Research Article

Fe₂O₃/GRAPHENE NANOSENSOR FOR ELECTROCHEMICAL ANALYSIS OF CHLORNITROFEN IN ENVIRONMENTAL SAMPLES

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ABSTRACT

Fe₂O₃/Graphene nanosensor is developed for the determination of chlornitrofen was studied by cyclic and differential pulse voltammetry. The peak observed for the chlornitrofen are attributed to the reduction of nitro groups at pH 4.0 (universal buffer). A systematic study of various experimental conditions, such as pH, accumulation potential, accumulation time and scan rate were studied. The relationship between peak current and chlornitrofen concentration was linear within the concentration range of 0.002–40.0 µg mL^{-1} with detection limit is found to be 0.0064 µg mL^{-1} (S/N=3). The proposed method is sensitive and free from interferences of other foreign ions. The proposed method has been satisfactorily applied to the determination of chlornitrofen in environmental samples.

INTRODUCTION

Pesticides are widely used to protect the crops from a variety of pests. The use of pesticides benefits in increasing agricultural production, but the repeated and indiscriminate usage of certain pesticides have led to their accumulation in plants, animals, soils and sediments, thus effecting widespread contamination of the environment [1]. After application, the pesticide molecules may undergo different pathways in the environment, depending on the types of interaction with the soil components [2,3]. In soils rich in organic matter or/and clay, pesticide molecules may become immobilized by strong absorption [4,5] that facilitates their degradation by sunlight, microorganisms or chemical reactions. In these cases, the degradation products may be toxic or not. In mineral soils, where the interaction is commonly very weak, they may be leached by rain or irrigation waters reaching rivers, dams or under-ground waters. Under such circumstances, the risk of contamination of potable sources is quite serious.

Chlornitrofen (N,N-diethyl-2,6-dinitro-4-(trifluloromethyl) benzene-1,3-diamine) has been widely used as a diphenyl-ether-derived herbicide for the rice paddy fields. Due to the continuous increase in the application of such pesticide, the necessity of water analysis is always growing. Generally, the traditional techniques used for such purpose are liquid chromatography and gas chromatography with electron capture detection, which is one of the most adequate due to the very low value obtainable for the detection limit [6-11]. However, the above techniques very expensive and demanding well-equipped laboratory installations and a well-trained analysis team. On the other hand, electro analytical procedures can overcome many of such difficulties by analyzing environmental samples without extractions and purification steps, thus shortening and undervaluing the pesticide analysis [12-16].

Graphene, the 2D honey comb lattice of sp²-bonded carbon atoms, has attracted tremendous attention from both the theoretical and experimental scientific communities in recent years because of its unique nanostructure and extraordinary electronic properties [17-21]. In general, graphene has a large surface area, excellent conductivity, and strong mechanical strength [22-32]. Furthermore, the oxidized rings of functionalized and defective graphene sheets contain abundant C–O–C (epoxide) and C–OH groups, while the sheets are terminated with C–OH and –COOH groups [33,34]. Defects of graphene may change its electronic and chemical properties [19]. The functionalized and defective graphene sheets are more hydrophilic and can be easily dispersed in solvents with long-term stability [35]. Moreover, they more easily produce in mass quantities as compared with the carbon nanotubes. They may be used to prepare some novel graphene-based nanocomposite films, which could facilitate the further manipulation and processing of these materials for developing novel electronic devices, such as nanosensors. Nanostructure materials have enormous significance due to their remarkable

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applications in various areas such as optical, electrical and magnetic devices, catalysis and sensors [22-32, 36, 37].

The aim of this work is to study the electrochemical behaviour of the chlornitrofen by differential pulse voltammetry and to establish the initial steps in the development of an electroanalytical procedure to analyze chlornitrofen in environmental samples. The GO modified Fe_2O_3 nanocomposite were prepared and the parameters that would affect the enrichment such as elution solvent and its volume, sample pH, salting out effect, adsorption time and desorption time were investigated in detail.

EXPERIMENTAL

Reagents and Apparatus

Graphene, Fe_2O_3 and citric acid procured from Sigma Aldrich. Chlornitrofen ($C_{12}H_6C_{13}NO_3$) was obtained from Rallis India Ltd.,. The purity of the compound was tested by a melting point determination. Boric acid, trisodium orthophosphate and sodium hydroxide were acquired from SD fine chemicals.

A stock solution was prepared by dissolving the required amount of compound in dimethylformamide. Universal buffers of pH range 2.0 to 10.0 was prepared using 0.2 M boric acid, 0.05 M citric acid and 0.1M trisodium orthophosphate. All the chemicals used were of analytical grade.

Analysis was carried out with an Autolab PGSTAT 101 supplied by Metrohm, Netherlands, with a conventional three-electrode system consisting of platinum wire as the auxiliary electrode, Ag/AgCl as the reference, a GO, Fe_2O_3, graphene oxide and Fe_2O_3 nanocomposite modi ed glassy carbon electrode (Fe_2O_3/GO/GCE) as the working electrode. The pH measurements were carried out with Elico digital pH meter. Dissolved air was removed from the solutions by degassing with oxygen–free nitrogen for 5 minutes. All the experiments were performed at room temperature.

Preparation of nanosensor

After a 5 mg of GO and 10 mg of Fe_2O_3 were dispersed in 10 ml of water by ultrasonication agitation for about 15 min, a homogeneous and stable black suspension was obtained. Prior to modification, the glassy carbon electrode was mechanically polished with alumina paste of different grades to a mirror finish, rinsed and sonicated (3 min) in ultrapure water. Finally, the GCE was coated with 10 µL of the Fe_2O_3/GO suspension and allowed to evaporate water at room temperature in the air. The Fe_2O_3 and GO coated GCE was prepared by the same procedure as explained above.

Voltammetric procedure

After 10 mL of pH 4.0 universal buffer (0.1 mol/L) was placed in the voltammetric cell, the required volume of chlornitrofen standard solutions was added by a micropipette. The solution was deaerated with nitrogen for 10 min, and accumulation was carried out under an open-circuit for 3 min. The reduction-peak current was measured at –0.78 V. Prior to and after every measurement, the Fe_2O_3/GO coated GCE was activated by five successive cyclic voltammetric sweeps between 0.0 to –1.20 V at 100 mV/s in a pH 4.0 universal buffer to produce a reproducible electrode surface.

RESULTS AND DISCUSSION

The electrochemical behaviors of chlornitrofen at a GO, Fe_2O_3 and Fe_2O_3/GO coated GCE have been investigated by cyclic and differential pulse voltammetry in a pH 4.0 universal buffer (0.1 mol/L). Fig. 1 showed the CVs of the GCE, Fe_2O_3/GCE, GO/GCE and Fe_2O_3/GO/GCE in pH 4.0 universal buffer solution in the presence of 5.0 µg mL^{-1} chlornitrofen. There was no obvious peak observed at the bare GCE (Fig. 1a) and the GO (Fig.1b), Fe_2O_3 (Fig.1c) modified GCE showed very weak current response.
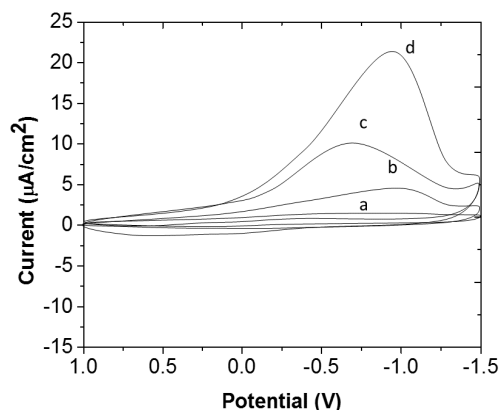
Figure 1 Typical cyclic voltammogram of chlornitrofen for an accumulation time of 80 s at GO/GCE (a); Fe_2O_3/GCE (b); Fe_2O_3-GO/GCE(c); rest time: 10 sec; scan rate: 20 mVs^{-1}; concentration: 5.0 µg mL^{-1}; pH: 4.0 (BR buffer).

However, the strong cathodic peak at +1.02V was observed at the Fe_2O_3/GO/GCE, which is more prominent than those obtained at the bare GCE, GO/GCE and Fe_2O_3/GCE. In this connection the incorporation of GO into Fe_2O_3 nanocomposite possesses most prominent peak indication that the use of GO can significantly enhance the electron transfer between Fe_2O_3 nanocomposite and the electrode. Upon a reverse scan, no corresponding oxidation peak is observed, revealing that the electrode reaction of chlornitrofen is totally irreversible.
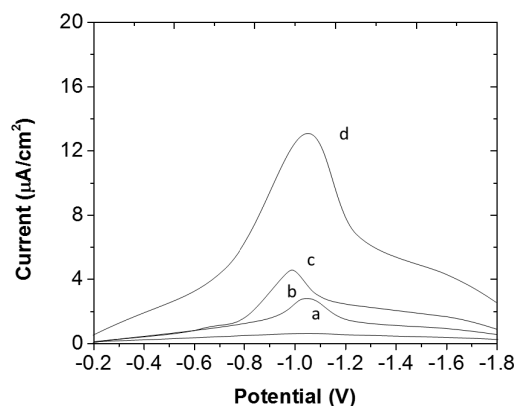
Figure.2 DPV of chlornitrofen at GO/GCE(a); Fe_2O_3/GCE (b); Fe_2O_3-GO/GCE (c); pH 4.0 (BR buffer) accumulation time: 80 s.; stirring rate: 1500 rpm; scan rate: 20 mVs^{-1}; pulse amplitude: 25 mV.

According to the currently accepted mechanism for the electroreduction of aromatic and heteroaromatic nitro compounds [16], the reduction peak is attributed to a four-

electron reduction of the nitro group to the corresponding hydroxylamine and see the Fig. 2. This phenomenon may be caused by the fact that the adsorption of chlornitrofen, or its reductive product, occurs at the electrode surface, and hence inactivates the electrode surface.

The voltammetric response of 5.0 µg.mL^{-1} chlornitrofen at four different electrodes was compared by differential pulse voltammetry (DPV). In a pH 4.0 universal buffer and after 3 min of open-circuit accumulation, a low reduction peak appeared at –0.78 V at the bare GCE (Fig. 3a). Under identical conditions, weak reduction peak current appeared at a GO/GCE, Fe$_2$O$_3$/GCE (Fig. 3b); however, it increased at the Fe$_2$O$_3$/GO film coated GCE (Fig. 3c). The peak current increase may have been caused by the fact that the Fe$_2$O$_3$/GO forms a perfect film on the GCE surface, and thus enhance electron transfer. Compared with that at both bare GCE and a graphite electrode, the reduction peak for the Fe$_2$O$_3$/GO coated GCE increases significantly under comparable conditions, and the reduction peak potential does not change much (Fig. 3d). The remarkable peak current enhancement undoubtedly attributes to the extraordinary properties of GO, such as subtle electronic properties, high aspect ratio and strong absorptive ability.
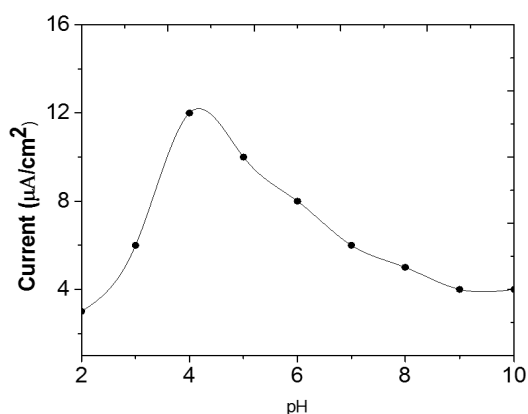

Figure 3 Effect of pH on chlornitrofen at Fe$_2$O$_3$-GO/GCE; accumulation time: 80 s.; rest time: 10 s., stirring rate: 1500 rpm; scan rate: 20 mVs^{-1}; pulse amplitude: 25 mV.

The electrochemical properties of 5.0 µg.mL^{-1} chlornitrofen in various mediums, such as pH 5.0–8.0 phosphate buffer, pH 2.0–8.0 MacIlvaine buffer, and pH 2.0–11.0 Universal buffer (each 0.1 mol/L), were investigated by DPV.
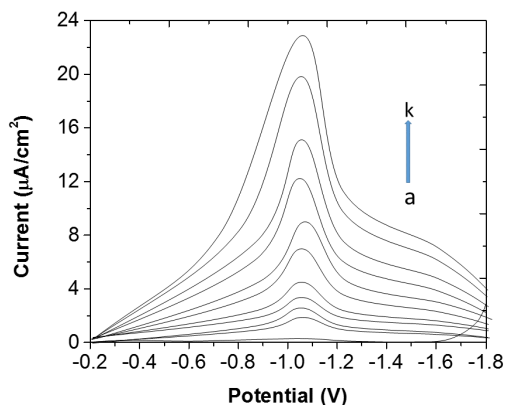

Figure 4 DPV of the NiO-GO/GCE by (a) 0.2, (b) 0.4, (c) 0.8, (d) 1.0 (e) 2.0 (f) 4.0, (g) 8.0, (h) 16, (i) 32 (j) 50 µg mL^{-1} dinoterbon; accumulation time of 80 s, stirring rate:1500 rpm; scan rate: 20 mVs^{-1}; pH: 4.0 (BR buffer); pulse amplitude:25 mV.

It was found that the peak current is highest and the peak shape is well-defined in pH 4.0 Universal buffer as shown in Fig.4. In a 0.1 mol/L Britton–Robinson buffer, the influences of the pH on the reduction peak potential were examined by differential pulse voltammetry. The reduction peak potential (*E*pc) shifts positively as the pH decreases from 11.0 to 3.0, and obeys the following equations: $E_{pc} = -0.21 - 0.057$ pH ($r = 0.997$). The slope of 57 mV/pH indicates that an equal number of electrons and protons are involved in the reduction of chlornitrofen.

Generally, the thickness of the Fe$_2$O$_3$/GO cast film, which is determined by the amount of the Fe$_2$O$_3$/GO suspension on the GCE surface, has an obvious effect on the current responses of chlornitrofen. Fig. 5, represents the reduction-peak current responses for various amounts of the Fe$_2$O$_3$/GO suspension. The reduction peak current gradually increases while gradually increasing the volume of the Fe$_2$O$_3$/GO suspension from 0 to 10 µL. When the amount of Fe$_2$O$_3$/GO suspension increases from 10 to 15 µL, the peak current changes slightly. However, when it exceeds 15 µL, the peak current conversely decreases. GO are ideal electrode materials with excellent electrical conductivity. In principle, the reduction peak current is almost independent of the thickness of the GO cast film. However, Fe$_2$O$_3$ is an insulator, and can lower the electrical conductivity of the cast film, and finally lowers the electron-transfer rate. Hence, the peak current contrarily decreases when the Fe$_2$O$_3$/GO film is too thick.
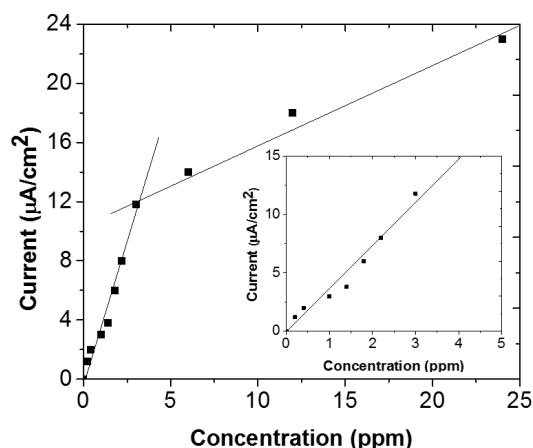
Figure 5 Calibration plot of DPV of dinoterbon

The reduction peak current of 5 µg mL^{-1} chlornitrofen was compared after 3 min of accumulation under different potential by DPV. The peak current almost remained unchangeable as the accumulation potential shifted from 0.50 to –0.60 V, revealing that the accumulation potential had no influence on the reduction peak current of chlornitrofen at the GO-film coated GCE. Thus, an open-circuit accumulation was employed.

The influences of the accumulation time on the reduction peak current of 5 µg mL^{-1} chlornitrofen have been examined; the results are illustrated in Fig. 4. The reduction peak current increases greatly within the first 3 min and then levels off, suggesting that the accumulation of chlornitrofen is very rapid to reach saturation at the Fe$_2$O$_3$/GO.
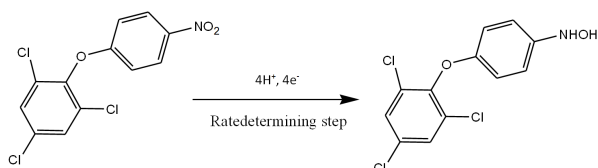
Scheme 1 Reduction mechanism of chlornitrofen

Interferences

To evaluate the interferences of foreign compounds on the determination of chlornitrofen at the 5 μg mL^{-1} level, a systematic study was carried out and the results are given in Table 1. It is found that a 500-fold concentration of uric acid (UA), dopamine (DA), ascorbic acid (AA), xanthine (XA), vitamine E, vitamine A, progesterone, caffeine and cholesterol almost do not influence the current response of 5 μg mL^{-1} chlornitrofen (signal change below 5%). However, some compounds containing a nitro group, such as metronidazole and nitrophenols, interfere with the determination of chlornitrofen, because they contain the same reductive groups that can be reduced near the potentials of chlornitrofen.

Table 1 Determination of chlornitrofen in water samples

Sample	Amount added (μg/ml)	Found (μg/ml)	Recovery (%)*	RSD (%)
Agricultural Run-off-1	5.0	4.99	99.80	0.05
	10.0	9.99	99.90	0.12
	20.0	19.90	99.50	0.03
Agricultural Run-off-2	5.0	4.95	99.00	0.14
	10.0	9.89	98.90	0.06
	20.0	19.89	99.45	0.05
River water	5.0	4.97	99.40	0.08
	10.0	9.89	98.90	0.01
	20.0	19.99	99.95	0.06

*Average of five determinations ± standard deviation.

Calibration graph

The calibration curve for chlornitrofen in pH 5.0 Britton–Robinson buffer was measured by DPV. The best parameters on the Fe$_2$O$_3$-GO coated GCE are an accumulation time of 3 min, a pulse amplitude of 50 mV, a scan rate of 20 mV/s, and a pulse width of 50 ms. The linear segment increases from 0,02 to 40 μg mL-1 (r = 0.998) with a slope of 1.01×10^7 μA (mol/L)$^{-1}$ an intercept of 0.03 μA. The detection limit of 0.064 μg mL^{-1} was obtained at 3 min of accumulation. The relative standard deviation (RSD) of 5.8% for 5 μg mL^{-1} chlornitrofen (n = 5) showed excellent reproducibility.

The long-term stability of the GO-film coated GCE was evaluated by measuring the current responses at a fixed chlornitrofen concentration of 5 μg mL^{-1} over a period of 4 weeks. The GO-film coated GCE was used daily and stored in the air. The experimental results indicated that the current responses deviated by only 5%, suggesting that the GO-film coated GCE possesses long-term stability.

Applications

Water samples, which received run-off water from agricultural field, were collected from penna river belt, Nellore district, A.P., India. These samples were filtered through a Whatman No.41 filter paper. Aliquots of water samples were taken in a 25 mL graduated tube, to it buffer solution was added and analysed as described above. The recoveries of chlornitrofen ranged from 97.50 to 100.0% and the results are summarized in Table. 1.

Vegetable samples, each of 25gm, were taken, collected from agricultural field, where chlornitrofen had been sprayed as an herbicide. The samples were macerated with two 20mL portions of ethanol-demineralized water(1+1), filtered through a Whatman filter paper No.41 and the filtrate was centrifuged at 1850g for10min. In the filtrate was quantitatively transferred into a 50mL calibrated flask and made up to the mark with 50% ethanol. Washings were collected in a 25mL calibrated flask and aliquots were analysed as recommended procedure. The residue of chlornitrofen was dissolved in dimethylformamide and transferred to a 100 mL volumetric flask. Results obtained for the determination of the herbicides in vegetable samples are presented in Table 2. Recoveries of chlornitrofen ranged from 98.00 to 99.87%, which indicates the accuracy and reproducibility of the proposed differential pulse polarographic method.

Table 2 Determination of chlornitrofen in agricultural samples

Sample	Amount added (μg/ml)	Found (μg/ml)	Recovery (%)	RSD (%)
Tomato	5.0	4.99	99.80	0.08
	10.0	9.99	99.90	0.12
	20.0	19.98	99.90	0.04
Brinzal	5.0	4.98	99.60	0.18
	10.0	9.98	99.80	0.02
	20.0	19.95	99.70	0.06

*Average of five determinations ± standard deviation.

CONCLUSIONS

The electrochemical reduction of chlornitrofen was successfully studied by differential pulse polarography. Several voltammetric parameters were optimized and their influence in the peak current or peak potential were adequately described by theoretical models involving electrode process, with the reagent strongly adsorbed on the surface and the transference of eight electrons per chlornitrofen molecule. In the analytical application, differential pulse polarography showed to be a very rapid and sensitive technique that allows reaching detection limits in the range of trace analysis in environmental samples. This is one major advantage of this electroanalytical technique since it allows an economy of time and money in the environmental monitoring of pesticide contamination.

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