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Voltammetric Determination of Pendimethalin with Nafion-Graphene Modified Glassy Carbon Electrode

Nafyon-Grafenle Modifiye Edilmiş Camsı Karbon Elektrot ile Pendimethalinin Voltametrik Tayini

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Abstract

In this study, the voltammetric behavior of pendimethalin was investigated at a glassy carbon electrode (GCE) and a nafion-graphene modified glassy carbon electrode (n-GR/GCE). The electrochemical characterization of pendimethalin was carried out using cyclic voltammetry (CV) technique. For the determination studies performed with GCE, the differential pulse voltammetry (DPV) technique was employed, while the differential pulse adsorptive stripping voltammetry (DPAdSV) method was used for the determination studies with n-GR/GCE. First of all, optimal experimental conditions were established for both electrodes, a calibration curve was plotted and linear working ranges were identified. For the 1st peak current of pendimethalin, the working range of the calibration curve drawn by DPV technique with GCE was 1.56×10^{-6}-1.08×10^{-3} M with the limit of detection (LOD) value calculated as 3.09×10^{-5} M. For the 2nd peak current of pendimethalin, the working range of the calibration curve created by DPV technique with GCE was 1.56×10^{-6}-9.73×10^{-4} M and the LOD value was found to be 3.36×10^{-6} M. For the 1st peak current of pendimethalin, the working range of the calibration curve constructed by DPAdSV technique with n-GR/GCE was determined to be 1.76×10^{-6}-4.01×10^{-4} M with the LOD value being 8.69×10^{-6} M. For the 2nd peak current of pendimethalin, the working range of the calibration curve obtained by DPAdSV technique with n-GR/GCE was 1.96×10^{-9}-7.53×10^{-4} M with the LOD value calculated as 1.05×10^{-9} M.

Keywords: Graphene, Modified electrode, Pendimethalin, Pesticide, Voltammetry

Öz

Bu çalışmada, pendimethalinin voltametrik davranışı camsı karbon elektrot (GCE) ve nafyon-grafenle ile modifiye edilmiş camsı karbon elektrot (n-GR/GCE) ile incelenmiştir. Pendimethalinin elektrokimyasal karakterizasyonu dönüşümlü voltametri (CV) yöntemi ile belirlenerek, GCE ile yapılan tayin çalışmalarında diferansiyel puls voltametrisi (DPV), n-GR/GCE ile yapılan tayin çalışmalarında diferansiyel puls adsorptive sıyırma voltametrisi (DPAdSV) yöntemi kullanılmıştır. Öncelikle her iki elektrot için optimum deney şartları belirlenerek, kalibrasyon grafiği oluşturulmuş ve doğrusal çalışma aralığı belirlenmiştir. Pendimethalinin 1.pik akımı için GCE'la DPV yöntemiyle oluşturulan kalibrasyon grafiğinin çalışma aralığı $1,56\times10^{-6}$-$1,08\times10^{-3}$M ve gözlenebilme sınırı (LOD) değeri $3,09\times10^{-5}$ M olarak bulunmuştur. Pendimethalinin 2.pik akımı için GCE'la DPV yöntemiyle oluşturulan kalibrasyon grafiğinin çalışma aralığı $1,56\times10^{-6}$-$9,73\times10^{-4}$M ve LOD değeri $3,36\times10^{-6}$ M olarak bulunmuştur. Pendimethalinin 1.pik akımı için n-GR/GCE'la DPAdSV yöntemiyle oluşturulan kalibrasyon grafiğinin çalışma aralığı $1,76\times10^{-6}$-$4,01\times10^{-4}$M ve gözlenebilme sınırı (LOD) değeri $8,69\times10^{-6}$M olarak bulunmuştur. Pendimethalinin 2.pik akımı için n-GR/CKE'la DPAdSV yöntemiyle oluşturulan kalibrasyon grafiğinin çalışma aralığı $1,96\times10^{-9}$-$7,53\times10^{-4}$ M ve LOD değeri $1,05\times10^{-9}$ olarak bulunmuştur.

Anahtar Kelimeler: Grafen, Modifiye elektrot, Pendimethalin, Pestisit, Voltametri

1. Introduction

Pendimethalin (Figure 1) is an herbicide in the dinitroaniline family used to control grassy and broadleaf weeds in crops such as corn, rice, potatoes, cotton, tobacco, black pepper, soybeans, wheat, tomatoes, peanuts, sunflowers, and onions (Zimdahl et al. 1984, Gerent et al. 2015, Saha et al.2015, Galli et al. 2018,).

Pendimethalin is resistant to microbial degradation, has a half-life of 90 days, and is strongly absorbed in the soil (Ni et al. 2011). The excess of pendimethalin used in the

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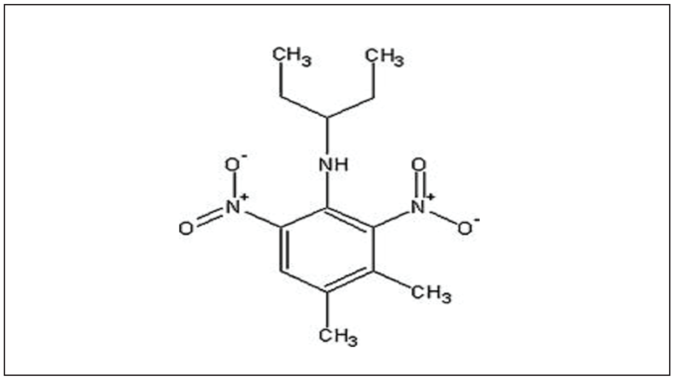


Figure 1. Chemical structure of pendimethalin (Gerent et al. 2015).

agricultural sector causes various environmental problems such as soil, water and air pollution (Gerent et al. 2015).

Recent studies have shown that pendimethalin leads to a series of physiological changes and endocrine effects such as liver, kidney damage and mutagenic effect, thus causing increased environmental and toxicological concerns (Shah et al. 2011). For this reason, it is of great importance to develop fast, low-cost, simple and large-scale methods for the determination of pendimethalin.

The literature review shows that several methods that required specialized technicians, expensive devices, and time-consuming processes such as pre-compilation were employed for the determination of pendimethalin including high-performance liquid chromatography-triple quadrupole mass spectrometry (Yang et al. 2018, Yang et al. 2019), gas chromatography-electron capture detector (Zhang et al. 2019), ultra-performance liquid chromatography–sequential mass spectrometry (Lim et al. 2017), liquid chromatography-sequential mass spectrometry (LC-MS / MS) (Saha et al.2015, Bordin et al. 2017, Pavlidis et al. 2019), gas chromatography-sequential mass spectrometry (Penetra et al. 2010, Wu et al. 2013,). Instead of these methods, low-cost, sensitive, and highly selective electrochemical methods may be preferred for the determination of pendimethalin (Kotouček et al.1996, Vaňková et al. 1997, Sreedhar et al. 2000, Galli et al. 2011, Ni et al. 2011 Gerent et al. 2015de Lima et al. 2016).

Graphene, discovered in 2004, is a two-dimensional carbon allotrope and has a hexagonal structure (Novoselov et al., 2004, Neto et al., 2009). Due to its electrical conductivity, large surface area, affordability, and easy accessibility, graphene is an ideal material for electrochemistry (Pumera et al., 2010, Fan et al. 2011, Sun et al., 2011). Graphene nanosheets tend to form irreversible stacks through strong π-π stacking, and since this Van der Waals interaction limits the applications of graphene, nafion is applied to prevent this (Xue et al. 2013). Nafion exfoliates graphene by electrosteric mechanism and is strongly absorbed into the graphene surface by hydrophobic interaction. It is an amphiphilic polymer that can solve graphene nanocomposite effectively and can be used for antifouling coating and to reduce the effect of surface-active macromolecules (Li et al. 2009, Fan et al. 2011, Filik et al., 2014). Besides, the properties nafion has, including chemical inertness, thermal stability, mechanical strength, capacity, huge cation exchange, and antifouling features cause the polymer to be widely applied for electrode modification (Tajeu et al. 2020).

In this study, electrochemical behavior and voltammetric determination of pendimethalin were performed with GCE and n-GR/GCE. The electrochemical behavior of pendimethalin was investigated for both electrodes using the CV method. The voltammetric determination of pendimethalin with n-GR/GCE was conducted by the DPAdSV method and with GCE by DPV method. The working ranges, LOD and Limit of Qualification (LOQ) were calculated for both electrodes. The results obtained showed that n-GR/GCE performs better for the determination of pendimethalin. In addition, the interference effect of some cations on pendimethalin was analyzed with n-GR/GCE and the selectivity of the method was determined. A sensitive, fast and selective method was developed for the determination of pendimethalin with n-GR/GCE without any pre-dissociation process. And there were no preceding studies investigating the electrochemical behavior and voltammetric analysis of pendimethalin with these electrodes.

2. Material and Method

2.1. Devices

Electrochemical experiments were carried out by Ivium pocketstat (potentiostat/galvanostat impedance analyzer). The data obtained were evaluated using Ivium software. C4 Cell Stand was used and pH measurements were performed with the Ohaus starter 3000 Bench pH meter. Prior to measurement, the pH meter was calibrated at three points using Ohaus standard pH buffer solutions. A Bell balance (±0.0001 g precision) was used for weighing. Ultra-pure water obtained from Millipore direct-3QV was used for preparing aqueous solutions and cleaning electrodes.

2.2. Electrodes

During experimental studies, the three-electrode system was applied. GCE (CHI 104) was employed as the working electrode, Ag/AgCI (3 M NaCI) electrode (MF-2052, BASi) served as the reference electrode and Pt wire acted as the counter electrode.

2.3. Chemicals

The chemicals used for the study include acetonitrile, sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), calcium chloride ($CaCl_2$), lead nitrate ($Pb(NO_3)_2$), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), and all of them were of analytical grade and were received from Merck. In this study, graphene synthesized and characterized by Kocak et al., 2015 was applied to modify the electrode surface (Kocak et al.2015).

2.4. Solutions

The stock solution of pendimethalin at a concentration of 1.0×0^{-2} M was prepared in acetonitrile and stored at $+4^{o}$C. In order to determine the working conditions of pendimethalin, H_2SO_4 solution was used for pH 1 and pH 2, phosphate buffer solution for the range between pH 3 and 12, and NaOH solution for pH 13.

2.5. Polishing Process of GCE and Modification of GCE with n-GR

A small amount of aluminum oxide (alumina, Al_2O_3, 0.05 µm) was poured on polishing pad and turned into a slurry with ultra-pure water. After cleaning the GCE surface by circular movements on this slurry, it was washed with ultra-pure water. Then, to clean the surface of the electrode, it was placed in a beaker containing ultra-pure water for 5 minutes in the ultrasonic bath.1.0 mg/ml graphene was dispersed in the ultrasonic bath by adding 25 % nafion. 5 µl was taken from this mixture and dripped on the surface of GCE and left in room conditions for the solvent to evaporate.

3. Results and Discussion

3.1. Electrochemical Behavior of Pendimethalin

When the electrochemical behavior of pendimethalin was examined by cyclic voltammetry between 0 V and -1.5 V in the pH 7 phosphate buffer solution with a GCE, two well-defined peaks were observed at -1.056 V (1st peak) and -0.954 V (2nd peak). No peak was present in the opposite direction scanning. This suggests that the reaction is irreversible (Galli et al. 2011). In voltammetric analyses, the type and pH value of the supporting electrolyte solution have a significant effect on the reduction and oxidation of the substance to be analyzed (Tabanlıgil 2019).

To determine the working conditions of pendimethalin, the change in peak current with pH was studied by differential pulse voltammetry using GCE. Two well-defined peaks were observed in all the solutions between pH 2 and 12. Considering the change in the 1st peak current with pH, the pH 7 phosphate buffer was selected as the supporting electrolyte, where the highest peak current was obtained (Figure 2). In subsequent analyses, pH 7 phosphate buffer solution was used.

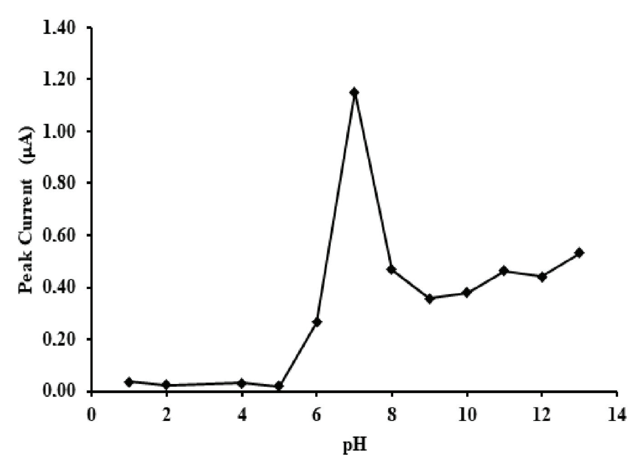


Figure 2. The effect of pH on the 1st peak current of 9.99×10^{-6} M pendimethalin using GCE with DPV method

3.2. Effect of Scan Rate on Electrochemical Behavior of Pendimethalin on GCE and n-GR/GCE

Cyclic voltammograms of pendimethalin were obtained from the pH 7.0 phosphate buffer solution, scanning the potential in the negative direction in the range of 0 V to -1.5 V. Scan rate voltammograms of 9.99×10^{-6} M pendimethalin were obtained with GCE in the range of 5 mV/s and 750 mV/s (Figure 3a) and scan rate voltammograms of 3.0×10^{-5} M pendimethalin were taken between 5 mV/s and 1000 mV/s using n-GR/GCE (Figure 3b).

To determine the electrochemical behavior of pendimethalin on the surfaces of GCE and n-GR/GCE, the logarithm of the peak current (log *Ip*) was plotted against the logarithm of the scan rate (log *v*) (Figure 4). The equation of the obtained lines was given in Table 1.

It can be seen from Table 1 that for GCE; when the logarithm of the peak current was plotted against the logarithm of the scan rate, the values of slope of the line were found as 0.435 (for 1st peak current) and 0.388 (for 2nd peak current). For n-GR/GCE; when the logarithm of the peak current versus the logarithm of the scan rate was plotted, the values of slope of the line were calculated as 0.819 (for 1st peak current) and 0.587 (for 2nd peak current). From the Randless-Sevcik equation, a linear slope of 0.5 is obtained between log *ip* and log*v* for diffusion-controlled reactions. If the reaction is adsorption controlled, the slope is equal to 1. Experimental data obtained for GCE show that the electrode reaction is diffusion-controlled, the reaction on n-GR/GCE surface is diffusion-controlled, as well as effective in adsorption (Laviron et al. 1980).

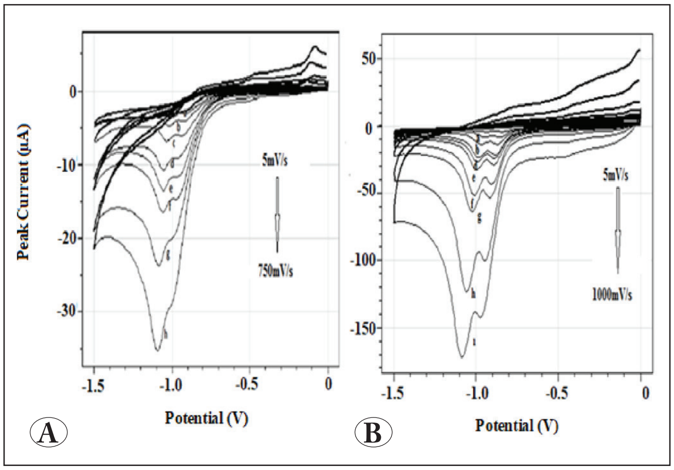


Figure 3. A) Cyclic voltammograms of 9.99×10^{-6} M pendimethalin with GCE from pH 7 phosphate buffer in the range of 5 - 750 mV/s scan rate a) 5, b) 10, c) 25, d) 50, e) 100, f) 150, g) 250, h) 750 mV/s. **B)** Cyclic voltammograms of 3.0×10^{-5} M pendimethalin in the range of 5 – 1000 mV/s scan rate with n-GR/GCE from pH 7 phosphate buffer solution a) 5, b) 10, c) 25, d) 50, e) 75, g) 150, h) 250, i) 500, j) 1000 mV/s.

3.3.Voltammetric Determination of Pendimethalin

3.3.1.Determination of the Working Range, LOD and LOQ of Pendimethalin by DPV at GCE

In the calibration studies of pendimethalin with GCE, DPV was employed to determine the working range. By adding standard pendimethalin solutions to a 5 ml pH 7 phosphate buffer solution, DPVs were obtained (Figure 5) and a calibration curve (Figure 6) was drawn.

A linear increase in both peak currents depending on the concentration of pendimethalin indicates that this pesticide can be determined by the DPV technique with GCE. When peak currents versus pendimethalin concentration were plotted, the calibration curve and working range were determined for 1st peak current and 2nd peak current separately. The calibration curve of the 1st and 2nd peak currents of pendimethalin is shown in Figure 6.

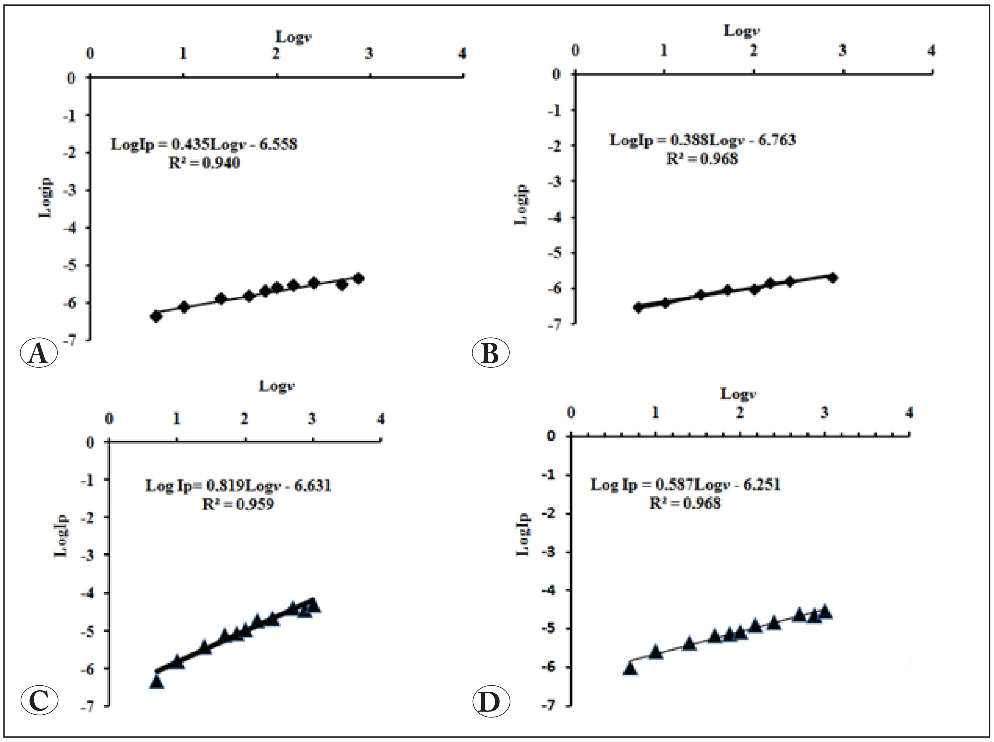
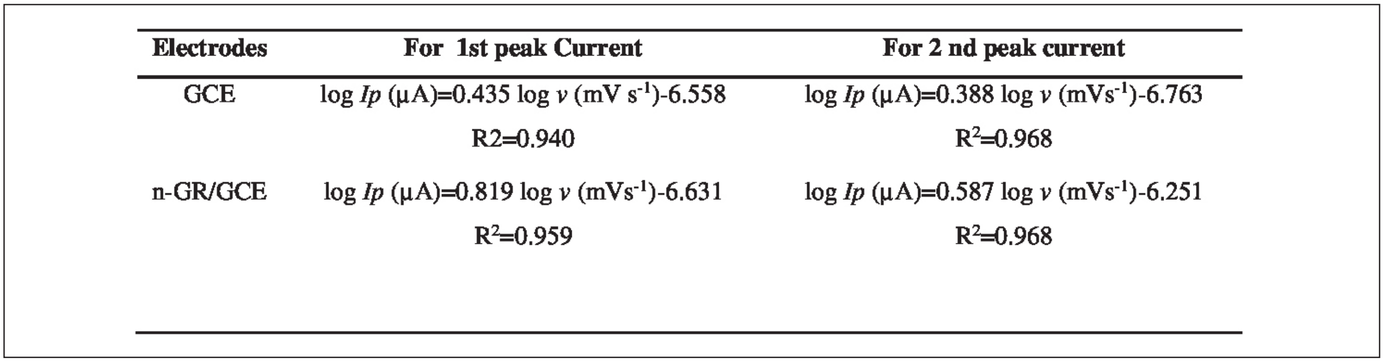


Figure 4. A) log *v*-log *Ip* graph of 9.99×10^{-6} M pendimethalin in the range of 5 - 750 mV/s scan rate at pH 7 phosphate buffer with GCE for 1st peak current, **B)** for 2nd peak current; **C)** log *v*-log *Ip* graph of 3×10^{-5} M pendimethalin in the range of 5-1000 mV/s scan rate at pH 7 phosphate buffer solution with n-GR/GCE for 1st peak current, **D)** for 2nd peak current.

Table 1. The linear equations obtained for GCE and n-GR/GCE (for 1st and 2nd peak current)



Electrodes	For 1st peak Current	For 2 nd peak current
GCE	log Ip (μA)=0.435 log v (mV s^{-1})-6.558 R2=0.940	log Ip (μA)=0.388 log v (mVs^{-1})-6.763 R^2=0.968
n-GR/GCE	log Ip (μA)=0.819 log v (mVs^{-1})-6.631 R^2=0.959	log Ip (μA)=0.587 log v (mVs^{-1})-6.251 R^2=0.968

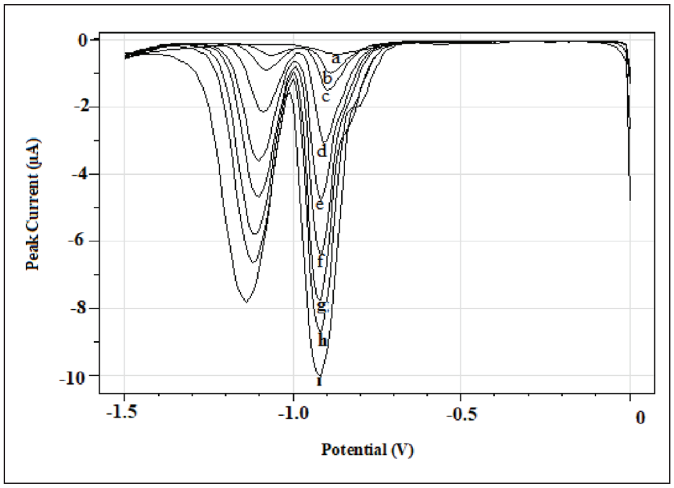


Figure 5. Voltammograms showing changes in concentration and peak currents of pendimethalin using DPV technique with GCE in pH 7 phosphate buffer solution; a) phosphate buffer solution (pH 7.0) b) 3.50×10^{-5} c) 8.69×10^{-5} d) 2.79×10^{-4} e) 5.21×10^{-4} f) 6.38×10^{-4} g) 8.64×10^{-4} h) 1.08×10^{-3}, i)1.58×10^{-3} M.

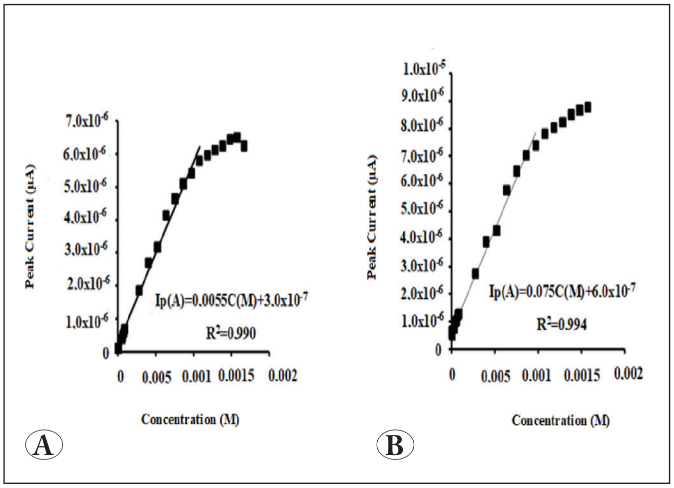


Figure 6. Peak current graph of pendimethalin versus concentration using GCE at pH 7 phosphate buffer solution **A)** for 1st peak current **B)** for 2nd peak current.

From the calibration curve given in Figure 6a, the working range of the 1st peak current was calculated as 1.56×10^{-6}-1.08×10^{-3} M.

The linear equation is as follows:

Ip (A)= 0.0055 C (M) – 3.0×10^{-7}; R^2 = 0.990)

On the other hand, the calibration curve of pendimethalin for 2nd peak current was shown in Figure 6b. From this calibration curve, the working range for 2nd peak current was found as 1.56×10^{-6} – 9.73×10^{-4} M.

The linear equation is as follows:

Ip (A)= 0.0075 C (M) – 6.0×10^{-7}; R^2 = 0.994)

At the next concentration (4.0×10^{-5} M) following the lowest one on the calibration curve of pendimethalin drawn by the DPV technique with GCE, the voltammograms were recorded, each of them repeated 3 times in 5 separate cells, and mean and standard deviation of 5 current values which were close to each other were calculated. The LOD value was calculated by the 3*S*/m formula, while the LOQ value by the 10*S*/m formula. For the 1st peak, LOD value was 3.09×10^{-5} M, and LOQ value was 1.03×10^{-4} M. As for 2nd peak, LOD value was 3.36×10^{-6} M, while the LOQ value was 1.12×10^{-5} M.

Within-day reproducibility of 1st and 2nd peak currents and peak potential of 1.0×10^{-4} M pendimethalin was investigated by DPV technique using GCE. When the reproducibility of GCE was examined, the values of RSD % of 1st peak current and 2nd peak current were found as 2.24 % and 1.64, respectively. And reproducibility of peak potential was RSD % 5.63 (1st peak) and RSD % 1.47 (2nd peak).

3.3.2. Determination of the Working Range of Pendimethalin by DPAdSV at n-GR/GCE

First, the accumulation potential (E_{acc}) of 1.0×10^{-6} M pendimethalin on the surface of n-GR/GCE was analyzed using the DPV technique in pH 7 phosphate buffer (20 % acetonitrile) solution varying from 0.1 V to -0.8 V by -0.1 V steps. From Figure 7a, when the effect of the accumulation potential on the current was examined, it was clear that the best current was obtained at 0 V. In subsequent studies, 0 V was used as E_{acc}.

When the accumulation time (t_{acc}) was changed from 0s to 350s and its effect on the peak current was examined, the highest peak current at 0 V accumulation potential was obtained at 300s (Figure 7b). In subsequent studies, the accumulation time was used as 300s.

The optimum accumulation potential of 1.0×10^{-6} M pendimethalin solution with n-GR/GCE was identified as 0 V and the accumulation potential as 300 s. After optimizing the parameters, DPAdS voltammograms were obtained (Figure 8) and a calibration curve was plotted (Figure 9).

In calibration studies of pendimethalin by the DPAdSV technique with n-GR/GCE, working solutions were prepared by adding a known amount of different pendimethalin stock solution to the pH 7 phosphate buffer solution (20 % acetonitrile). Shifts were observed in peak potential when concentration increased. This indicates a strong adsorption on the modified electrode surface (Galli et al. 2010). The calibration graph of the pendimethalin was drawn by using the peak currents measured from the voltammograms obtained with the addition of pendimethalin under optimum conditions. Working range of n-GR/GCE for pendimethalin determination for 1st peak current by DPAdSV technique was 1.7×10^{-6} -4.01×10^{-4} M, while for 2nd peak, it was 1.96×10^{-9}-7.53×10^{-4} M. Calibration curves of pendimethalin drawn by the DPAdSV technique with n-GR/GCE (1st peak current and 2nd peak current) were shown in Figure 9.

3.3.3. Calculation of LOD and LOQ Parameters of Pendimethalin by DPAdSV with n-GR/GCE

At the next concentration (3.0×10^{-6} M) of pendimethalin following the lowest one on the working range calibration curve for 1st peak, voltammograms were recorded, each of them repeated 3 times in 5 separate cells, and their mean and standard deviation were calculated by averaging the peak currents of voltammograms obtained in each cell. The LOD value was calculated using the $3S/m$ formula, while the LOQ value by the $10S/m$ formula. For the 1st peak, the LOD value was found to be 8.69×10^{-6} M, and the LOQ value was calculated as 2.90×10^{-5} M. At the next concentration (4.0×10^{-8} M) following the lowest one on the calibration curve for the 1st working range of 2nd peak, voltammograms were recorded, each of them repeated 3 times in 5 separate cells, and their mean and standard deviation were calculated by averaging the peak currents of

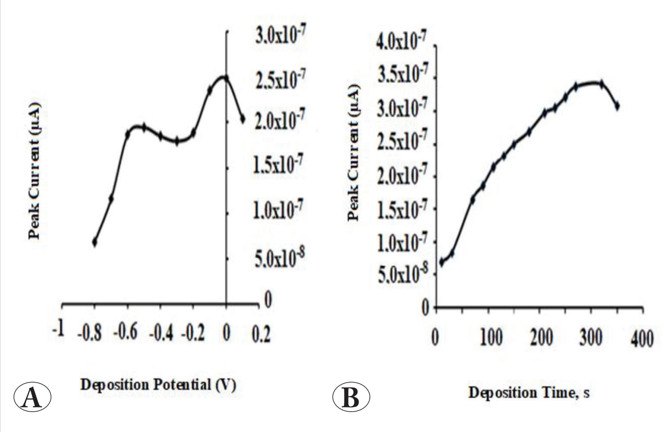


Figure 7. A) The effect of accumulation potential of 1.0×10^{-6} M pendimethalin on peak current (scan rate: 50 mV/s, potential range from 0.1 V to -0.8 V), **B)** the effect of accumulation time on peak current (scan rate: 50 mV/s, E_{acc}: 0V).

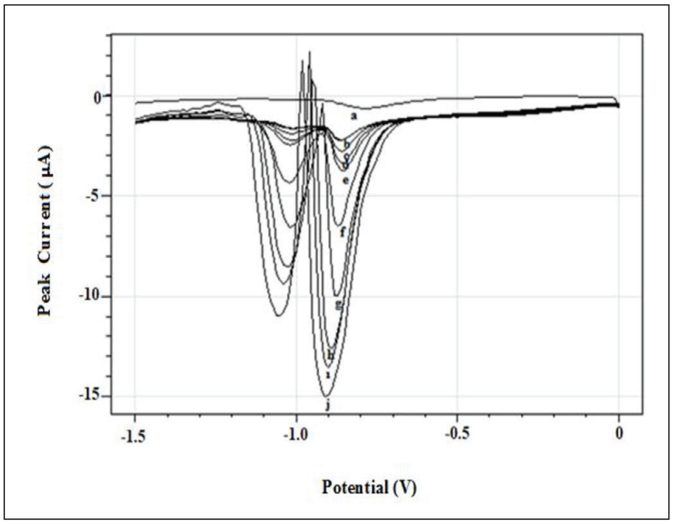


Figure 8. Voltammograms showing changes in concentration and peak currents of pendimethalin using DPAdSV technique with n-GR/GCE in pH 7.0 phosphate buffer solution (20 % acetonitrile); a)Phosphate buffer solution (pH 7.0) b)8.49×10^{-6} c)3.50×10^{-5} d)4.85×10^{-5} e)7.44×10^{-5}, f)1.51×10^{-4}, g)2.78×10^{-4}, h)4.01×10^{-4}, i)5.21×10^{-4}, j)8.64×10^{-4} M.

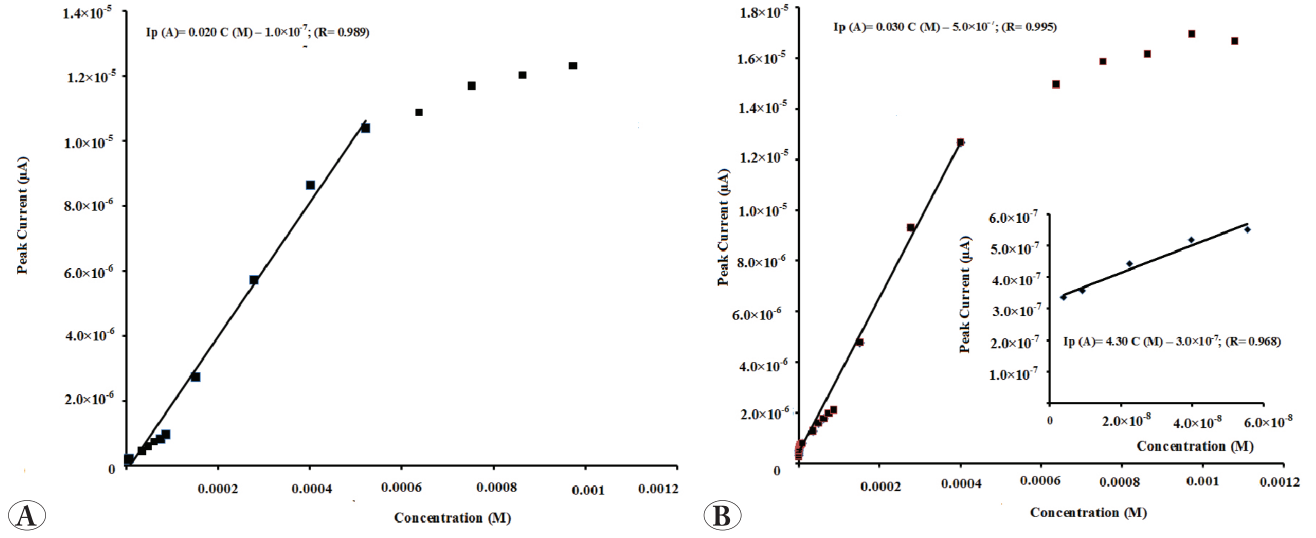


Figure 9. Peak current graph of pendimethalin versus concentration at pH 7 phosphate buffer solution (20 % acetonitrile) with n-GR/GCE **A)** For 1st peak current (E_{acc}: 0V, t_{acc}: 300s) **B)** For 2nd peak current.

voltammograms obtained in each cell. The LOD value was 1.05×10^{-9} M, while the LOQ value was 3.48×10^{-9} M.

At the next concentration (3.0×10^{-6} M) following the lowest one on the calibration curve for the 2nd working range of 2nd peak, voltammograms were recorded, each of them repeated 3 times in 5 separate cells, and their mean and standard deviation were calculated by averaging the peak currents of voltammograms obtained in each cell. The LOD value was calculated by the $3S/m$ formula, while the LOQ value by the $10S/m$ formula. For the 2nd working range of the 2nd peak, the LOD value was found to be 3.45×10^{-6}, while the LOQ value was 1.15×10^{-5} M.

Within-day reproducibility of 1st and 2nd peak current and peak potential was investigated for 1.0×10^{-4} M pendimethalin. Reproducibility of peak current was RSD % 3.26 (1st peak) and RSD % 1.34 (2nd peak). Reproducibility of peak potential was RSD % 1.01 (1st peak current) and RSD % 1.76 (2nd peak current)

3.4. Interference Effect

The interference effect of some metal cations (Cu^{2+}, Ni^{2+}, Ca^{2+}, $Pb^{2+)}$ possibly present in the same environment as pendimethalin, was investigated to demonstrate the selectivity and preciseness of the method. The interference effect was studied with the ratio of interference species to pendimethalin concentration in 1.0×10^{-4} M pendimethalin being 1:1 and 1:5. The ratio of the 1st and 2nd peak currents of pendimethalin obtained when there were no species capable of interference to the peak current obtained in the presence of these species was calculated as % recovery.

From Table 3, it is clear that interference species did not affect the 1st peak current, with the ratio of interference species to pendimethalin concentration being 1:1 and 1:5 in 1.0×10^{-4} M pendimethalin. According to the results on the 1st peak current, pendimethalin can be selectively determined with n-GR/GCE in the presence of Cu^{2+}, Ni^{2+}, Ca^{2+}, Pb^{2+} cations whose interference effects were investigated 1:1.

4. Conclusion

In this paper, the voltammetric determination and electrochemical behavior of pendimethalin were performed on the surfaces of GCE and n-GR/GCE. When GCE and n-GR/GCE were compared for voltammetric determination of pendimethalin, it was clear that n-GR/GCE was more suitable due to the advantageous features of graphene such as good electrical conductivity, large surface area, good π–π interaction, and strong adsorptive ability. A wider working range, a lower LOD and LOQ were obtained in the determination of pendimethalin with n-GR/GCE using the DPAdSV technique. When the interference effect of some cations on pendimethalin was examined using the n-GR/GCE, the method was found to be more sensitive and selective, based on the 1st peak current, indicating that this method can be used for the determination of pendimethalin

Table 2. Analytical parameters for determination of pendimethalin using GCE and n-GR/GCE

Parameters	1st peak (GCE)	2nd peak (GCE)	1stpeak (n-graphene/GCE)	2nd peak (n-graphene/GCE)
Linear Working Range (M)	1.56×10^{-6}-1.08×10^{-3}	1.56×10^{-6}-9.73×10^{-4}	1.76×10^{-6}-4.01×10^{-4}	1.96×10^{-9}-7.53×10^{-4}
Slope (A/M)	0.0055	0.0075	0.0055	0.0075
Correlation Coefficient	0.990	0.994	0.099	0.094
LOD	3.09×10^{-5}	3.36×10^{-6}	8.69×10^{-6}	1.05×10^{-9}
LOQ	1.03×10^{-4}	1.12×10^{-5}	2.90×10^{-5}	3.48×10^{-9}
Reproducibility of peak potential	5.60	1.64	1.01	1.76
Reproducibility of peak current	2.24	1.47	3.26	1.34

Table 3. Interference effect of some cations in the determination of 1.0×10^{-4} M pendimethalin on n-GR/GCE using DPAdSV method and % recovery values (pH 7)

İnterfering Species (1:1)	**% Recovery For 1st peak**	**% Recovery For 2nd peak**	**İnterfering Species (1:5)**	**% Recovery For 1st peak**	**% Recovery For 2nd peak**
Cu^{2+}	106	107	Cu^{2+}	123	122
Ni^{2+}	100	101	Ni^{2+}	102	117
Ca^{2+}	98.3	103	Ca^{2+}	100	116
Pb^{2+}	99.8	11.1	Pb^{2+}	110	125

in real samples. In this study, voltammetric determination of pendimethalin was carried out by a convenient, practical and low-cost technique. In addition, there are no preceding voltammetric studies of pendimethalin with GCE and n-GR/GCE in the literature.

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