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A Novel and Highly Sensitive Reduced Graphene Oxide Modified Electrochemical Sensor for the Determination of Chlorpyrifos in Real Sample

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Abstract

In this study, the voltammetric behavior of chlorpyrifos(CPF) was investigated using reduced graphene oxide-modified glassy carbon electrode(RGO/GCE). FT-IR, XRD and TEM methods were employed in the characterization of graphene oxide and reduced graphene oxide prepared by Hummers' method. Electrochemical characterization of CPF was determined by cyclic voltammetry(CV) and differential pulse voltammetry(DPV). Determination of CPF was performed by differential pulse adsorptive stripping voltammetry (DPAdSV) on RGO/GCE. Two working ranges between 5.19×10^{-7}-8.12×10^{-6}M and 8.12×10^{-6}-2.18×10^{-3}M were obtained in the CPF calibration curve created by DPAdSV method on RGO/GCE and the limit of detection was found to be 1.56×10^{-7}M. Recovery of CPF from tap water samples on RGO/GCE was 101.0%. In conclusion, a selective and sensitive sensor was developed for the determination of CPF, which can be used in real samples.

Keywords: Chlorpyrifos, modified electrode, reduced graphene oxide

Klorpirifosun Gerçek Örnekte Tayini İçin Yeni ve Yüksek Hassasiyetli İndirgenmiş Grafen Oksitle Modifiye Edilmiş Elektrokimyasal Sensör

Öz

Bu çalışmada, klorpirifosun(CPF) voltametrik davranışı, indirgenmiş grafen oksitle modifiye edilmiş camsı karbon elektrot(RGO/GCE) kullanılarak incelendi. Hummers yöntemiyle hazırlanan grafen oksit ve indirgenmiş grafenoksitin karakterizasyonunda FT-IR, XRD ve TEM yöntemleri kullanıldı. CPF'nin elektrokimyasal karakterizasyonu, dönüşümlü voltametri(CV) ve diferansiyel puls voltametriyle(DPV) ile belirlendi. RGO/GCE'ta CPF'nin tayini diferansiyel puls adsorptif sıyırma voltametrisiyle(DPAdSV) yapıldı. RGO/GCE'ta CPF'nin DPAdSV yöntemiyle oluşturulan kalibrasyon grafiğinde 5.19×10^{-7}-8.12×10^{-6}M ve 8.12×10^{-6}-2.18×10^{-3}M olmak üzere iki çalışma aralığı belirlendi. LOD değeri 1.56×10^{-7}M'dir. RGO / GCE ile musluk suyu örneklerinde CPF geri kazanımı %101,0'dir. Sonuç olarak,CPF tayini için gerçek numunelerde kullanılabilen seçici ve duyarlı bir sensör geliştirilmiştir.

Anahtar kelimeler: Klorpyrifos, modifiye elektrot, indirgenmiş grafen oksit

INTRODUCTION

Chlorpyrifos(CPF) is a broad-spectrum organophosphate insecticide that is widely used in agriculture, urban life, and household pest control(Pope et al., 2005; Nallapaneni et al., 2005; Sirisha et al., 2007).

This pesticide is applied to cereal crops, cotton, field crops, fruits, hazelnut, vegetables, ornamental plants, and grass. CPF is also effective in controlling worms, cockroaches, fleas, flies, termites and, lice. CPF acts on the central nervous system, heart, and respiratory system. Exposure to CPF is linked to acute symptoms such as coordination disorders, dizziness, headache, shivering, cramps, blurred vision, and dyspnea(difficulty in breath). When exposed to higher levels, it leads to loss of consciousness, the paroxysm of laughter, and death(Nallapaneni et al., 2005). The determination of CPF is, therefore, of vital importance. Methods such as HPLC-UV-VIS(Handajani et al., 2017), HPLC-MS/MS(Huan et al., 2019), GC-MS(Sinha et al., 2006), colorimetry (Mane et al., 2020) were developed for the determination of CPF. However, despite the accuracy and high sensitivity of these methods, they come with certain drawbacks including high costs, time-consuming processes such as pre-concentration, and bulky devices that are not suitable for fieldwork. Therefore, a simpler, faster and, cost-efficient method is required to detect CPF(Huang et al., 2020). Electrochemical methods were employed for simple, fast and cost-efficient determination of CPF(Al-Meqbali et al., 1998; Manisankar et al., 2005; Sirisha et al., 2007; Pelit et al., 2011; Kumaravel et al., 2015; Sreedar et al.,2015; Fischer et al. J.,2016; Melo et al.,2018; Joshi et al., 2020)

Being one of the most prominent elements of the periodic table, carbon has a total of five allotropes including fullerene, carbon nanotube, graphene, graphite, and diamond. While diamond and graphite which have been known since ancient times are three-dimensional allotropes, nanotube discovered in the 90s is one-dimensional and fullerene is zero-dimensional. On the other hand, the recently-discovered graphene which attracted a great deal of attention after its discovery is two-dimensional. The electronic structure of the graphene layers was first discussed by Wallace in 1947(Wallace, 1947). In 2004, Novoselov and Geim mechanically extracted a single-layer of graphene using the exfoliation method and characterized, with various methods, the graphene compressed as a preliminary process of the research for making electrochemical sensors (Novoselov et al., 2004). Graphene is widely used in electrochemical and electroanalytical applications thanks to its relatively low cost, wide specific surface area(theoretically 2630 m^2/g)(Manisankar et al., 2008)and higher electron mobility(15 000 cm $V^{-1}s^{-1}$)(Geim et al., 2010; Yang et al., 2010) compared to carbon nanotube and fullerene.

In this study, a new-generation, simple, sensitive, reliable, and easily-preparable electrode modified with reduced graphene oxide(RGO/GCE) was employed in the electrochemical determination of CPF. To obtain the RGO used in GCE modification, GO was first synthesized from graphite using the Hummers method and then was reduced by $NaBH_4$. And lastly, it was characterized using FT-IR, XRD, and TEM methods. Differential pulse adsorptive stripping voltammetry(DPAdSV) was performed and the conditions for the quantitative determination of CPF on RGO/GCE were unveiled.

MATERIAL AND METHODS

Instrumentation and chemicals

Iviumpocketstat(potentiostat galvanostat impedance analyzer) was used for voltammetric measurements of CPF and the data collected through this device were evaluated with the Ivium software. Shimadzu IR Affinity-1was used to determine the functional groups of graphene oxide and graphite via FT-IR spectroscopy. Atomic force microscope(Nanosurf Easy scan2, Nanosurf Instruments Inc.) and transmission electron microscope(JEOL TEM 1400) were used respectively for the determination of thickness and size of graphene layers. A three-electrode system was employed during the experimental studies, where glassy carbon electrode(CHI104) served as the working electrode, while Ag/AgCI(3M NaCI) electrode(MF-2052, BAS) was used as the reference electrode and Pt wire as the counter electrode.

All the chemicals used in the experimental studies were in analytical purity. Sulfuric acid(H_2SO_4) was purchased from Carbo Erba(CAS no:7664-93-9); sodium hydroxide (NaOH) (CAS no: 1310-73-2), sodium nitrate ($NaNO_3$) (CAS no : 7631-99-4), sodium chloride (NaCl)(CAS no: 7647-14-5), sodium carbonate(Na_2CO_3) (CAS Number: 497-19-8), calcium chloride dihydrate ($CaCI_2.2H_2O$) (CAS No: 10035-04-8), lead nitrate ($Pb(NO_3)_2$) (CAS No: 10099-74-8), nickel nitrate hexahydrate($Ni(NO_3)_2.6H_2O$) (CAS No: 13478-00-7), cobalt nitrate($Co(NO_3)_2$) (CAS No: 10026-22-9), copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) (CAS No: 10031-43-3) from Merck and CPF($C_9H_{11}CI_3NO_3PS$) (CAS no:2921-88-2) from Dr. Ehrenstorfer GmbH. The purity of the argon gas(Ar) used was 99.99%. All of the experiments were conducted in room conditions.

Synthesis of reduced graphene oxide(graphene)

Chemical synthesis of the reduced graphene oxide(graphene)(RGO) was performed in two steps. The first step included the production of graphene oxide(GO) from graphite, while the second step

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involved producing RGO by reducing the graphene oxide. The synthetic graphite was converted into graphene oxide(GO) using the Hummers method(Al-Meqbali et al., 1998). To this end, the graphite was put into a beaker and then placed inside an ice bath. After the addition of concentrated H_2SO_4 and $KMnO_4$, it was stirred for 30 minutes while maintaining the temperature below 20 °C. Then, the solution was removed from the ice bath and stirred for a further 30 minutes at room temperature, and then deionized water was slowly and carefully added. Stirring continued for another 30 minutes after the temperature reached 98°C. After that, pure water H_2O_2 was added to the solution, which turned into a yellow-brown color. At this point, non-reactive potassium permanganate and manganese dioxide were reduced to Mn^{2+} with the addition of H_2O_2. Following the completion of the stirring process, the solution was centrifuged. The precipitate was washed 5 times with 5% HCl solution. To confirm the completion of the washing process, $BaCl_2$ was added to the washing water. In case the $BaSO_4$ precipitate was observed, the washing process resumed. After the washing process was completed, the solid graphene oxide was dried in a vacuum drying oven at 60ºC.

Step two: the GO solution was obtained at 1mg mL^{-1} concentration with deionized water. It was sonicated in the ultrasonic bath for 2 hours to ensure the homogeneous suspension of GO. Then a 1 M NaOH solution was used to bring the pH of the GO solution to 10. To reduce graphene oxide, $NaBH_4$ was slowly added to this solution and it was mixed at 80°C for 6 hours. The obtained RGO suspension was washed 5 times with distilled water. Finally, the volume of the solution was completed with deionized water to 100 mL. The prepared RGO suspension with 1 mg mL^{-1} concentration was used to modify the electrode surface. The obtained RGO solution was then dried for 2 days in a vacuum oven at a temperature of 60 °C for characterization.

Preparation of RGO modified glassy carbon electrode

The RGO solution that had a concentration of 1 mg mL^{-1} in water was kept in an ultrasonic bath until it was dispersed. 5 µL was taken from the dispersed RGO solution, dripped on the cleaned and dried surface of the GCE, and left to dry under room conditions. The electrode that dried up during the day was used for electrochemical studies after it was washed with deionized water(Kang et al.,2010).

Voltammetric measurements

All voltammetric studies of CPF were conducted in 10 ml 0.1 M NaOH solution(Manisankar et al.,2005). Before the voltammetric analysis, high purity argon (99.99%) was purged into the electrochemical cell for 5 minutes to remove the oxygen. Conditioning of graphene modified glassy carbon electrode (RGO/GCE) was performed by cyclic voltammograms(25 times) in the potential range of 0 V to -2.1 V at a scan rate of 100 mVs^{-1}. CPF was determined by differential pulse adsorptive stripping voltammetry(DPAdSV) on RGO/GCE(pulse amplitude: 80 mV, staircase potential: 6 mV, scan rate: 50 mV s^{-1}, pulse time: 7 ms, quiet time: 15 s).

Preparation of tap water samples of chlorpyrifos

A stock solution of $1.0x10^{-4}$M CPF was prepared by mixing 1mL tap water, 1mL acetonitrile, and 8 mL 0.1M NaOH solution.The same solution without CPF was used as a blank solution for further experiments.

RESULTS AND DISCUSSION

Characterization of GO and RGO

FT-IR spectroscopy was applied to determine the functional groups of GO and RGO. Figure 1a depicts the FT-IR spectra of GO and RGO. From Figure 1a, FT-IR spectrum of GO showed the broadband of O-H stretching vibrations around 3300 cm^{-1}, the sharp band of C=O stretching vibrations at 1717 cm^{-1}, C=C stretching of unoxidized graphitic domain at 1617 cm^{-1}, C-O stretching of carboxylic acid at 1041 cm^{-1}(William et al., 1958; Paredes et al., 2008; Konios et al.,2014; Çiplak et al., 2015)

From Figure 1a, it can be concluded that after the reduction of graphene oxide, the main difference was the absence of the broad band of O-H stretching. The other vibrations of oxygen-containing functional groups at the RGO spectrum were decreased by the reduction process of GO(Koçak et al., 2015).

XRD spectra of GO and RGO were shown in Figure 1b. XRD technique is very useful to confirm the reduction of graphene oxide regarding the decrease of interlayer distance. The characteristic sharp peak of (002) plane of GO at 2ϴ=11.1 was related to the

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distance of 0.79 nm between GO layers(Figure 1b). The corresponding broad peak of RGO at 2Ɵ=23.8 was the(002) plane of RGO with 0.37 nm of interlayer distance(Figure 1b). This decrease verified that GO was successfully reduced to RGO(Johra et al., 2014; Emiru et al., 2017)

The surface morphologies and flake dimensions of GO and RGO were depicted by TEM images in Figure 2a and Figure 2b, respectively. GO sheets were typically wrinkled and consisted of few layers (n<5) due to stacking. In Figure 2b, RGO sheets were less wrinkled and folded than the oxidized form.

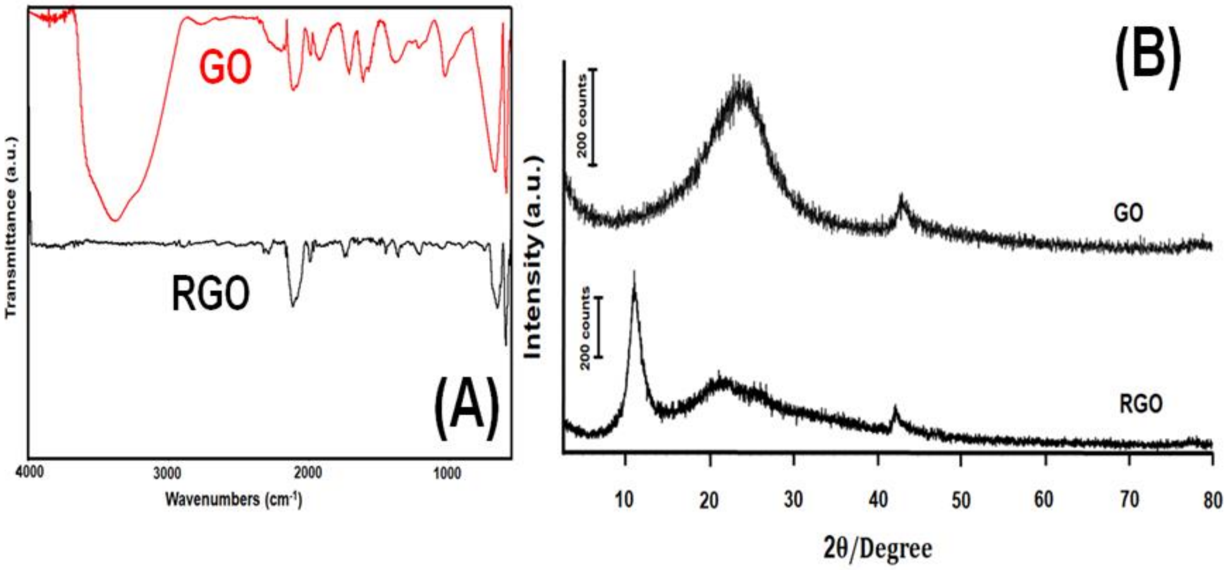

Figure 1. FTIR spectra of GO and RGO (A), XRD images of GO and RGO (B)

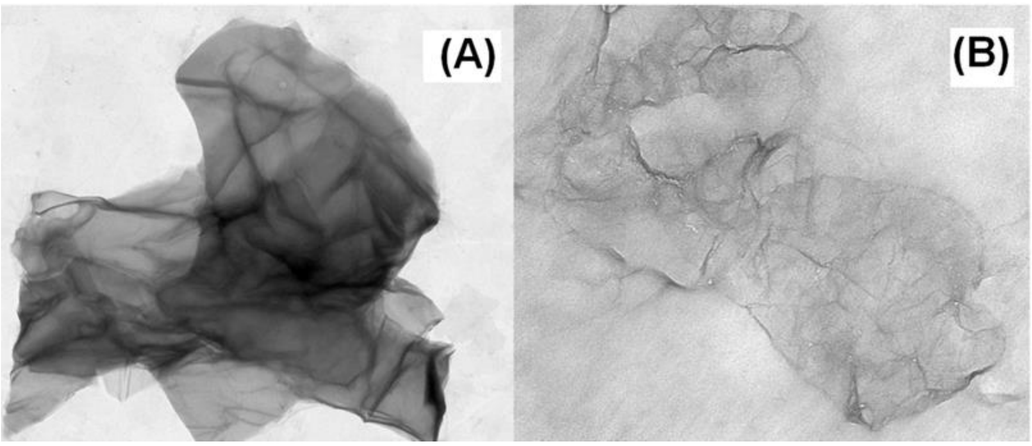

Figure 2. FTIR spectra of GO and RGO (A), XRD images of GO and RGO (B)

Electrochemical behavior of CPF.

CV analyses of CPF were performed on RGO/GCE and GCE in 0.1M NaOH. CV of CPF were scanned from 0 V to -2.1 V in negative direction and from -2.1 V to 0 V in positive direction.

In the CVs of 4.98x10^{-5}M CPF in 0.1 M NaOH taken at GCE, the first peak was -1.620V(1.27µA), the second peak was -1.749V(1.25µA) and the third

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peak was -1892(1,31µA), while at RGO/GCE, the first peak was -1.623V(0.78µA), the second peak was -1.754V(1.09µA) and the peak peak was -1.903V (0.84µA)(Figure 3).

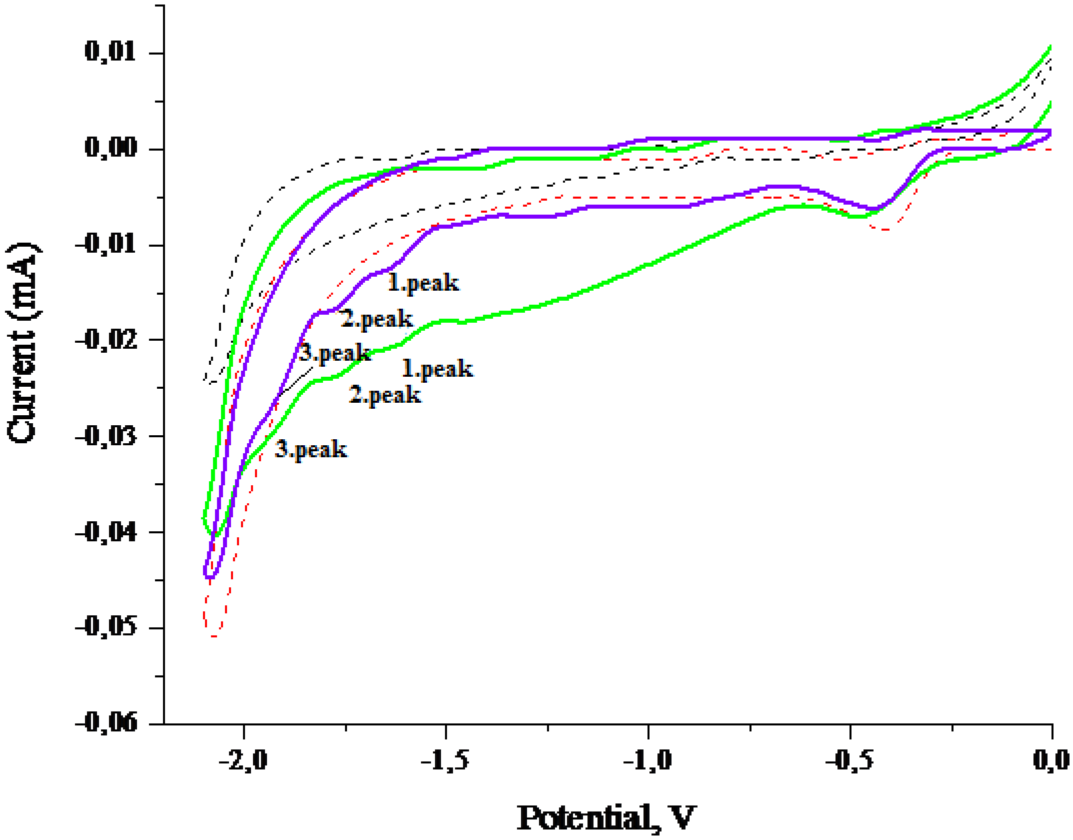

Figure 3.CVs of 4.98x10^{-5} M CPF peak currents at GCE (purple line) and RGO/GCE (green line) in 0.1 M NaOH solution; 5 ml 0.1M NaOH solution at GCE(black line) and RGO/GCE(red line) (scan rate:50 mV s^{-1})

The reason for the peak of CPF at a potential close to the hydrogen evolution area is the electro negativity of chlorine atoms in the molecule. From the literature, the electron density of C=N was decreased by the chlorine atoms, which caused the observation at a more negative potential of electrochemical reduction of CPF (Stobinski et al., 2014; Kumaravel et al., 2015).

The diagnosis of adsorbed CPF was explored by the effect of scan rate on the voltammetric response, which should give a linear response for the case of logip-logv with 1 of slope value(Manisankar et al., 2005).The voltammograms showing current responses at different scan rates and the plots of logip-logv for CPF at RGO/GCE were presented in Figure 4a and Figure 4b, respectively. From Figure 4a, three reduction peaks were observed in the cathodic scan(negative direction), but no peak was present in the reverse scan. It was clearly understood that CPF was irreversibly reduced and electron transfer occurred in 3 separate reduction steps. The first reduction peak was the reduction of the C=N structure of pyridine and the second peak was the reduction which occurred with the result of 2e$^-$ of the intermediate product.In the study they carried out in 1998, El-Shawi and Kamal examined the electrochemical behavior of CPF in the buffer solutions of pH=3, pH=5, pH=7.5, and pH≥9.5. In

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this study, the peak was divided into two consecutive small peaks in the strong alkaline environment of CPF PH≥9.5. They argued that this behavior was due to the emergence of two consecutive single-electron reduction stages of trichloropyridol, a degradation product of CPF, or the reduction of two different oriented types. In our study, the appearance of three peaks can be attributed to the electrochemical reduction of chlorpyrifos and trichloropyridol, the degradation product, in a strong basic environment.

Although the literature reports that these peaks are diffusion-controlled(Stobinski et al., 2014; Kumaravel et al., 2015), RGO/GCE showed the adsorption effect of CPF and its intermediate products onto the electrode surface from the plot of logip-log v in Figure 4b).

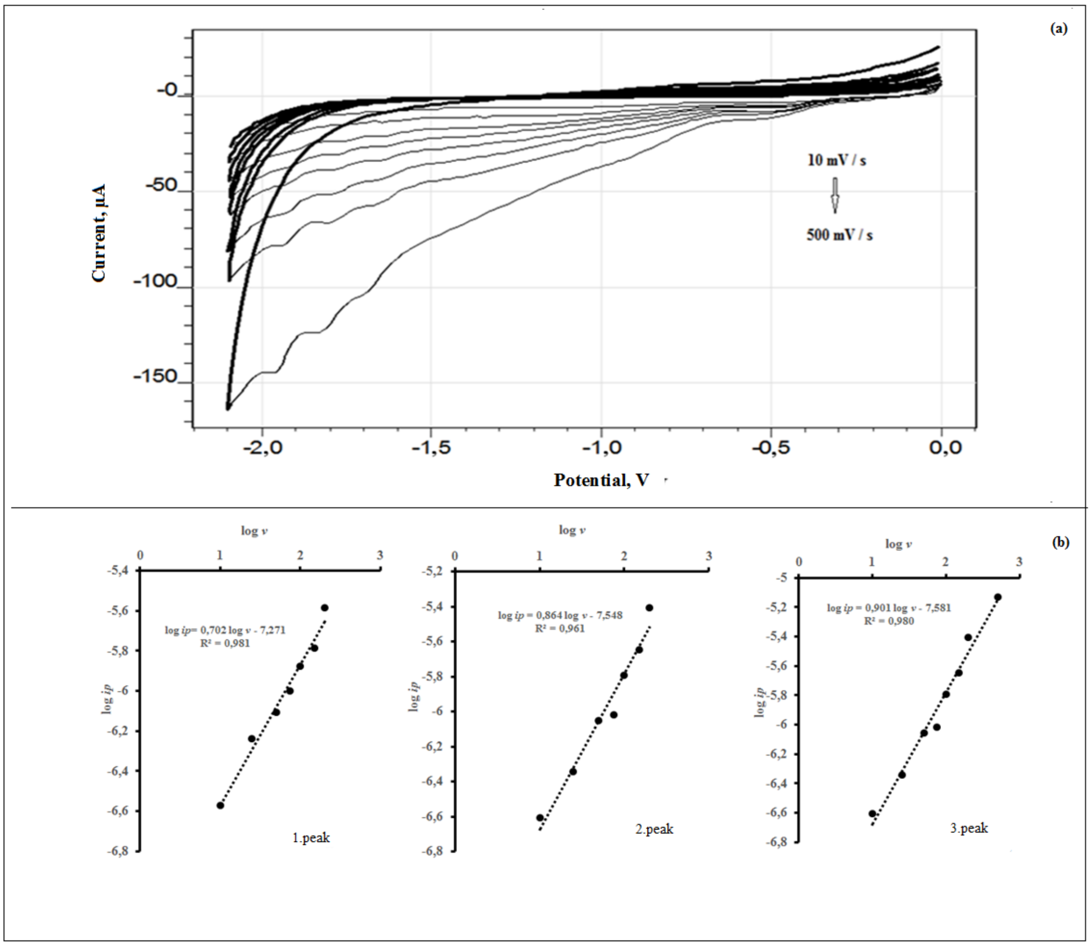

Figure 4.CVs of 4.98x10^{-5}M CPF taken with RGO/GCE at different potential scanrates(a) and log ip-logv grap(b) (0.1 M NaOH, pH: 13)

From the equations, the perfect mixing conditions of diffusion and adsorption controlled processes on the modified electrode surface were observed with the slope values closeto 0.75 for every three peaks(Manisankar et al., 2005). Besides, the adsorption effect of CPF on RGO/GCE was considered that RGO modification resulted in the objectives as well as utilizing in an adsorptive stripping method such as DPAdSV.

Effect of accumulation potential and time on the peak current

The accumulation step is highly useful to increase the current response of the analyte for

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adsorption-controlled electrochemical reactions. The conditions of the accumulation step were determined by an optimization procedure with three replicate measurements. Figure 5a and Figure 5b show the current responses of 4.98x10^{-5} M of CPF with accumulation potential(E_{acc}) and period(t_{acc}) carried out between 0 V and 1.2 V, and from 10 to 140s by incrementing at 10s intervals, respectively. The maximum current response for the electrochemical reduction of CPF was observed at E_{acc} of 0 V and t_{acc} of 30s.In addition, the highest current response was obtained at the third peak of CPF at -1.80 V and it was decided to use the third peak of CPF for the electrochemical determination of CPF.

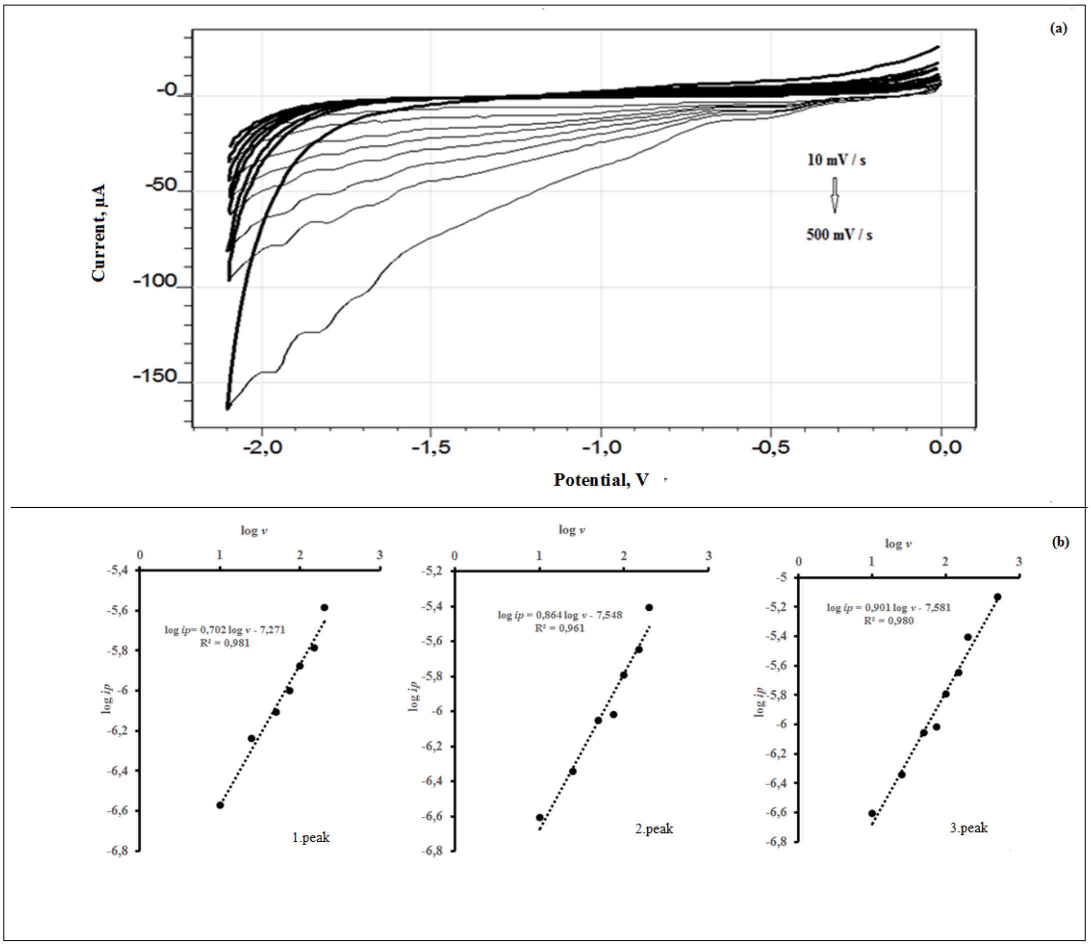

Figure 5. Change of 4.98x10^{-5} M CPF by the accumulation potential of peak current obtained by DPAdSV method on RGO/GCE (●: peak 1, ▲: peak 2, ■: peak 3, ΔE=80 mV, Es=6 mV, v=50 mV s^{-1}, t_{aac} =15s)(a), change of 4.98x10^{-5} M CPF by the accumulation potential of peak current obtained by DPAdSV method on RGO/GCE (●: peak 1, ▲: peak 2, ■: peak 3, ΔE=80 mV, Es=6 mV, scan rate=50 mV s^{-1}, t_{acc} =15 s) (b)

Determination of CPF by DPAdSV

The quantitative analysis of CPF was carried out by DPAdSV using the calibration curve at RGO/GCE under optimal conditions (0.1 M NaOH, E_{acc}: 0 V, t_{acc}: 30 s). The pulse voltammograms at increased concentrations of CPF were shown in Figure 6a., and the corresponding calibration graph was presented in Figure 6b. From Figure 6b, the sensor developed for the analysis of CPF gave two linear ranges with the following equations:

First: I (µA)= 2167 C (mM)+1.345 R^2=0.996 (between 5.19x10^{-7} M and 8.12x10^{-6} M)

Second: I (µA)=6.448 C (mM)+ 19.32 R^2=0.993 (between 8.12x10^{-6}M and 2.18x10^{-3}M)

The limit of detection(LOD) and limit of quantification(LOQ)were calculated to be 156 nm

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and 519 nm using the equation of LOD = 3 s/m and LOQ = 10 s/m, respectively. The validation results of the RGO modified sensor were presented in Table 1, it was shown that the obtained LOD value was the lowest for CPF determination with modified solid electrodes from Table 2.

In Table 2, when the LOD values of CPF at GCE and RGO/GCE were compared, a lower (17.46%) limit of detection was calculated at RGO/GCE. Besides, RGO/GCE is more advantageous than GCE due to its repeated use without cleaning the surface. The enhanced response to CPF arises from the electrocatalytic activity of oxygen-containing functional groups of RGO as a modifier. Although mercury electrodes show lower LODs for the quantitative determination of CPF, the use of mercury may cause environmental problems. In addition, the determination studies performed at RGO/GCE appear to have a lower LOD value compared to those carried out by Sreedar et al., 2015, Kumaravel et al., 2015 and Fischer et al. J., 2016

Repeatability and Selectivity

Repeatability and reproducibility of the proposed sensor were confirmed by taking DPAdSV measurements of 6.03x10^{-8}M CPF in 0.1M NaOH at various times using modified electrodes. The RSD value of the peak currents showing the repeatability was 0.069 % with the data obtained at different times using the same electrode. The RSD values of repeatability were found to be less than 5%, and the proposed modified electrode was found to show good precision.

To evaluate the selectivity of the proposed sensor, it was utilized against several inorganic compounds probably existing in soil and water. No interference effect was observed for 0.1mM and 0.5mM of Co^{2+}, Ni^{2+}, Pb^{2+}, and Ca^{2+} nitrates (approximately 1 and 5 folds concentration) with the recovery between 99.9% and 111.0%, but Cu^{2+} resulted in an excess deviation with the recovery value of 78.2% from Table 3.

Assay of CPF intap water

To confirm the suitability and reliability of the proposed sensor, the standard solution of CPF and tap water was spiked into 0.1 M NaOH, and then the determination of CPF in optimized conditions was carried out without following an extraction procedure. Recovery studies of CPF in the tap water were calculated at a 95% confidence level as listed in Table 4.

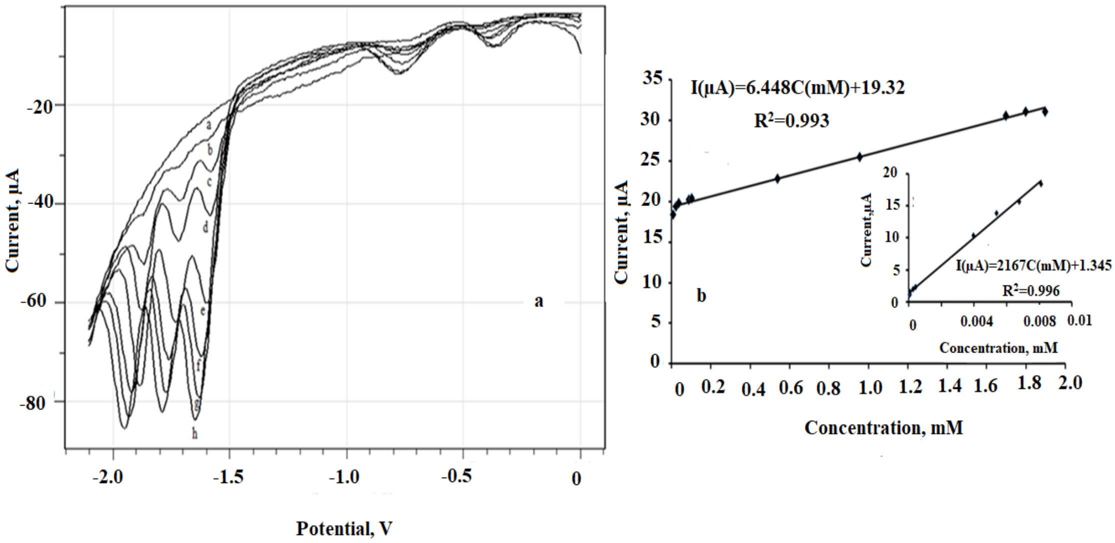

Figure 6. Voltammograms of CPF in different concentrations in 0.1 M NaOH solution obtained by means of DPAdSV method on RGO/GCE: a) 0.1 M NaOH, b) 6.03x10^{-8} M, c) 7.19x10^{-7} M, d) 3.91x10^{-6} M, e) 3.64x10^{-5}M f) 1.59x10^{-3} M, g) 1.80x10^{-3} M, h) 2.08x10^{-3} M CPF (ΔE=80 mV, Es=6 mV, E_{acc}=0 V, t_{acc}=30 s v=50 mV s^{-1})(a), peak current change with concentration of CPF in 0.1 M NaOH solution by DPAdSV method on RGO/GCE (ΔE=80 mV, Es=6 mV, E_{acc}=0 V, t_{acc}=30 s, v=50 mV s^{-1})(b)

Table 1.*Analytic parameters identified for determination of CPF using DPAdSV method with RGO/GCE in 0.1 M NaOH solution*

Parameters	**1. Calibration Curve**	**2. Calibration Curve**
Linear working range (M)	5.19x10^{-7}-8.12x10^{-6}	8.12x10^{-6}-2.18x10^{-3}
Slope (µA /mM)	2167.4	6.6448
Correlation coefficient	0.996	0.993
LOD (M)	1.56x10^{-7}	
LOQ (M)	5.19x10^{-7}	
Peak Potential Repeatability (% BSS)	0.005*	
Peak Current Repeatability (% BSS)	0.069*	

Table 2. *LOD values of studies on electrochemical determination of CPF (LOD values were convertedin to molarity)*

Electrode	**LOD**	**Method**	**Literature**
Dripping mercury electrode (DME)	8.7x10^{-7} M	Differential pulse polarographic	(Al-Meqbali et al., 1998)
Poly 3,4-ethylenedioxythiophene modified glassy carbon electrode (PEDOT/GCE	8.0x10^{-10}M	Square wave stripping voltammetry	(Manisankar et al., 2005)
Hanging mercury drop electrode (HMDE)	9.9x10^{-9}M	Differential pulse cathodic adsorptive stripping voltammetry	(Al-Meqbali et al., 1998)
Hanging mercury drop electrode (HMDE)	3.9x10^{-10}M	DPAdSV	(Pelit et al., 2011)
Clay modified carbon paste electrode	2.28x10^{-10}M	DPAdSV	(Sirisha et al., 2007)
Ag/Cu alloy nanoparticles and graphene composite paste electrode	4.4x10^{-6}M	DPAdSV	Sreedar et al., 2015)
NanoTiO2/cellulose acetate modified glassy carbon electrode	3.5x10^{-6}M	DPV	(Kumaravel et al., 2015)
Mercury Meniscus Modified Silver Solid Amalgam Electrode	2.6 × 10^{-6} M	DPV	(Fischer et al. J.,2016)
Hanging mercurydrop electrode	4.4 × 10^{-10}M	Square wave adsorptive stripping voltammetry	(Melo et al.,2018)
GCE	1.89x10^{-7} M	DPV	Presentstudy
RGO/GCE	1.57x10^{-7} M	DPAdSV	Presentstudy

Table 3. *Interference effect of certain cations on CPF using DPAdSV method with RGO/GCE*

Interfering ions	For 1. peak recovery at the preference of 1.0x10^{-4} M interferent (%)	For 2.peak recovery at the preference of 1.0 x10^{-4} M interferent (%)	For 3. peak recovery at the preference of 1.0x10^{-4} M interferent (%)	For 1.peak recovery at the preference of 5.0x10^{-4} M interferent (%)	For 2.peak recovery at the preference of 5.0x10^{-4} M interferent (%)	For 3.peak recovery at the preference of 5.0x10^{-4} M interferent (%)
Cu^{2+}	106.9	101.4	78.2	46.6	35.7	17.0
Ni^{2+}	96.9	101.0	99.9	92.2	80.1	84.8
Co^{2+}	95.6	101.0	105.0	76.4	46.9	51.3
Ca^{2+}	95.2	98.5	111.0	91.4	59.2	59.9
Pb^{2+}	98.1	111.0	111.0	85.4	38.2	27.7

Table 4. *Recovery values of CPF in tap water using DPAdSV method with RGO/GCE*

Added (µg mL^{-1})	Found (µg mL^{-1})	Recovery (%)	Relative standard deviation (%)	Relative error(%)
3.51	3.5±0.3	101.0	3.26	0.99
7.01	7.1±0.4	101.0	2.46	0.97

CONCLUSION

The RGO / GCE, which is novel, sensitive, selective, easily producible and applicable, was proposed as a sensor for determining the CPF.

Two linear working ranges were found in the range of 5.19x10^{-7}M - 8.12x10^{-6} M and 8.12x10^{-6}M-2.18x10^{-3}M in the determination of CPF by DPAdSV method using the modified electrode. The detection limit was found to be 1.56×10^{-7}M. These results indicated that the proposed modified electrode has a wide working range and a low limit of detection for the determination of CPF. The proposed method was applied sensitively and selectively to the determination of CPF in tap water, as a true sample.

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CONFLICT OF INTEREST

The Author report no conflict of interest relevant to this article.

RESEARCH AND PUBLICATION ETHICS STATEMENT

The author declares that this study complies with research and publication ethics.

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