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A New Hydroxylamine Electrochemical Sensor Based on an Oxadiazol Derivative and Multi-wall Carbon Nanotubes Modified Glassy Carbon Electrode

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ABSTRACT

A new hydroxylamine sensor has been fabricated by immobilizing oxadiazal derivative at the surface of a glassy carbon electrode (GCE) modified by multi-wall carbon nanotube (MWCNT). The adsorbed thin films of oxadiazol derivative on the MWCNT modified GCE show a pair of peaks with surface confined characteristics. The oxadiazol derivative MWCNT (OMWCNT) modified GCE shows highly catalytic activity toward electrooxidation of hydroxylamine. The results show that the peak potential of hydroxylamine at OMWCNT modified GCE surface shifted by about 331 and 346 mV toward negative values compared with those of MWCNT and activated GCE surface, respectively. In addition, the sensitivity of hydroxylamine determination is improved remarkably by DMWCNT modified electrode. The kinetic parameters, such as the electron transfer coefficient, α, the standard heterogeneous rate constant, k', and exchange current, i_0, for oxidation of hydroxylamine at the OMWCNT modified GCE (OMWCNT-GCE) were determined by cyclic voltammetry measurements. Also diffusion coefficient of hydroxylamine was determined as 4.05×10^{-7} cm^2 s^{-1} by using chronoamperometry technique. Furthermore, the linear dynamic range (2.0-600.0 μM), seasitivity and detection limit (0.61 μM) for hydroxylamine determination was evaluated using differential pulse voltammetry. Excellent electrochemical reversibility of the redox cauple, technical simplicity, good electrocatalytic activity for hydroxylamine and good reproducibility are the advantages af this modified electrode. Finally, the activity of OMWCNT-GCE was also investigated for hydroxylamine determinatian in two natural water samples.

Keywards: Hydroxylamine, Multi-wall carbon nanotubes; Oxadiazol derivatives; Differential pulse voltammetry

INTRODUCTION

Hydroxylamine is knawn as a kind of reducing agent widely used in industry and pharmacy. It is one of the intermediate products of nitrogen-cycle and plays an important role in life science [1]. Hydroxylamine is a natural product found in mammalian cells and bacteria. In the former, NH_2OH may be formed from decompositian of nitrosothiols [2]. Moreover, some hydroxylamine derivatives also constitute a great part of anticancer drugs [3]. In addition, hydroxylamine has been shown to inactivate or inhibit a number of cellular enzymes and some viruses *in vitro*. It is also a skin irritant and sensitizer. Until now, a number of methods have been developed for the determination of hydroxylamine [4-14]. For example, chromatographic [4,5], spectrophotometric [6,7] and electrochemical [8-13] methods have been successfully applied to the determination of hydroxylamine.

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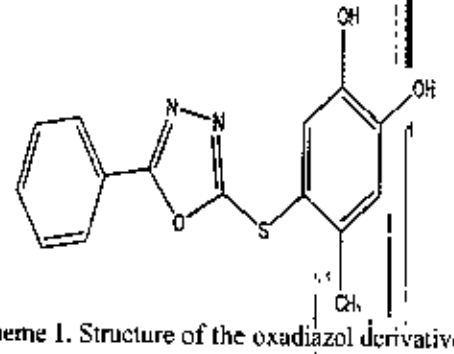
Unfortunately, hydroxylamine with a large overpotential for oxidation at ordinary electrodes is not a suitable analyte for electrochemical measurement techniques. One promising approach for minimizing overvoltage effects is the use of carbon modified electrodes (CMEs) containing specifically selected redox mediators immobilized on conventional electrode surfaces. In recent years, various CMEs have been prepared and applied for determination of hydroxylamine [14–16].

Carbon nanotubes, as a new kind of porous nanostructure material which are 10,000 times thinner than a human hair and 100 times stronger than steel [17], exhibit several unique electrical, geometrical and mechanical properties. Thus, they can be used for promotion of electron transfer reactions when used as electrode material in electrochemical devices. Direct electrocatalytic activity of important chemical and biochemical compounds, such as hydrazine [18], epinephrine [19], cholesterol [20], nicotinamide adenine dinucleotide NADH and hydrogen peroxide [21], ascorbic acid [22], uric acid [23], proteins [24], nitric oxide [25], hydrogen sulfide [26] and glucose [27,28] on the surface of different electrodes modified with carbon nanotubes have been investigated. Thus, these nanomaterials can be used as electrode materials for a wide range of important chemical and biological species [29-35]. Owing to the importance of para-hydroquinone ring substituents on the reactivity of the mediator, in this paper we report the characteristics of another modified electrode, prepared from the electrodeposition of an oxadiazol derivative (see scheme 1 for structure) on the MWCNTs modified GCE (OMWCNT–GCE). The reactivity of this modified electrode is also examined toward the electrocatalytic oxidation of hydroxylamine with the aim of finding its capabilities as an electron transfer mediator. In this report, we also investigate the electrochemical oxidation of hydroxylamine at the MWCNTs modified GCE (MWCNT-GCE) and the oxadiazol derivative modified GCE (OMGCE). The results show that the sensitivity of hydroxylamine determination at an OMWCNT–GCE is remarkably improved and also its overpotential is reduced, when compared to MWCNT–GCE and OMGCE. Finally, the analytical application of OMWCNT-GCE is described as a voltammetric detector for hydroxylamine determination in two water samples.



Scheme 1. Structure of the oxadiazol derivative.

EXPERIMENTAL

Electrochemical apparatus and chemicals

An Autolab potentiostat–galvanostat PGSTAT 30 (Eco Chemie, Utrecht, the Netherlands) equipped with GPES 4.9 software, in conjunction with a three-electrode system and a personal computer was used for electrochemical measurements. A saturated calomel reference electrode (SCE), a platinum wire counter electrode, an oxadiazol derivative electrodeposited on a GCE (OMGCE), multi-wall carbon nanotubes modified GCE (MWCNT-GCE), and an oxadiazol derivative electrodeposited on multi-wall carbon nanotubes modified GCE (OMWCNT–GCE) were employed as working electrodes for the electrochemical studies. The pH was measured with a Metrohm model 691 pH/mV meter.

The multi-wall carbon nanotubes with diameter of 10-20 nm, length of 5-20 μm, and purity of >95% were purchased from Nanolab Inc. (Brighton, MA). Hydroxylamine, the chemicals used for preparation of buffer solutions, and other reagents were of analytical grades from Merck and were used as received. The oxadiazol derivative (5-phenyl-1,3,4-oxadiazole-2-thiol), (scheme 1 for structure), was synthesized and purified according to the procedure described recently [36]. In the present paper, we refer to this oxadiazol derivative as oxadiazol for convenience. Doubly distilled water was used to prepare all the solutions. Buffer solutions (0.1 M) were prepared from H_3PO_4, and the pH was adjusted with saturated NaOH solution. Hydroxylamine solution was freshly prepared just prior to use and all the experiments were carried out at room temperature.

Electrode preparation

The procedure for preparation of the working electrode was as follows. At first, the GCE was carefully polished mechanically with 0.05 μm Al_2O_3 slurry on a piece of polishing cloth and then rinsed with doubly distilled water. For the

electrochemical activation of the electrode, it was immersed in 0.1 M sodium bicarbonate solution and was activated by a continuous potential cycling from 1.4 to 1.7 V at a sweep rate of 100 mV s^{-1} until a stable voltammogram was obtained. For the preparation of oxadiazol modified GCE (OMGCE), the activated GCE (AGCE) was rinsed with doubly distilled water and was modified by 10 cycles of potential sweep 300 to 500 mV at a scan rate of 50 mV s^{-1} in a 0.1 M phosphate buffer solution (pH 7.0) containing 0.10 mM oxadiazol. For the preparation of the MWCNT modified GCE (MWCNT-GCE), 3 µL of MWCNT–OMF suspension (1 mg/1 mL) was placed directly onto the activated GCE surface and dried at room temperature to form a MWCNT film at the GCE surface. The oxadiazol MWCNT modified GCE (OMWCNT-GCE) was prepared by immersing of MWCNT-GCE in a 0.1 M phosphate buffer (pH 7.0) containing 0.1 mM oxadiazol by 8 continuous potential cycles from 300 to 500 mV at scan rate of 50 mV s^{-1}.

RESULTS AND DISCUSSION

Factors influencing the current response of OMWCNT modified GCE

The effect of number of potential cycles and MWCNT value, used for GCE surface modification, on the current response of the OMWCNT-GCE were investigated to optimize test performance. Current response of the modified electrode is expected to be affected by the amount of oxadiazol on the surface of MWCNT modified GCE, which can be controlled by number of potential cycles during the modification of the electrode. The results show that with increasing the number of potential cycles, the current response increased and higher current was found around eight cycles of potential. However, eight cycles of potential is considered as the optimum since for more than eight cycles a decrease in current response is observed, probably, due to the formation of a thick and compact film, which do not facilitate the electron transfer. Current response of the OMWCNT-GCE is also affected by the amount of MWCNT on the surface of GCE, which can be controlled by using the same concentration of MWCNT with different volume of the suspension. After the oxadiazol film was formed on MWCNT modified GCE, the current responses of the modified electrode were recorded. The relationship between the current response and the MWCNT value was shown with the increment of MWCNT value, the current response increased, which implies that higher MWCNT value results in higher sensitivity. However, it was observed in the experiment that the background current also increased with increasing the MWCNT value, which did not facilitate the determination of the hydroxylamine. Therefore, in this work, a moderate MWCNT value of 3 µL of DMF-MWCNT solution (1 mg/1 mL) was selected for fabrication of OMWCNT-GCE.

Electrocatalytic oxidation of hydroxylamine at an OMWCNT modified GCE

Fig. 1 shows the cyclic voltammetric responses of a 0.1 M phosphate buffer solution (pH 7.0) containing 5.0 mM hydroxylamine at OMWCNT-GCE (curve b), MWCNT-GCE (curve c), OMGCE (curve d), and active GCE (curve f). In the absence of hydroxylamine (Fig. 1, curve e), a well behaved redox response corresponding to the electrodeposited oxadiazol can be observed. Upon the addition of 5.0 mM of hydroxylamine, there is an enhancement of the anodic current peak and a very small current is observed in the cathodic peak (Fig. 1, curve d). This is indicative of a very strong electrocatalytic effect. As illustrated, the anodic peak potential for hydroxylamine oxidation at OMWCNT-GCE (curve b) is about 241 mV which is close to that of the surface confined mediator anodic peak potential in the absence of hydroxylamine. Moreover, MWCNT-GCE (curve c) and OMGCE (curve d), peak potentials are about 572 and 347 mV respectively, and at the bare GCE, no current is observed in the presence of hydroxylamine. Table 1 shows the electrochemical characteristics of hydroxylamine oxidation on various electrode surfaces at pH 7.0. From Table 1, it is concluded that the best electrocatalytic effect for hydroxylamine oxidation is at OMWCNT–GCE. For example, according to the results, there is a dramatic enhancement of the anodic peak current at OMWCNT-GCE (curve b) relative to the value obtained at the MWCNT-GCE (curve c) and OMGCE (curve d). Also, the peak potential of hydroxylamine oxidation at OMWCNT-GCE (curve b) shifts by about 331 mV and 106 mV toward the negative values compared with that at a MWCNT-GCE (curve c) and OMGCE (curve d) respectively. In other words, as the data obtained clearly show, the combination of MWCNT and a mediator (the oxadiazol) definitely

improves the characteristics of hydroxylamine oxidation. It can be seen that for the oxadiazol film attached to MWCNT, there exist a pair of well defined redox peaks. Compared to the bare electrode, and considering the porous interfacial layer of the MWCNT-modified GCE, an electron may penetrate through the conductive porous channels onto the electrode more easily, leading to a higher sensitivity. Therefore, MWCNT can be used as a new material for immobilization and electron transfer reactions of oxadiazol

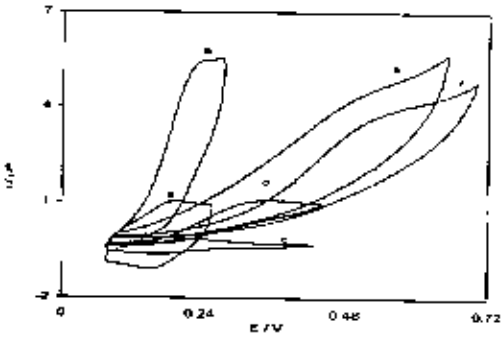


Fig. 1. Cyclic voltammograms of the OMWCNT–GCE in 0.1 M phasphate buffer solution (pH 7.0) at scan rate 20 mV s^{-1} in (a) absence and (b) presence of 5.0 mM hydroxylamine (d), (e) and (f) as (b) for OMGCE, MWCNT–GCE and activeted GCE respectively. (c) as (a) for OMGCE.

The effect of scan rate on the electrocatalytic oxidation of hydroxylamine at OMWCNT-GCE was used to get information about the rate determining step. Fig. 2 shows the cyclic voltammograms of the modified electrode in a 0.1 M phosphate buffer (pH 7.0) containing 1.5 mM hydroxylamine at different scan rates. Inset of Fig. 2 shows that a plot of the catalytic peak current versus the square root of scan rate is linear. This result indicates that, at an appropriate overpotential, the process is diffusion rather than surface controlled, which it is the ideal case for quantitative applications [37]. Also, from this plot, one can calculate an approximate total number of electrons in the overall oxidation of hydroxylamine (n) using the following equation for diffusion controlled electrochemically irreversible reaction [38].

$$I_p = 3.01\times10^5 n[(1-\alpha)n_\alpha]^{1/2} A C_b D^{1/2} \nu^{1/2} \quad (1)$$

Table 1. Comparison of electrocatalytic oxidation characteristics of hydroxylamine (5.0 mM) on various electrode surfaces at pH 7.0

Name of electrode[a]	Oxidation peak potential (mV)	Oxidation peak current (μA)
AGCE	587	3.48
MWCNT–GCE	572	3.85
OMGCE	347	1.19
OMWCNT–GCE	241	4.10

[a]AGCE: activated glassy carbon electrode, MWCNT–GCE: multi–wall carbon nanotubes modified glassy carbon electrode, OMCCE: oxadiazol modified glassy carbon electrode, OMWCNT–GCE: oxadiazol multi–wall carbon nanotubes modified glassy carbon electrode.

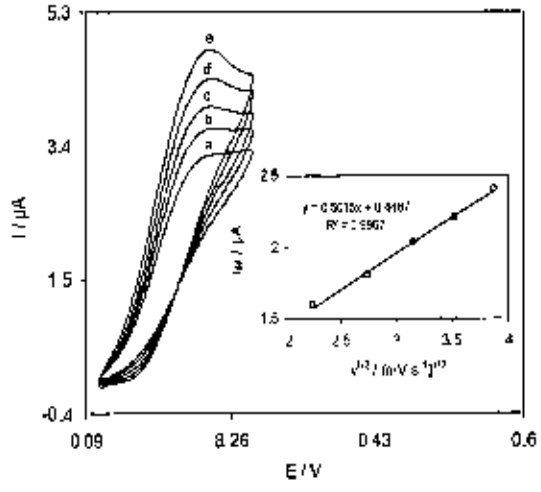


Fig. 2. Cyclic voltammograms of the OMWCNT modified GCE in 0.1 M phosphate buffer solution (pH 7.0) containing 1.5 mM hydroxylamine at scan rates: (a) 5, (b) 7.5, (c) 10.0, (d) 12.5 and (e) 15.0 mV s^{-1}. Inset: Variation of the electrocatalytic current versus the square root of scan rate.

where D is the diffusion coefficient of hydroxylamine ($D=4.05\times10^{-7}$ cm^2 s^{-1} obtained by chronoamperometry), C_b is the bulk concentration of hydroxylamine (1.5 mM), and A is the electrode surface area (0.0314 cm^2). Values for α and n_a which are deduced from Tafel plots (see below) are 0.30 and 1 respectively. This produces an approximate value, $n = 2.1\cong2$, for the total number of electrons involved in the anodic oxidation of hydroxylamine. Thus, the rate determining step is given in Eq. (3) with a rate constant k. In above conditions, for E_rC_i catalytic (EC_i') mechanism, Andrieux and Saveant theoretical model [39] can be used to calculate the catalytic rate constant, k. Based on this theory, the average value of the catalytic rate constant between hydroxylamine and oxadiazol, k', is calculated to be $(6.9\pm0.14)\times10^{-4}$ cm s^{-1}.

$$Oxadiazol_{(reduced\ form)} \rightleftarrows Oxadiazol_{(oxidized\ form)} + 2H^+ + 2e \quad (2)$$

$$2\ Oxadiazol_{(oxidized\ form)} + 2NH_2OH \rightarrow 2\ Oxadiazol_{(reduced\ form)} + N_2O + H_2O \quad (3)$$

The overall oxidation of hydroxylamine by the modified electrode is given in Eq. (4).

$$2NH_2OH \rightarrow N_2O + H_2O + 4H^+ + 4e \quad (4)$$

In order to obtain information about the rate determining step, Tafel plots were drawn (Inset of Fig. 3), derived from points of the Tafel region of the linear sweep voltammograms in Fig. 3. The results of polarization studies for electrooxidation of hydroxylamine at OMWCNT-GCE show that, for all potential sweep rates, the average Tafel slope is 12.6 V^{-1}. Referring to equation (5) [37], the average Tafel slope of 12.6 V^{-1} agrees well with the involvement of one electron in the rate determining step of electrode process, assuming a charge transfer coefficient of α=0.30.

$$\text{Tafel slope} = (1-\alpha)n_aF/\ 2.3RT \quad (5)$$

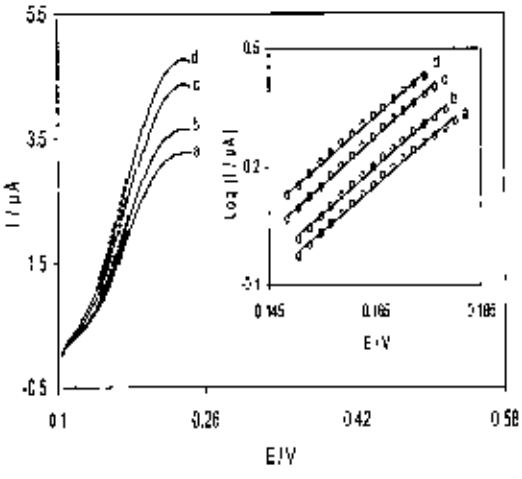


Fig. 3. Linear sweep voltammogram of the OMWCNT modified GCE in 0.1 M phosphate buffer solution (pH 7.0) containing 1.5 mM hydroxylamine at scan rates: (a) 5, (b) 7.5, (c) 12.5 and (d) 15.0 mV s^{-1}. Inset shows the Tafel plot derived from the linear sweep voltammogram.

In addition, the exchange current, i_0, is obviously readily accessible from the intercept of the Tafel plots [37]. The average value of the exchange current, i_0, of hydroxylamine at OMWCNT is found to be 0.0121 μA

Chronoamperometric studies

The catalytic oxidation of hydroxylamine at OMWCNT-GCE surface was also studied by chronoamperometry. Chronoamperograms were obtained at different concentrations of hydroxylamine at a potential step of 270 mV (Fig. 4). For an electroactive material (hydroxylamine in this case) with a diffusion coefficient, D, the current corresponding to the electrochemical reaction (under diffusion control) is described by Cottrell equation [37]:

$$I = nFAD^{1/2}C/\pi^{1/2}t^{1/2} \quad (6)$$

where D and C are the diffusion coefficient (cm^2 s^{-1}) and bulk concentration (mol cm^{-3}) of the

analyte respectively. Fig. 4A, shows the experimental plots of I versus $t^{-1/2}$ with the best fits for different concentrations of hydroxylamine employed. The slopes of the resulting straight lines were then plotted versus the hydroxylamine concentration, from whose slope and using the Cottrell equation [37] we calculated the average diffusion coefficient of 4.05×10^{-7} cm^2 s^{-1} for hydroxylamine. The calculated diffusion coefficient is in a good agreement with that previously reported for hydroxylamine [1].

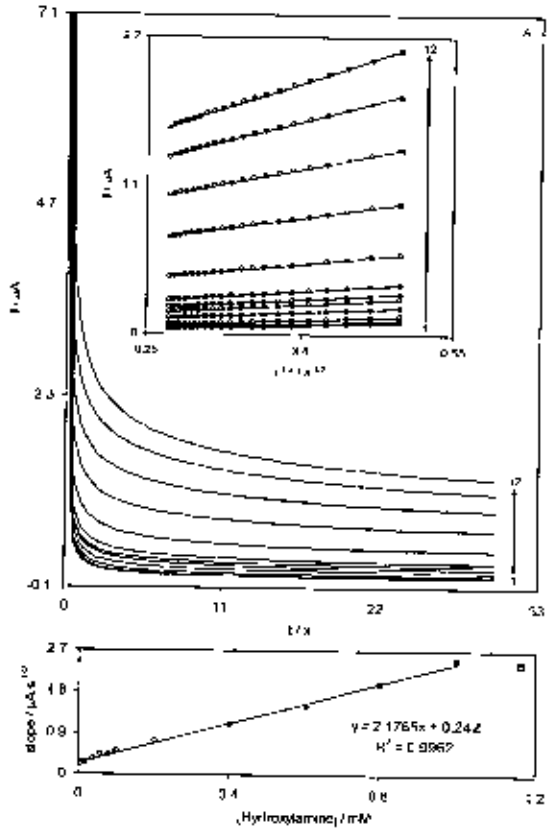


Fig. 4. (A) Chronoamperometric response of the OMWCNT-GCE in 0.1 M phosphate buffer solution (pH 7.0) at potential step of 270 mV for different concentrations of hydroxylamine. The number of 1 to 12 correspond to 0.008, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mM hydroxylamine. Inset A: Plots of I versus $t^{-1/2}$ obtained from the chronoamperograms (B) Shows plot of the slope of straight lines against the hydroxylamine concentration.

Differential pulse voltammetry investigations

Fig. 5 shows the differential pulse voltammograms (DPVs) of various concentrations of hydroxylamine in a 0.1 M phosphate buffer (pH 7.0) at OMWCNT-GCE. The plot of the electrocatalytic peak current of hydroxylamine at the surface of OMWCNT modified GCE, corrected for any residual current of the modified electrode in supporting electrolyte, versus hydroxylamine concentration is shown in inset of Fig. 5. This figure shows clearly that the calibration plot is linear, between 2.0 to 600.0 μM hydroxylamine. The lower detection limit of hydroxylamine, C_m, was obtained using the equation $C_m=3s_{bi}/m$ [40], where s_{bi} is the standard deviation of the blank response (μA) and m is the slope of the calibration plot 7.84 μA mM^{-1}. In this experiment, eleven replicate measurements were performed on the blank solution and the resulting data were then treated statistically to obtain s_{bi}=0.0016 μA. From the analysis of these data, we estimate that the limit of detection of hydroxylamine is 0.61 μM. Also the average voltammetric peak current I and the precision estimated in terms of the coefficient of variation for repeated measurements (n=15) of 10.0 μM hydroxylamine at OMWCNT-GCE were 0.463 ± 0.011 μA and 2.38%, respectively. The value of variation coefficient indicates that the OMWCNT-GCE is stable and does not undergo surface fouling during the voltammetric measurements., It also demonstrates the fact that the result obtained at the OMWCNT-GCE is reproducible, and is a proof of the OMWCNT-GCE reproducibility in analytical applications

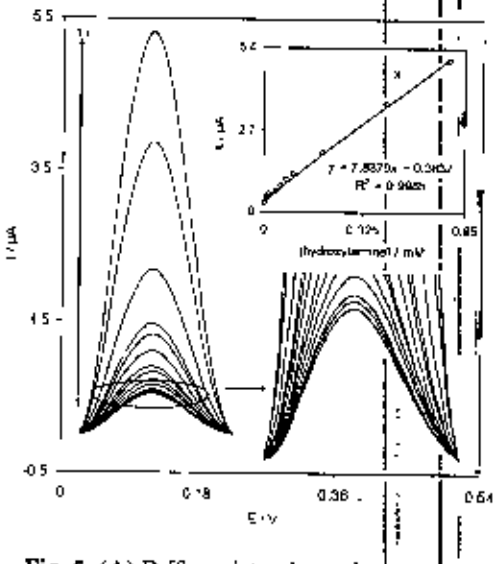


Fig. 5. (A) Differential pulse voltammograms at OMWCNT-GCE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of hydroxylamine. The numbers 1 to 13 correspond to 2.0, 4.0, 6.0, 8.0, 10.0, 20.0, 40.0, 60.0, 80.0, 100.0, 200.0, 400.0 and 600.0 μM hydroxylamine. Inset shows Plot of the electrocatalytic peak current, corrected for any residual current, as a function of hydroxylamine concentration.

Determination of hydroxylamine in tap and well water samples

From the results that are mentioned in the previous section, it is apparent that OMWCNT-GCE possesses a high sensitivity and a good detection limit to determine hydroxylamine in real samples. In order to test its practical applieation. the modified electrode was used to determine hydroxylamine in two natural water samples. For this propose, 4 mL of natural water sample was diluted to 10 mL with a 0.1 M phosphate buffer solution (pH 7.0). Then, certain amounts of hydroxylamine were added and their recovery were determined by differential pulse voltammetry. The results (Table 2) show that the recoveries are within the range from 99.2 to 103.7%. The results that were obtained using the proposed method were validated against a calibration graph for hydroxylamine within a range of 2.0 to 600.0 μM (see section 3 4). The results of the proposed methad proved to match well with the calibration graph.

CONCLUSIONS

The results nf this study show that oxadiazol can be immobilized easily on the surface of multi-wall earbon uanotubes (MWCNT) modified glassy carbon electrode (GCE). The oxadiazol MWCNT modified GCE (OMWCNT-GCE) presents a stable and excellent electrocatalytic activity for hydroxylamine. The diffusion coeffieient of hydroxylamine is calculated for experimental conditions, using chronoamperometric results. It has been shown that differential pulse voltammetry can be used as analytical method for determination of hydroxylamine in varinus solutions.

Table 2. Determination of hydroxylamine in water samples using calibration plots obtained by OMWCNT–GCE.

Samples	Added (μM)	Found (μM)	RSO (%)	Recovery %
Drinking water	–	<DL	–	–
	15.0	15.3	2 1	102.0
	30.0	31.1	2.7	103.7
Tap water	–	<DC	–	–
	25.0	24.8	3 2	99.2
	50.0	50.7	1.7	101 4

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