

Full Paper

A Sensitive Electrochemical Sensor for Hydroxylamine Determination: Using Ionic Liquids and Magnetic Core-shell $\text{Fe}_3\text{O}_4@ \text{TiO}_2/\text{MWCNT}$ Nanocomposite and 2-(4-Oxo-3-phenyl-3,4-dihydroquinazoliny)- N' -phenyl-Hydrazinecarbothioamide as Mediator

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Abstract- A sensitive electrochemical sensor for determination of hydroxylamine has been introduced. This sensor profits by 2-(4-Oxo-3-phenyl-3,4-dihydroquinazoliny)- N' -phenyl-hydrazinecarbothioamide (2PHC) as mediator and magnetic core-shell $\text{Fe}_3\text{O}_4@ \text{TiO}_2/\text{MWCNT}$ nanocomposite and ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) to improve the working electrode behavior. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry, and differential pulse voltammetry (DPV) are used to study of the suitability of 2PHC, at the surface of modified electrode, as a mediator for the electrocatalytic oxidation of hydroxylamine in aqueous solutions. The electrocatalytic peak current of hydroxylamine oxidation shows a linear dependence on hydroxylamine concentration in the range of 0.1–500.0 μM , by DPV in optimized conditions at pH 7.0. The detection limit (3σ) was obtained 52.0 nM. Electrochemical parameters such as electron transfer coefficient, α and diffusion coefficient, D , are also determined. The proposed method was successfully applied as a highly sensitive, selective, simple, and precise method for hydroxylamine determination in the water samples.

Keywords- Hydroxylamine, $\text{Fe}_3\text{O}_4@ \text{TiO}_2/\text{MWCNT}$ nanocomposite, Ionic liquids, Modified electrodes

1. INTRODUCTION

Hydroxylamine belongs to an important class of reducing agents, which are commonly used for synthesis of pharmaceutical intermediates and final drug substances. In contrast, hydroxylamine well-known as a mutation agent, moderately toxic and harmful to human, animals, and even plants, even at modest level [1-7]. Likewise in environmental viewpoint, oceanic hydroxylamine produced along nitrous oxide production, considered as a hazardous compound [8-10]. Thereupon, existence of a method for determination of hydroxylamine in low level, is highly important [11]. Many of approaches developed and successfully applied for hydroxylamine determination such as spectrophotometry, high performance liquid chromatography, gas chromatography, potentiometry, polarography, biamperometry and electrochemical [12-19]. However, the processes involved in many of these methods are extremely complex, and the linear ranges are relatively narrow and have low precision [20-23]. Fortunately, electrochemical techniques offer the opportunity for portable, cheap and rapid methodologies [24-29].

However, many analytes cannot be electrooxidized at bare carbon electrodes. One promising approach is the use of chemically modified electrodes (CMEs) containing specifically selected redox mediators immobilized on conventional electrode materials [30]. Recently, various chemically modified electrodes (CMEs) have been prepared and applied in the determination of materials, which can significantly lower the overpotentials and increase the oxidation current response [31-34].

Carbon nanotubes (CNTs) have excellent optical, electric, and magnetic properties due to their unique coiled structures. Recently, many researchers have focused on the surface functionalization of multi-walled CNTs (MWCNTs) and the use of MWCNTs in composite materials. But the excellent performance of CNTs is limited due to their easy agglomeration in aqueous solution [35-44]. The magnetism of Fe_3O_4 nanoparticles is strong, so it has wide potential applications in many fields such as magnetic recording, sensor, microwave absorbing, catalyst, electrochemistry, and especially in the biomedicine due to its magnetic response. Furthermore, Fe_3O_4 nanoparticles has excellent magnetic response. It can be used in many potential applications such as cell separation, immobilized enzyme, immunodiagnosis, tumor targeting therapy, DNA separation, and nucleic acid hybridization [45-50]. Core-shell particles consist of at least two phases with different chemical compositions [51-54]. Usually core-shell particles are composed of magnetic or luminescent core, which is coated with inert or inactive shell like SiO_2 , TiO_2 or polymer one [55-58]. The presence of a magnetic element in core-shell particles is additionally attractive owing to their applications on biomedicine, biotechnology, biosensors, enzyme and protein immobilization. Also, external layer can protect the core or may be functionalized, using suitable functional groups and further used in many bioapplications [59-61].

Ionic liquids (ILs) are either organic salts or mixtures of salts that are fluid at room or near-room temperature. Due to the excellent physicochemical properties of room temperature ionic liquids (RTILs), such as high ionic conductivity, wide electrochemical windows, negligible vapor pressure, chemical and thermal stability, good antifouling ability, well biocompatibility, and inherent catalytic ability; they can be used as the modifier or the supporting electrolyte in electroanalysis [62-66].

Thus, in this paper, initially the preparation and suitability of a 2-(4-Oxo-3-phenyl-3,4-dihydroquinazoliny)-*N'*-phenyl-hydrazinecarbothioamide/ ionic liquid/ magnetic core-shell $\text{Fe}_3\text{O}_4@ \text{TiO}_2/\text{MWCNT}$ nanocomposite modified carbon paste electrode (2PHC/IL/FTCNT/CPE) as a new electrode in the electrocatalysis and determination of hydroxylamine in an aqueous buffer solution was described. Then the analytical performance of the modified electrode in quantification of hydroxylamine was also evaluated. Finally this new constructed electrochemical sensor was used for determination of hydroxylamine in real samples.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode (Azar Electrode, Urmia, Iran), a platinum wire (Azar Electrode, Urmia, Iran), and 2PHC/IL/FTCNT/CPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. Hydroxylamine and all of the other reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0. Ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) was purchased from Sigma Aldrich. 2-(4-Oxo-3-phenyl-3,4-dihydroquinazoliny)-*N'*-phenyl-hydrazinecarbothioamide was synthesized in our laboratory as reported previously [20].

2.2. Preparation of the electrode

To obtain the best conditions in the preparation of the 2PHC/IL/FTCNT/CPEs, we optimized the ratio of 2PHC, IL and $\text{Fe}_3\text{O}_4@ \text{TiO}_2/\text{MWCNT}$ nanocomposite. The results of our studied showed that the maximum peak current intensity of hydroxylamine could be obtained at the surface of 2PHC/IL/FTCNT/CPE with optimum ratio of 2PHC, IL and $\text{Fe}_3\text{O}_4@ \text{TiO}_2/\text{MWCNT}$ nanocomposite.

The 2PHC/IL/FTCNT/CPEs were prepared by dissolving 0.01 g 2PHC in CH₃Cl and then added in 0.95 g graphite powder and 0.04 g Fe₃O₄@TiO₂/MWCNT nanocomposite with a mortar and pestle. Then, 0.3 mL IL and 0.6 mL of paraffin oil were added to the above mixture and mixed for 15 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a glass tube. A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, 2PHC modified CPE electrode (2PHC /CPE) without Fe₃O₄@TiO₂/MWCNT nanocomposite and IL, Fe₃O₄@TiO₂/MWCNT nanocomposite carbon paste electrode (FCPE) without 2PHC and IL, and unmodified CPE in the absence of 2PHC, IL, and Fe₃O₄@TiO₂/MWCNT nanocomposite were also prepared in the same way.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of 2PHC/IL/FTCNT/CPE

2PHC/IL/FTCNT/CPE was prepared and its electrochemical behaviors were studied using cyclic voltammetry (CV) technique. A pair of reversible peaks observed at $E_{pa}=0.21$ V and $E_{pc}=0.11$ V. The half-wave potential ($E_{1/2}$) and ΔE_p were 0.16 and 0.10 V, respectively. The peak separation potential, ($\Delta E_p=E_{pa}-E_{pc}$), is greater than the $(59/n)$ mV expected for a reversible system, which indicates a quasi reversible behavior for the mediator in an aqueous medium [68]. The electrode capability for the generation of a reproducible surface was examined by cyclic voltammetric data obtained in optimum solution pH 7.0 from five separately prepared 2PHC/IL/FTCNT/CPEs. The calculated RSD for various parameters accepted as the criteria for a satisfactory surface reproducibility (about 1–4%), which is virtually the same as that expected for the renewal or ordinary carbon paste surface. However we regenerated the surface of 2PHC/IL/FTCNT/CPE before each experiment according to our previous results.

In addition, the long-term stability of the 2PHC/IL/FTCNT/CPE was tested over a three-week period. When CVs were recorded after the modified electrode was stored in atmosphere at an ambient temperature, the peak potential for hydroxylamine oxidation was unchanged and the current signals showed less than 2.7% decrease relative to the initial response. The antifouling properties of the modified electrode toward hydroxylamine and its oxidation products were investigated by recording the CVs of the modified electrode before and after use in the presence of hydroxylamine. CVs were recorded in the presence of hydroxylamine after having cycled the potential 15 times at a scan rate of 10 mV s⁻¹. The peak potentials were unchanged and the currents decreased by less than 2.6%. Therefore, at the surface of 2PHC/IL/FTCNT/CPE, not only the sensitivity increases, but the fouling effect of the analyte and its oxidation product also decreases.

3.2. Electrocatalytic oxidation of hydroxylamine at a 2PHC/IL/FTCNT/CPE

The electrochemical behavior of hydroxylamine and 2PHC are dependent on the pH value of the aqueous solution. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of hydroxylamine. Thus the electrochemical behavior of hydroxylamine was studied in 0.1 M PBS in different pH values ($2.0 < \text{pH} < 9.0$) at the surface of 2PHC/IL/FTCNT/CPE by CV. It was found that the electrocatalytic oxidation of hydroxylamine at the surface of 2PHC/IL/FTCNT/CPE was more favored under neutral conditions than in acidic or basic neutral medium. This appears as a gradual growth in the anodic peak current and a simultaneous decrease in the cathodic peak current in the CVs of 2PHC/IL/FTCNT/CPE. Thus, the pH 7.0 was chosen as the optimum pH for electrocatalysis of hydroxylamine oxidation at the surface of 2PHC/IL/FTCNT/CPE.

Fig. 1 depicts the CV responses for the electrochemical oxidation of 0.15 mM hydroxylamine at unmodified CPE (curve b), FTCNT/CPE (curve d), 2PHC/CPE (curve e) and 2PHC/IL/FTCNT/CPE (curve f). As shown, the anodic peak potential for the oxidation of hydroxylamine at 2PHC/IL/FTCNT/CPE (curve f) and 2PHC/CPE (curve e) was about 210 mV, while at the FTCNT/CPE (curve d) and bare CPE (curve b), hydroxylamine was not oxidized until the potential reached +1,200 mV. These results demonstrate that the best electrocatalytic effect for hydroxylamine oxidation was observed at 2PHC/IL/FTCNT/CPE (curve f). However, 2PHC/IL/FTCNT/CPE shows much higher anodic peak current for the oxidation of hydroxylamine compared to 2PHC/CPE, indicating that the combination of ionic liquid, $\text{Fe}_3\text{O}_4@ \text{TiO}_2/\text{MWCNT}$ nanocomposite and the mediator (2PHC) has significantly improved the performance of the electrode toward hydroxylamine oxidation. In fact, 2PHC/IL/FTCNT/CPE in the absence of hydroxylamine exhibited a well-behaved redox reaction (Fig. 1, curve c) in 0.1 M PBS (pH 7.0). However, there was a drastic increase in the anodic peak current in the presence of 0.25 mM hydroxylamine (curve f), which can be related to the strong electrocatalytic effect of the 2PHC/IL/FTCNT/CPE towards this compound [68]. Also, unmodified CPE (curve a) in 0.1 M PBS (pH 7.0) did not show any oxidation peak.

The effect of potential scan rate on the electrocatalytic oxidation of hydroxylamine at the 2PHC/IL/FTCNT/CPE was investigated by LSV (Fig. 2). As can be observed in Fig. 2, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height (I_p) vs. the square root of scan rate ($v^{1/2}$) was found to be linear in the range of 10-50 mV s^{-1} , suggesting that, at sufficient over potential, the process is diffusion rather than surface controlled (Fig. 2A). A plot of the scan rate-normalized current ($I_p/v^{1/2}$) vs. scan rate (Fig. 2B) exhibits the characteristic shape typical of an EC' process [68].

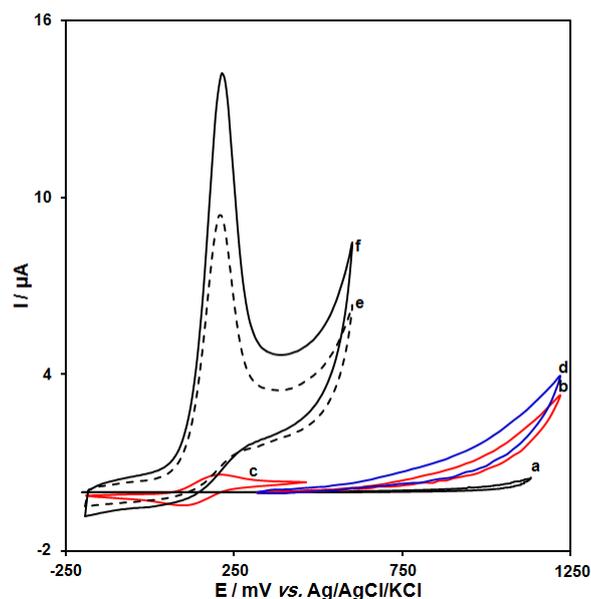


Fig. 1. CVs of (a) unmodified CPE in 0.1 M PBS (pH 7.0); (b) unmodified CPE in 0.1 M PBS (pH 7.0) containing 0.15 mM hydroxylamine; (c) 2PHC/IL/FTCNT/CPE in 0.1 M PBS (pH 7.0); (d) FTCNT/CPE in 0.1 M PBS (pH 7.0) containing 0.15 mM hydroxylamine; (e) 2PHC/CPE in 0.1 M PBS (pH 7.0) containing 0.15 mM hydroxylamine and (f) 2PHC/IL/FTCNT/CPE in 0.1 M PBS (pH 7.0) containing 0.15 mM hydroxylamine. In all cases the scan rate was 10 mV s^{-1}

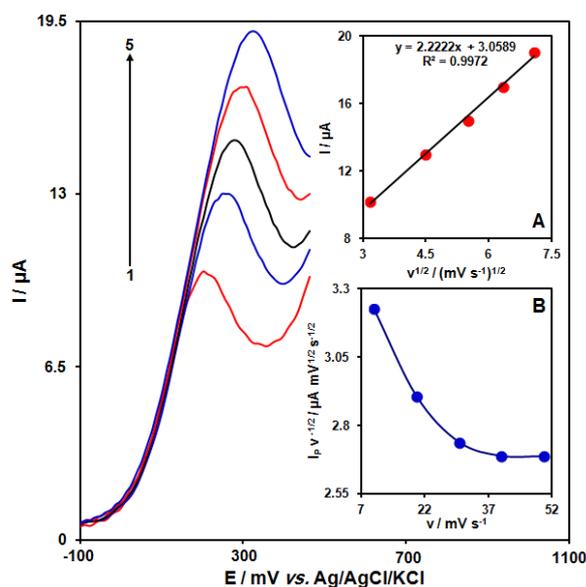


Fig. 2. LSVs of 2PHC/IL/FTCNT/CPE in 0.1 M PBS (pH 7.0) containing $150.0 \mu\text{M}$ hydroxylamine at various scan rates; numbers 1-5 correspond to 10, 20, 30, 40 and 50 mV s^{-1} , respectively. Insets: Variation of (A) anodic peak current vs. $v^{1/2}$ and (B) normalized current ($I_p/v^{1/2}$) vs. v

Fig. 3 shows the LSV of a 2PHC/IL/FTCNT/CPE obtained in 0.1 M PBS (pH 7.0) containing 150.0 μM hydroxylamine, with a sweep rate of 10 mV s^{-1} . The points show the rising part of the voltammogram (known as the Tafel region), which is affected by the electron transfer kinetics between hydroxylamine and 2PHC/IL/FTCNT/CPE. If deprotonation of hydroxylamine is a sufficiently fast step, the number of electrons involved in the rate determining step can be estimated from the slope of the Tafel plot. The inset of Fig. 3 shows a Tafel plot that was drawn from points of the Tafel region of the linear sweep voltammogram. The Tafel slope of 0.1561 V obtained in this case agrees well with the involvement of one electron in the rate determining step of the electrode process, assuming a charge transfer coefficient of $\alpha=0.62$.

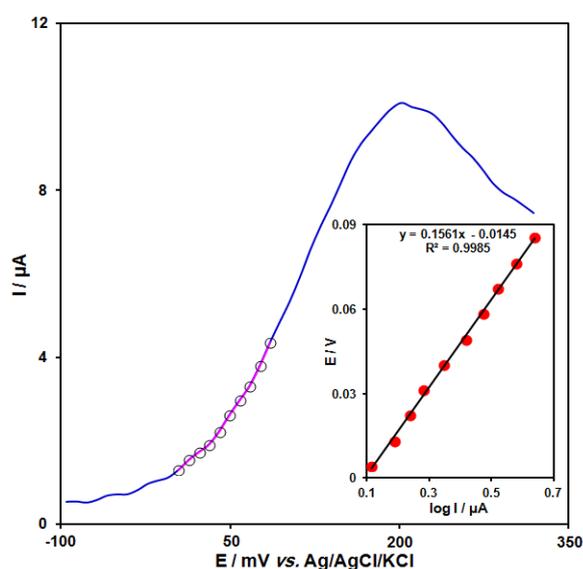


Fig. 3. LSV (at 10 mV s^{-1}) of electrode in 0.1 M PBS (pH 7.0) containing 150.0 μM hydroxylamine. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV.

3.3. Chronoamperometric measurements

Chronoamperometric measurements of hydroxylamine at 2PHC/IL/FTCNT/CPE were carried out by setting the working electrode potential at 0.3 V vs. Ag/AgCl/KCl (3.0 M) for the various concentration of hydroxylamine in 0.1 M PBS (pH 7.0) (Fig. 4). For an electroactive material (hydroxylamine in this case) with a diffusion coefficient of D , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [68].

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where D and C_b are the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of hydroxylamine (Fig. 4A). The slopes of the resulting straight lines were then plotted vs. hydroxylamine concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the D was found to be $1.7 \times 10^{-6} \text{ cm}^2/\text{s}$.

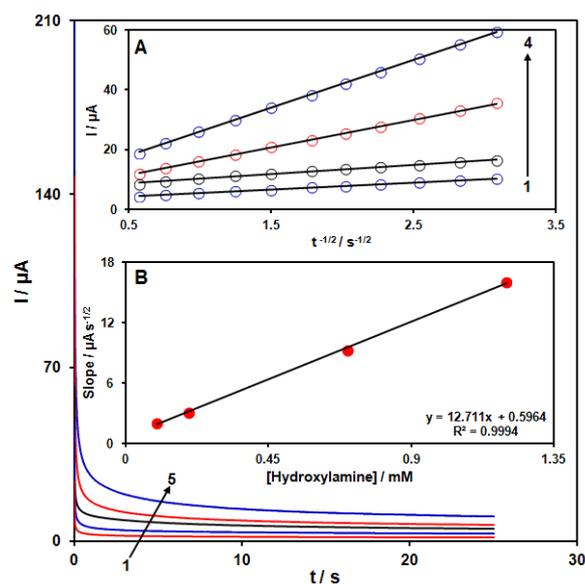


Fig. 4. Chronoamperograms obtained at 2PHC/IL/FTCNT/CPE in 0.1 M PBS (pH 7.0) for different concentration of hydroxylamine. The numbers 1–5 correspond to 0.0, 0.1, 0.2, 0.7 and 1.2 mM of hydroxylamine. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 2–5 and (B) Plot of the slope of the straight lines against hydroxylamine concentration

3.4. Calibration plot and limit of detection

The electrocatalytic peak current of hydroxylamine oxidation at the surface of the 2PHC/IL/FTCNT/CPE can be used for determination of hydroxylamine in solution. Therefore, DPVs were performed using modified electrode in 0.1 M PBS (pH 7.0) containing various concentration of hydroxylamine (Fig. 5).

The plot of peak current vs. hydroxylamine concentration consisted of a linear segments with slopes of $0.051 \mu\text{A}/\mu\text{M}$ in the concentration range of from 1.0×10^{-7} to 5.0×10^{-4} M. The detection limit (3σ) of hydroxylamine was found to be 52.0 nM.

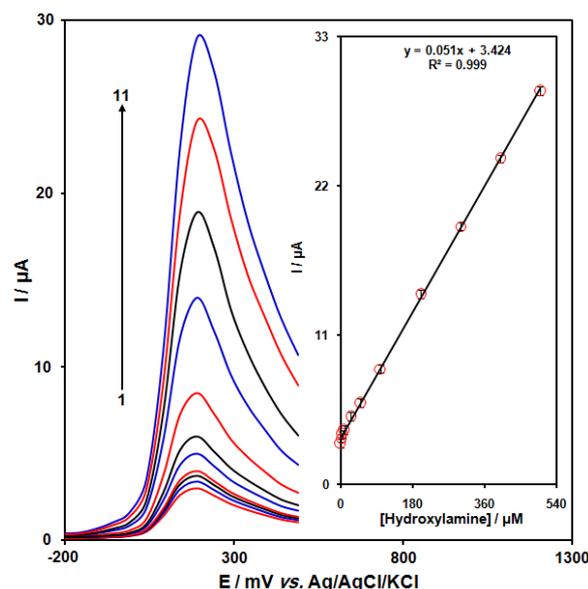


Fig. 5. DPVs of 2PHC/IL/FTCNT/CPE in 0.1 M (pH 7.0) containing different concentrations of hydroxylamine. Numbers 1–11 correspond to 0.1, 1.0, 5.0, 10.0, 25.0, 50.0, 100.0, 200.0, 300.0, 400.0 and 500.0 μM of hydroxylamine. Inset: plot of the electrocatalytic peak current as a function of hydroxylamine concentration in the range of 0.1–500.0 μM

3.5. Interference study

The influence of various substances as potential interfering compounds with the determination of hydroxylamine was studied under the optimum conditions. The potential interfering substances were chosen from the group of substances commonly found with hydroxylamine water samples. The tolerance limit was taken as the maximum concentration of the foreign substances, which caused an approximately $\pm 5\%$ relative error in the determination. The result of interfering studied shows that Ni^{2+} , CN^- , Br^- , K^+ , Li^+ , Ag^+ , Zn^{+2} , Pb^{+2} , Mg^{2+} , Mn^{+2} , Co^{3+} , Cr^{2+} , and SCN^- , glucose, sucrose, urea, lactose and fructose did not affect the selectivity. These results demonstrate that the modified electrode has a good selectivity for hydroxylamine.

3.6. Real sample analysis

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of hydroxylamine in water samples. Based on the repeated differential pulse voltammetric responses ($n=5$) of the diluted analytes and the samples that were spiked with specified concentration hydroxylamine was made for determination of hydroxylamine concentrations in water samples. The results are listed in Table 1.

Satisfactory recovery of the experimental results was found for hydroxylamine. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

Table 1. The application of 2PHC/IL/FTCNT/CPE for determination of hydroxylamine in water samples (n=5)

Sample	Spiked (μM)	Found (μM)	Recovery (%)	R.S.D. (%)
Tap water	0	-	-	-
	5.0	4.9	98.0	3.7
	10.0	10.3	103.0	2.8
	15.0	15.1	100.7	2.9
	20.0	20.2	101.0	1.6
River water	0	-	-	-
	7.5	7.6	101.3	2.4
	12.5	12.2	97.6	2.7
	17.5	18.1	103.4	3.5
	22.5	22.3	99.1	2.1

4. CONCLUSIONS

We propose an electrochemical sensor for highly sensitive and trace determination of hydroxylamine. This electrochemical sensor uses 2-(4-Oxo-3-phenyl-3,4-dihydroquinazolinyl)-*N'*-phenyl-hydrazinecarbothioamide (2PHC) as mediator. 2PHC shows high catalytic effects on the oxidation of hydroxylamine. Calibration curve using of DPV method was done and demonstrated applicability of this sensor for determination of hydroxylamine in the range from 1.0×10^{-7} to 5.0×10^{-4} M. Therefore, we propose this method as a rapid, reproducible, highly sensitive and selective for the hydroxylamine determination in very wide concentration ranges. Finally, this sensor applied successfully for determination of hydroxylamine in water samples.

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