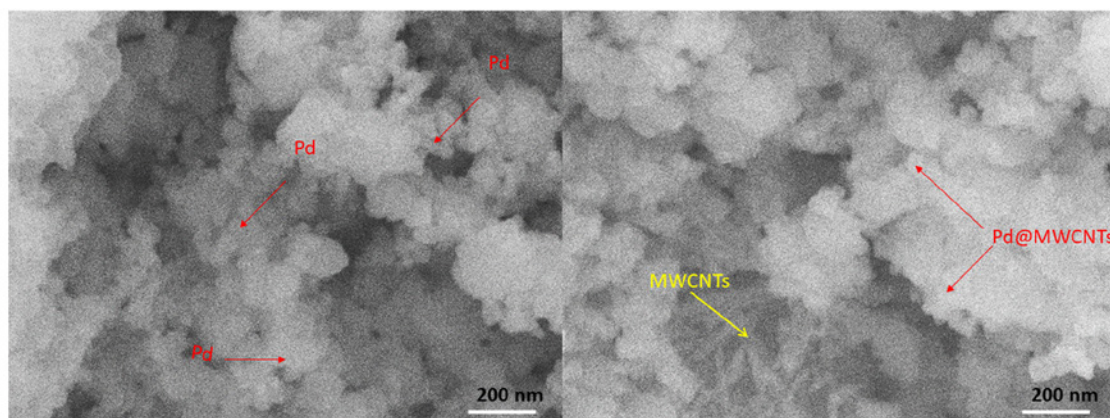Scheme 1. Schematic representation of the preparation of Pd@MWCNTs/GCE

Fig. 2. SEM images with two different magnifications of Pd (left) and Pd supported MWCNTs (right).

a suspension solution. The 10 mg of 0.02 mM of H_2PdCl_4 was added to 2 mL ultra-pure water and then mixed in an oxidized MWCNTs suspension solution. Afterward, after 1 hour of ultrasonication, 50 mL of 20 mM $NaBH_4$ was added dropwise to the reaction mixture and agitated at room temperature until the suspension was black. The resultant suspension was centrifuged and washed with ultrapure water and ethanol, followed by vacuum oven drying at 90 °C. Afterward annealed at 200 °C to strengthen the attachment of palladium on the surface of MWCNTs.

Before the electrodeposition process, the GCE was first cleaned with 0.3 μm alumina powder using a BAS polishing kit followed by an ultrasonic bath in ethanol for 10 minutes. Then, 10 mg of Pd@MWCNTs in acetone was dropped on the surface of the cleaned GCE. The GCE was then dried under the lamp for 30 minutes and rinsed in ultra-pure water several times. The resulting modified electrode denoted as Pd@MWCNTs composite film modified GCE was then rinsed with double distilled water and used for the electrochemical analysis. A similar procedure was repeated to modify the GCE with the Pd and MWCNTs. The preparation of Pd@MWCNTs/GCE is depicted schematically in Scheme 1.

RESULTS AND DISCUSSION

The surface morphology of Pd@MWCNTs nanocomposites was examined by scanning electron microscopy (Fig. 2A & B). Typical morphology of MWCNTs noticed in all two images are consistent for all examined samples showing that the agglomerated MWCNTs bundles. It was found to have an irregular shape and size, which indicates that the surface area is very large from SEM analysis (Fig. 2). However, the exact length is difficult to be measured because the bundle is always in the meandering form. The diameter of a meandering form of multiwalled carbon nanotubes is in the range of 9 nm while the length can reach more than several micrometers. The palladium nanoparticles are observed around spherical shapes or clusters on the surface of MWCNTs with a diameter of up to 12 nm. The energy dispersive X-ray (EDX) spectroscopy (Fig. 3) indicates the atomic and mass % of elements present in the Pd@
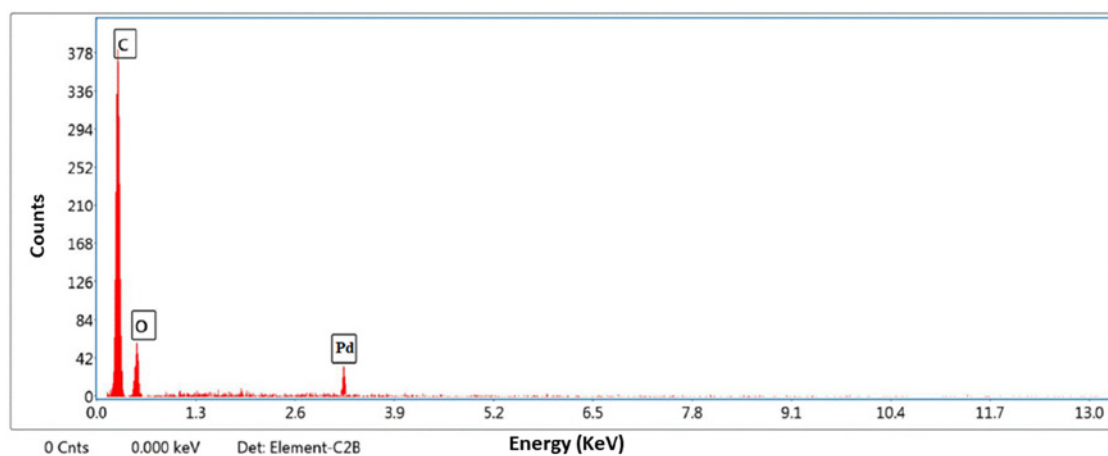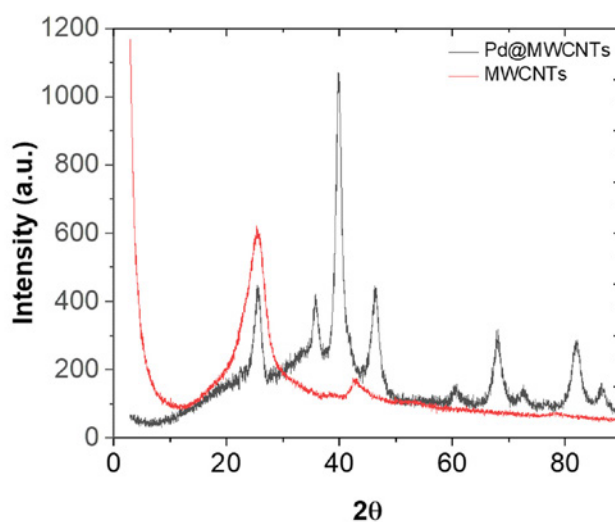
Fig. 3. EDX spectrum of Pd supported MWCNTs

Fig. 4. XRD spectrum of MWCNTs and Pd supported MWCNTs.

MWCNTs. The atomic percentage of C, O, and Pd was felt to be 52.66, 28.45, and 18.89 precisely. The mass percentage of C, O, and Pd was found to be 50.86, 34.90, and 14.24 respectively. From the spectrum, the peaks reveal that the presence of C, O, and Pd is 0.5, 0.8, and 2.9 KeV specifically.

As shown in Fig. 4, XRD pattern analysis was used to investigate the structural analysis of MWCNTs and Pd@MWCNTs. The pattern of the MWCNTs shows a high intense peak at $2\theta = 24.6°$ and a low intense peak at $2\theta = 43.9°$, corresponding to the (002) and (100) lattice space [26]. The three diffraction peaks in the Pd@MWCNTs composite, which correspond to the (111), (200), and (220) lattice plane diffraction of Pd, are centered at $2\theta = 40.15, 46.72$, and $68.24°$. These peaks match those found in the JCPDS No: 89-4897 [27], which were reported Pd nanocomposites. The pattern revealed that the particles have a face-centered cubic crystal structure with a cell dimension of 3.889 and a wavelength of 1.54 A°. Furthermore, no discernible peaks owing to $PdCl_2$ can be found in the XRD pattern, indicating that Pd (II) has been reduced to Pd (0). From the primary diffraction peak, the predicted average crystalline size of Pd NPs in MWCNTs is around 12 nm (111).

The preliminary studies on the electrochemical behavior of the Pd@MWCNTs-modified electrode
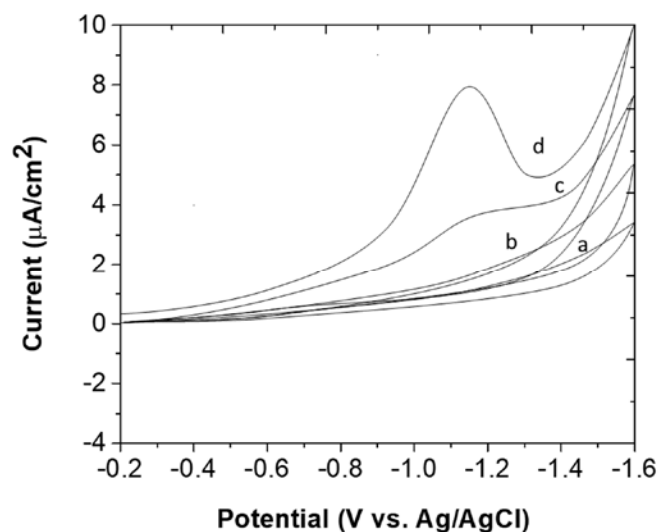
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Fig. 5. Cyclic voltammograms for butachlor (6.0 μg·mL⁻¹) at bare GCE (a), MWCNTs/GCE (b), Pd/GCE (c) and Pd@MWCNTs/GCE (d) in pH 6.0 (0.10 M of phosphate buffer); accumulation potential –1.13 V; accumulation time 80 s; pulse amplitude 30 mV; scan rate 50 mVs⁻¹.

were performed by cyclic voltammetry and differential pulse voltammetry in 0.10 M phosphate buffer solution (pH 6.0) at a scan rate of 50 mVs⁻¹. The differential pulse voltammogram measurements were performed to optimize the experimental conditions and determine the butachlor at room temperature in the potential range from −0.20 V to −1.60 V. The analyte solutions were thoroughly deoxygenated by bubbling high-purity nitrogen before each voltammetric analysis.

The cyclic voltammograms (CV) of butachlor in 0.10 M phosphate buffer at pH 6.0 in concentration 6.0 μg·mL⁻¹ and scan rate 50 mVs⁻¹. The reduction peak appears at -1.13 V, which may be due to the reduction of the carbonyl group (>C=O) of the butachlor and no oxidation peak is observed in the anodic area which suggests that the process is irreversible. Fig.5 shows comparative CVs of the bare GCE (Fig. 5a), MWCNTs/GCE (Fig. 5b), Pd/GCE (Fig. 5c), and Pd@MWCNTs/GCE (Fig. 5d). As can be seen from Fig.5a there is no prominent peak for the reduction of butachlor at bare GCE. While the MWCNTs/GCE and Pd/GCE displayed a slight reduction in peak current, it was assessed to be inadequate for the reduction of butachlor. Based on the above results, the palladium-supported MWCNTs were successfully immobilized on the GCE surface and shows synergistic electro-active nature with a strong reduction peak at -1.13 V based on the preceding results. Additionally, the

electrochemical sensor provides high electro-catalytic activity because of its large surface area and efficient electron transfer. As the scan rate is increased, the peak current also increased and no peak appeared in the reverse sweep, indicating the irreversible nature of the reaction process. The influence of diverse scan rate (ν) on the irreversible reduction peak current of butachlor at the Pd@MWCNTs/GCE was also studied by cyclic voltammetry. The irreversible reduction peak current increases upon the increase of scan rate. One can see that good linearity between the I_{pc} of the irreversible reduction peak and ν was obtained within the range of 50-250 mV s⁻¹, with linear regression equation $I_{pc}(\mu A)=-7.24-0.0204v^{1/2}$ (mVs⁻¹), R=0.998 [25]. This indicates that electrochemical kinetics is controlled by the adsorption of butachlor molecules.

The differential pulse voltammetric response of 6.0 μg·mL⁻¹ butachlor was studied at Pd@MWCNTs with 0.10 M phosphate buffer at pH 6.0 as a supporting electrolyte at the pulse amplitude of 30 mV and a scan rate of 50 mVs⁻¹ (Fig. 6). The bare GCE (Fig. 6 curve 'a') and MWCNTs/GCE (Fig. 6 curve 'b') whereas no obvious reduction peak was attained for 6.0 μg·mL⁻¹ butachlor in 0.10 M phosphate buffer at pH 6.0. At fabricated Pd/GCE (Fig. 6 curve"c') the minor reduction peak current was observed at significantly higher than the bare GCE and MWCNTs/GCE reduction current

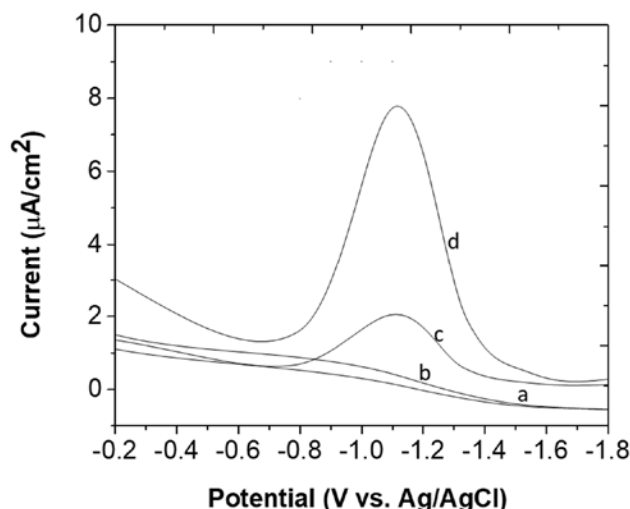*J. Water Environ. Nanotechnol., 7(2): 121-131 Spring 2022*

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Fig. 6. Differential pulse voltammograms for 6.0 μg·mL⁻¹ butachlor at bare GCE (a), MWCNTs/GCE (b), Pd/GCE (c) and Pd@MWCNTs/GCE (d) in pH 6.0 (0.10 M of phosphate buffer); accumulation potential –1.13 V; accumulation time 80 s; pulse amplitude 30 mV; scan rate 50 mV s⁻¹.
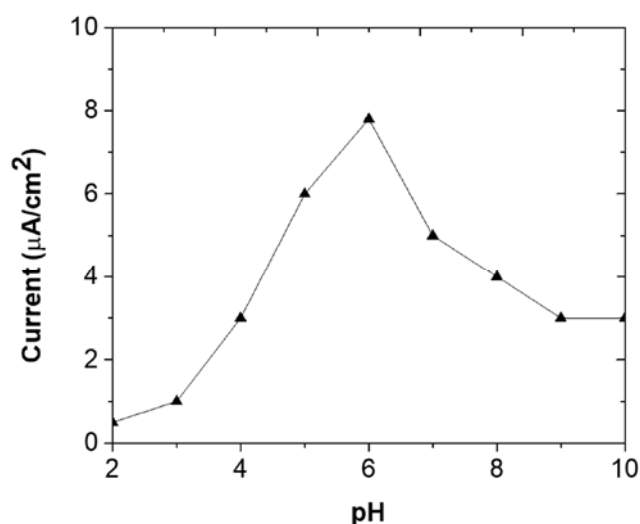

Fig. 7. Effect of pH on the electrochemical response of the Pd@MWCNTs/GCE. The concentration of butachlor is 6.0 μg·mL⁻¹; accumulation potential –1.13 V; accumulation time 80 s; pulse amplitude 30 mV; scan rate 50 mV s⁻¹.

respectively. The enrichment of the reduction peak current of the Pd@MWCNTs modified GCE was acquired owing to the expectant area and great electrical conductibility of the butachlor (Fig. 6 curve'd'). Therefore, the differential pulse voltammograms were observed for bare GCE, MWCNTs/GCE, and Pd@MWCNTs, and it was found to be not so effective for the reduction of the peak current of butachlor.

Optimum parameters on the response of butachlor
The effect of the pH of 0.1 M phosphate buffer

on the electrochemical behavior of butachlor at the modified electrode was studied using cyclic voltammetry over the pH range 2.0-12.0. Fig. 7, shows the cyclic voltammograms of 6.0 μg·mL⁻¹ butachlor in phosphate buffer at various pH values. The peak current increased with pH until it reached its maximum value at pH 6.0. then the peak current response decreased at pH values above 6.0. This is presumably due to the electrostatic attraction between the Pd@MWCNTs/GCE and the carbonyl group of butachlor pesticides. By observing that the I_{pc} and E_{pc} of butachlor were radically dependent
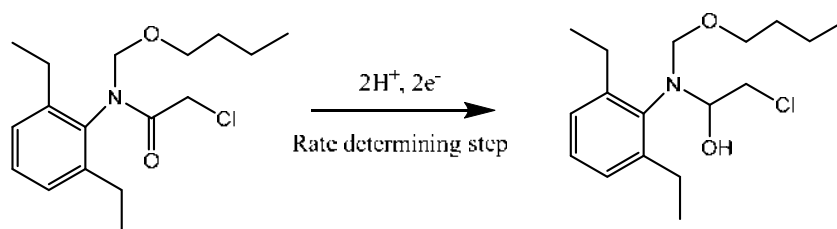
Fig.8. Schematic representation of possible electrochemical reduction mechanism of butachlor on Pd@MWCNTs/GCE
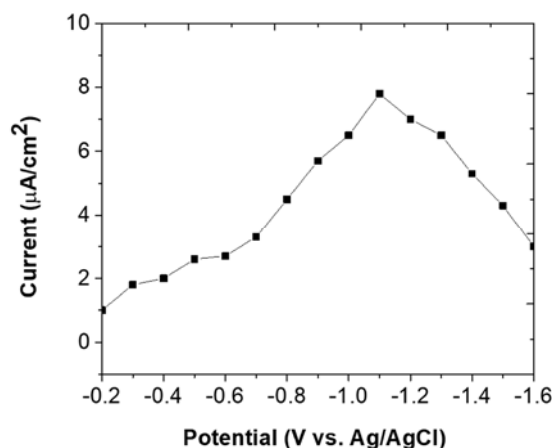

Fig. 9. Effect of accumulation potential on the electrochemical response of butachlor at Pd@MWCNTs; accumulation time 80 s; pulse amplitude 30 mV; scan rate 50 mV s^{-1}.

on pH, it can be concluded that protons are participating in the electro-reduction process of butachlor on the modified Pd@MWCNTs/GCE. The process responsible for this behavior must be the reduction of the carbonyl group in the butachlor and the maximum peak was observed at pH 6.0 on Pd@MWCNTs/GCE. Moreover, at 25 °C (equivalent to a Nernst system), the slope of E_{pc} vs. pH of butachlor was also 12 mV/pH, suggesting that the reduction process involves the same number of electrons and protons, i.e for two electrons and two protons. According to the cyclic study, the mechanism of the electrochemical reaction of butachlor is shown in Fig. 8.

The optimum parameter of the scan rate influence was investigated. The results suggested that the differential pulse voltammetric peak current reached maximum value when the scan rate was 50 mVs^{-1}. As for the scan rate the current response with increasing the scan rate from 10 mVs^{-1} to 150 mVs^{-1}, gives the maximum response at 50 mVs^{-1}. The optimal value of −1.13 V was chosen for accumulation potential which coincides with the reduction potential for butachlor at selected

conditions (Fig. 9). This interesting observation indicates that products of the electrochemical reduction of butachlor herbicide in a certain way influence maximum peak current by differential pulse voltammetry. Hence, enhanced absorption and the accumulation of butachlor on the Pd@MWCNTs/GCE after its pre-treatment at −1.13 V can be exploited here to significantly increase the sensitivity of the differential pulse voltammetry. Fig. 10 shows that the signal has a prolongation of the accumulation time (t_{acc}) up to 80 s. The peak current increased rapidly with the increase of accumulation time and almost reached a platform after 80 s. For analytical purposes, Pd@MWCNTs/GCE was initially pre-treated for 80 s into the solution of 6.0 μg·mL^{-1} of butachlor 0.10 M phosphate buffer solution before it was used for measuring the concentration of butachlor to achieve down to the low ppm-level. The additional preconcentration time of 80 s was employed before each measurement. Selected pre-treatment time is enough to obtain a stable analytical signal due to saturation of electrode surface. Therefore, the 80s was selected as the optimum accumulation
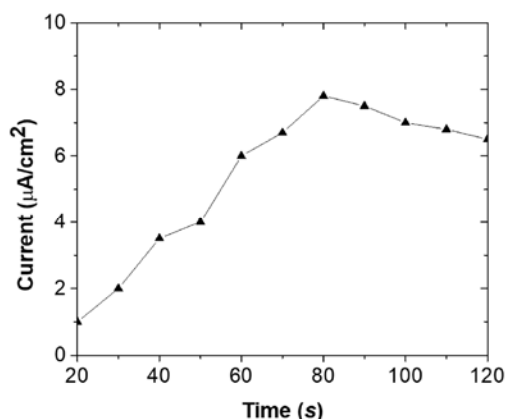
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Fig. 10. Effect of accumulation time on the electrochemical response of butachlor at Pd@MWCNTs; accumulation potential –1.13 V; pulse amplitude 30 mV; scan rate 50 mVs^{-1}.
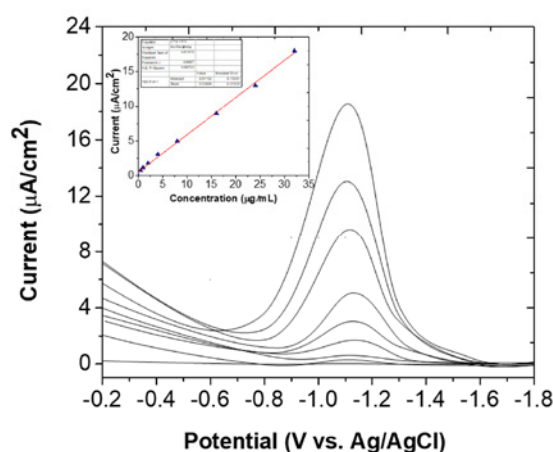

Fig.11. Differential pulse voltammograms recorded at Pd@MWCNTs/GCE for different concentrations of butachlor [0, 0.1, 1.0, 2.0, 4.0, 8.0, 16.0, 24.0 and 32.0 µg·mL^{-1} (from bottom to top)] in 0.10 M phosphate buffer solution (pH 6.0); accumulation potential –1.13 V; accumulation time 80 s; pulse amplitude 30 mV; scan rate 50 mV s^{-1}; Calibration curve of butachlor (insert).

time for the determination of butachlor on the electrochemical sensor. In addition, it should be emphasized that palladium nanoparticles are electrocatalysts which in synergism with a developed surface area of MWCNTs enables the successful application of this electrode for butachlor determination. Accordingly, the optimum conditions for recording a maximum developed and sharper peak for butachlor are accumulation time 80 s, accumulation potential -1.13 V, scan rate 50 mVs^{-1}, pulse amplitude 30 mV, and optimum temperature 25 ºC.

The influence of interference ions like Na$^+$, Ca^{2+}, K$^+$, Cl$^-$, Ag$^+$, HCO$_3^-$, NO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$ and some of the biomolecules (urea, ascorbic acid, linuron, and imidacloprid) on the determination of butachlor was also investigated. Initially,

differential pulse voltammograms signal of butachlor (6.0 µg·mL^{-1}) was recorded using the Pd@MWCNTs/GCE, then either the selected ion was added in a concentration that is 40 times higher than butachlor or selected biomolecules was added in the same final concentration as butachlor. The solutions were analyzed by the proposed method and all investigated ions or biomolecules neither influenced peak potential nor peak current intensity of butachlor expressively at optimized conditions.

Electrochemical characterization

The differential pulse voltammogram was recorded under the optimum experimental conditions at Pd@MWCNTs/GCE. Fig. 11 shows the typical differential pulse voltammogram

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Table 1. Application of the recommended method to the determination of butachlor in soil samples

Sample	Amount added ($\mu g \cdot mL^{-1}$)	Amount found ($\mu g \cdot mL^{-1}$)	Recovery* (%)	Standard Deviation
	5.0	4.85	97.0	0.012
Black soil	10.0	9.90	99.0	0.008
	25.0	24.9	99.6	0.014
	5.0	4.90	98.0	0.030
Red soil	10.0	9.92	99.2	0.050
	25.0	24.7	98.8	0.075

*n=5 (no. of determinations)

Table 2. Comparison between the proposed Pd@MWCNTs sensor with some published sensors for detection of other pesticides.

Electrode	pH	Pesticide	Linear range ($\mu g \cdot mL^{-1}$)	Limit of detection ($\mu g \cdot mL^{-1}$)	Ref.
rGO-Cu/CuO-Ag/GCE	3.0	Carbaryl	0.01-4.02	0.001	28
		Fenamiphos	0.02-6.03	0.001	
Graphene oxide/GCE	7.0	Thiamethoxam	10-200	2.42	29
	8.0	Imidacloprid		2.02	
Au/CNTs/GC	5.0	Parathion	0.001-7.0	0.0005	30
Au/MWCNTs	6.3	Methyl parathion	0.5-16.0	0.050	31
	6.62	Methiocarb	0.1-55	0.15	32
Pd/MWCNTs/GCE	6.0	Butachlor	0.10-32.0	0.044	Present work

rGO: reduced graphene oxide; CNTs: carbon nanotubes

recorded in various concentration ranges from 0.10 $\mu g \cdot mL^{-1}$ to 32 $\mu g \cdot mL^{-1}$ (0.0, 0.1, 1.0, 2.0, 4.0, 8.0, 16.0, 24.0 and 32.0 $\mu g \cdot mL^{-1}$) at 50 mV s^{-1}. Fig.11 (insert) shows the calibration curve of the sensor for the determination of butachlor. Under the optimized conditions, the sensor exhibits a linear relationship between the peak current and the concentration of butachlor in the range of 0.10 $\mu g \cdot mL^{-1}$ to 32 $\mu g \cdot mL^{-1}$. The linear regression equation was determined to be $I_{pc}(\mu A)$ = 0.54162+0.536 C $\mu g \cdot mL^{-1}$ with a correlation coefficient of 0.997, the limit of detection (LOD = 3(sd)/b) and limit of quantitation (LOQ = 10(sd)/b) were calculated, where sd is the standard deviation of the intercept and b is the slope of the calibration graph [14]. LOD and LOQ were found to be 0.044 $\mu g \cdot mL^{-1}$ and 0.835 $\mu g \cdot mL^{-1}$ of butachlor on Pd@MWCNTs/GCE.

Applications of the electrochemical sensor

Differential pulse voltammetry was applied to the determination of butachlor herbicide in soil samples at room temperature (~25 °C). The agricultural soil analysis of black and red soil samples was collected from around the agricultural field of Tirupati., A.P., India. The soil was collected at 10-15 cm deep, sieved, and stored in an airtight plastic container at room temperature. Then, the stored soil samples were centrifuged and filtered using 0.2 μm filter paper to free them from other impurities. Additionally, spiked with three different concentrations of butachlor herbicide into the filtered soil samples and it was analyzed by differential pulse voltammetry. The soil samples showed peak currents for different concentrations of spiked butachlor at the potential of -1.13 V. From the calibration graph, we found the results as tabulated in Table 1. To check the precision of the method, five replicates analyzed of each sample were carried out. The average recoveries obtained in soil samples were 97.0- 99.6% with a relative standard deviation of 1.89% respectively. The electrochemical performances viz., high sensitivity, detection limit, and dynamic range of the Pd@MWCNTs/GCE are compared with the other pesticides-based sensors. As per the results, the developed electrochemical sensor exhibits good detection limit and dynamic range than previous sensors, which illustrates the Pd@MWCNTs modified GCE could be enhancing the electronic and catalytic properties of butachlor herbicide (Table 2.).

The repeatability of Pd@MWCNTs/GCE was tested by taking five successive signals with a standard solution of 6.0 $\mu g \cdot mL^{-1}$ of butachlor on

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the same day under ideal conditions. The Pd@MWCNTs/GCE sensor succeeds on average peak current has retained the initial peak response of 98.5 %. Such findings supported the strong repeatability, great shelf life, and accuracy of the advanced Pd@MWCNTs/GCE sensor. Reproducibility relates to the difference in measurements produced under different conditions on a subject. The sensor reproducibility was investigated within the day at ambient temperatures, minimal deviations with an analogous standard deviation value (RSD) of 1.8 % were identified in the voltammetric signals. In addition, the electrode reproducibility was constantly analyzed for 3 days, and also the RSD level was determined found to be ~1.2%. This result reveals the modification of glassy carbon electrode with Pd@MWCNTs nanoparticles sustain the good qualities of greater stability as well as reproducibility as the notable voltammetric applications.

CONCLUSIONS

An electrochemical sensor of Pd@MWCNTs can be successfully prepared and fabricated on a glassy carbon electrode for differential pulse voltammetry. The proposed sensor has shown to be a fairly efficient method for rapid and sensitive determination of butachlor herbicide in soil samples. The obtained Pd@MWCNTs sensor possesses a favorable morphology with a fast electron-transport MWCNTs network decorated by palladium nanoparticles enabling advantageous electrocatalytic behavior for reduction of butachlor with attained relatively low limits of detection and quantitation. The sensing characteristics of Pd@MWCNTs/GCE toward butachlor were found to be superior to the MWCNTs/GCE and bare GCE and as well as very convenient and sensitive, indicating that the Pd@MWCNTs modified glassy carbon electrode is promising for the detection of butachlor in soil samples.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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