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Original scientific paper

Voltammetric determination of hydroxylamine in water and waste water samples using a NiO nanoparticle/new catechol derivative modified carbon paste electrode

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Abstract

A (9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-4-ethylbenzene-1,2-diol (DED) modified NiO/NPs carbon paste electrode "(DED/NiO nanoparticle (NiO/NPs)/CPE) was constructed for determination of hydroxylamine (HX). The cyclic voltammogram showed that the electrocatalytic oxidation of HX at the surface of DED/NiO/NPs/CPE occurs at a potential of about 800 mV less positive than with an unmodified electrode. Square-wave voltammetry results presented that the electrocatalytic oxidation peak currents of HX in pH 8.0 had two linear dynamic ranges in the range of 0.1 to 2.0 and 2.0 to 400.0 µM HX, with a detection limit of 0.07 µM. The kinetic parameters such as electron transfer coefficient α (0.47) and rate constant (2.454×10^3 M^{-1} s^{-1}) were determined for the chemical reaction between HX and DED. Finally, this method was evaluated for the determination of HX in water and waste water samples.

Keywords

Hydroxylamine; NiO nanoparticle; water and waste water analysis; sensor; voltammetry

Introduction

Hydroxylamine (HX) is known as a type of reducing agent and is widely used in industrial and pharmaceutical applications. It has been identified as a key intermediate in nitrogen cycles and nitrous oxide production [1]. The quantitative determination of HX is very important in both studies of biological processes and for industrial purposes. It has been confirmed that HX is produced during the reduction of nitrates by *Escherichia coli* and Torula yeast [2].

Electrochemical analysis is gaining significance within industrial process control, environmental monitoring and various pharmaceutical and biotechnology applications [3-7]. The use of unmodified electrodes for electrochemical detection has a number of limitations, such as low selectivity and sensitivity, poor reproducibility, slow electron transfer reaction, low stability over a wide range of solution compositions and the high overpotential at which the electron transfer process occurs [8-10]. Chemical modification of inert substrate electrodes with redox active thin films offers significant advantages in the design and development of electrochemical sensors. In operation, the redox active sites shuttle electrons between the analyte and the electrodes with a significant reduction in activation overpotential [11]. A further advantage of chemically modified electrodes is that they are less prone to surface fouling and oxide formation, compared to inert substrate electrodes [12-14]. A wide variety of compounds have been used as electron transfer mediators for the modification of electrode surfaces in various procedures [15-17].

Nanotechnology has become one of the most interesting disciplines in science and technology today. The intense interest in nanotechnology is being driven by various interesting fields and is creating a new industrial revolution [18]. Nano-materials such as nanoparticles, carbon nanotubes or nanocomposite connected with biomolecules are being used for several bioanalytical applications [19-21]. Electroanalysis is taking advantage of all the possibilities offered by nanomaterials that are easy to detect using conventional electrochemical methods. Nanocomposite of a variety of shapes, sizes and compositions continues to change the field of bioanalytical measurement.

In the present work, we describe the preparation and suitability of a DED modified NiO/NPs carbon paste electrode as a new electrode for electrocatalysis and determination of HX in an aqueous buffer solution. To demonstrate the catalytic ability of the modified electrode toward the electrooxidation of HX in real samples, we examined the utility of this method for the voltammetric determination of HX in water and waste water samples.

Experiment

Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany), unless otherwise stated. Doubly distilled water was used throughout.

1.0×10^{-2} mol L^{-1} HX solution was prepared daily by dissolving 0.064 g HX in water and the solution was diluted to 100 mL with water in a 100 mL volumetric flask. The solution was kept in a refrigerator at 4^{o}C and in the dark. Further dilution was made with water.

Phosphate buffer solutions (sodium dihydrogen phosphate and disodium monohydrogen phosphate, plus sodium hydroxide, 0.1 mol L^{-1}) (PBS) with different pH values were used.

High viscosity paraffin ($d = 0.88$ kg L^{-1}) from Merck was used as the pasting liquid for the preparation of the carbon paste electrode. Spectrally pure graphite powder (particle size <50 µm) from Merck was used as the substrate for the preparation of the carbon paste electrode as a working electrode.

Apparatus

Cyclic voltammetry (CV), chronoamperometry and square wave voltammetry (SWV) were performed using an analytical system, Autolab, with PGSTAT 302N (Eco Chemie, The Netherlands). The system was run on a PC using GPES software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl (KCl_{sat}) electrode as a reference electrode was used. The working electrode was either an unmodified carbon paste electrode (CPE) or a DED/NiO/NPs/CPE. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu–K_α radiation (l = 1.54 Å).

Preparation of the modified electrode

To prepare the modified electrode, 150.0 mg of NiO/NPs and 70.0 mg of DED was hand mixed with 780.0 mg of graphite powder using a mortar and pestle. Using a syringe, 15 drops of paraffin were added to the mixture and mixed well for 55 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. By pushing a copper wire down the glass tube into the back of the mixture, electrical contact was created. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on weighing paper. The unmodified carbon paste electrode (CPE) was prepared in the same way without NiO/NPs and DED to the mixture, to be used for comparison purposes.

Preparation of real samples

Water samples were stored in a refrigerator immediately after collection. Ten millilitres of the sample was centrifuged for 15 min at 1500 rpm. The supernatant was filtered using a 0.45 µm filter and then diluted three times with the PBS pH 8.0. The solution was transferred into the voltammetric cell to be analysed without any further pre-treatment. The standard addition method was used for the determination of HX in real samples.

Results and discussion

NiO/NPs characterisation

NiO/NPs were analysed by XRD analyses. The XRD pattern of NiO/NPs nanopowders in the 2θ range of 10-80° is shown in Fig. 1.

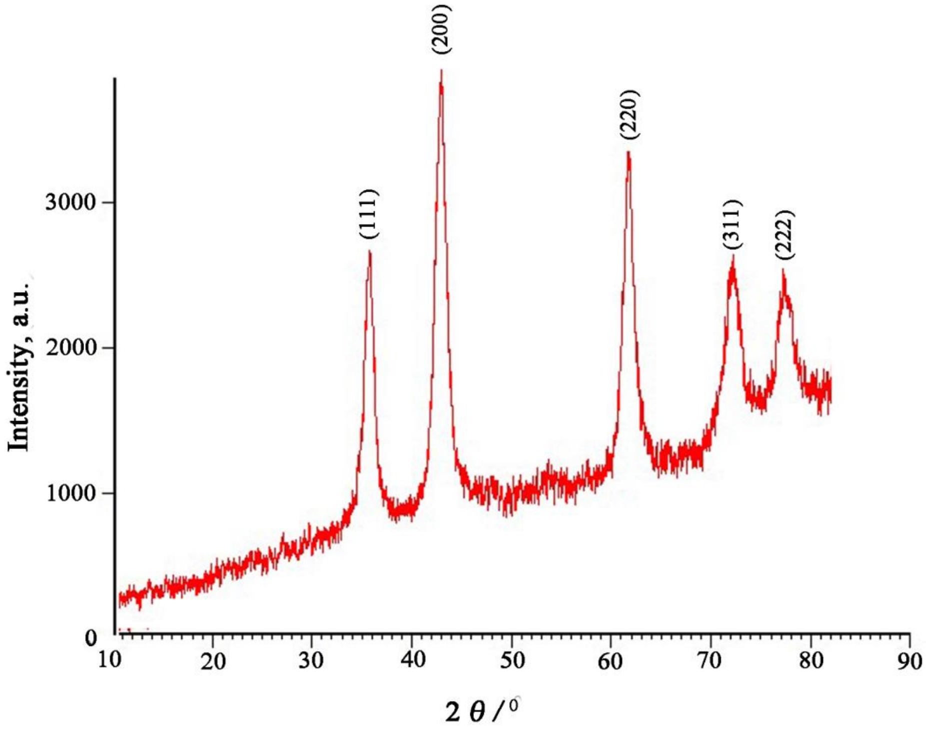

Figure 1. *XRD patterns of as-synthesised NiO/NPs nanoparticles.*

Figure 1 clearly proves the presence of NiO/NPs. An average diameter of as-synthesised NiO/NPs was calculated from the broadness peak ($2\theta = 44°$) by using the Scherrer equation $D = K\lambda/\beta\cos\theta$, and measured about 25.0 nm.

Electrochemical investigation

Figure 2 depicts the cyclic voltammetry responses from the electrochemical oxidation of 400 µM HX at DED/NiO/NPs/CPE (curve c), DED/CPE (curve b), NiO/NPs/CPE (curve d) and unmodified CPE (curve e). As shown, the anodic peak potential for HX oxidation at DED/NiO/NPs/CPE (curve c) and at DED/CPE (curve b) was about 200 mV, while at NiO/NPs/CPE (curve d); the peak potential was about 1000 mV. At the unmodified CPE, the peak potential of HX was about 1050 mV (curve e). From these results, it was concluded that the best electrocatalytic effect for HX oxidation was observed at DED/NiO/NPs/CPE (curve c).

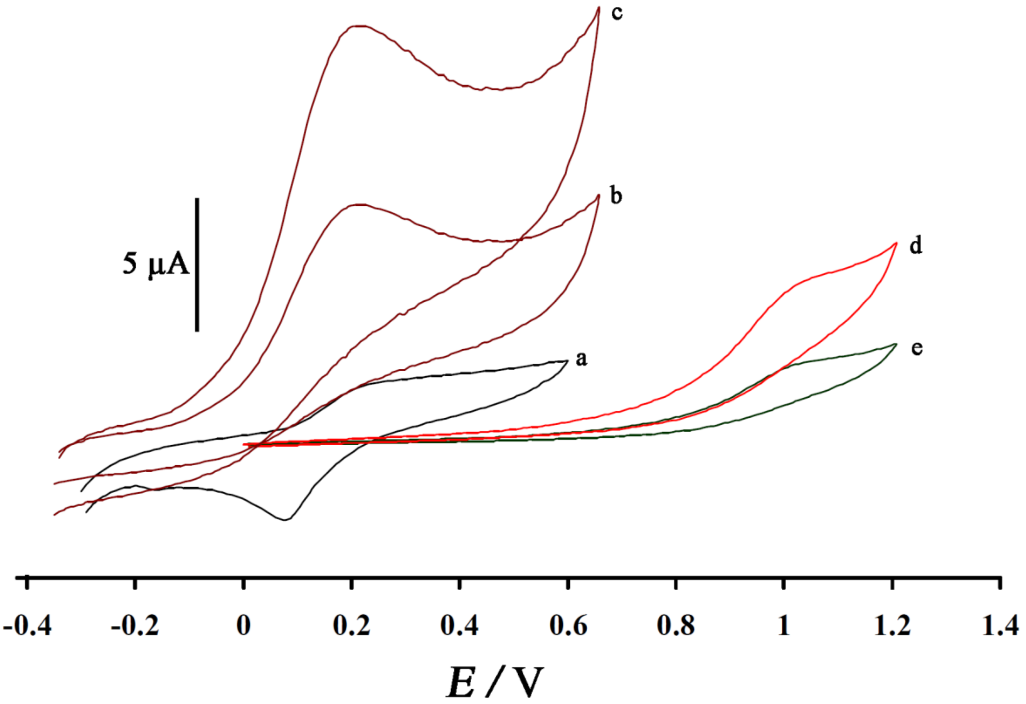

Figure 2. *Cyclic voltammograms of (a) the buffer solution at DED/NiO/NPs/CPE; (b) 400 µM HX at DED/CPE; (c) 400 µM HX at DED/NiO/NPs/CPE; (d) 400. µM HX at NiO/NPs/CPE; (e) 400 µM HX at CPE. Conditions: 0.1 mol* L^{-1} *PBS (pH 8.0), scan rate of 20 mV* s^{-1}.

For example, the results show that the peak potential of HX oxidation at DED/NiO/NPs/CPE (curve c) shifted by about 800 and 850 mV toward less positive values when compared with NiO/NPs/CPE (curve d) and unmodified CPE (curve e), respectively. Additionally, DED/NiO/NPs/CPE showed higher anodic peak current for the oxidation of HX compared to DED/CPE, indicating that the combination of NiO/NPs and the mediator significantly improved the performance of the electrode toward HX oxidation. In fact, DED/NiO/NPs/CPE in the absence of HX exhibited a well-behaved redox reaction (Figure 2a) in the buffer solution (pH 8.0). However, there was a drastic increase in the anodic peak current in the presence of 400 µM HX (curve c), which can be related to the electrocatalytic role of DED/NiO/NPs/CPE towards oxidation of HX.

We observed a linear variation of the peak current with the square root of scan rate ($v^{1/2}$) at scan rates ranging from 2-12 mV s^{-1} at pH 8.0 (Figure 3). This result clearly indicates a diffusion-controlled electrooxidation process [22].

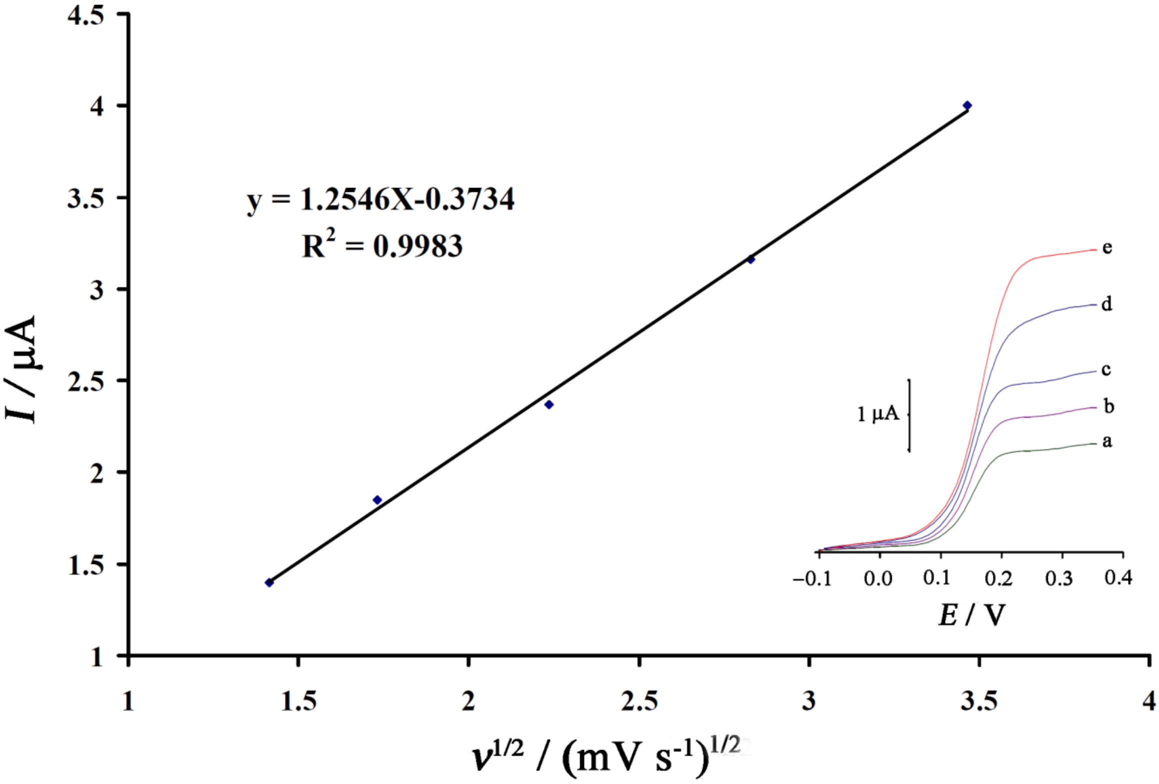

Figure 3 *Plot of* I_{pa} *versus* $v^{1/2}$ *for the oxidation of 100.0 µM HX at various scan rates of (a) 2.0; (b) 3.0; (c) 5.0; (d) 8.0; (e) 12.0 mV* s^{-1} *in 0.1 mol* L^{-1} *phosphate buffer solution (pH 8.0) at NiO/NPs/DED/CPE. Inset: Cyclic voltammograms of 100.0 µM HX at various scans.*

To obtain information about the rate-determining step, a Tafel plot was drawn, derived from points in the Tafel region of the linear sweep voltammogram (Figure 4). The slope of the Tafel plot was equal to $n(1-\alpha)F/2.3RT$, which resulted in 0.1115 V decade^{-1} [23]. Therefore, we obtained the value of α being equal to 0.47.

For further investigations, the value of α was calculated for the oxidation of HX at pH 8.0 for both the modified and unmodified paste electrodes using one other method (see equation 1):

$$\alpha n_{\alpha} = 0.048/(E_P - E_{P/2}) \quad (1)$$

where $E_{P/2}$ is the potential corresponding to $I_{P/2}$. The values for αn_{α} were found to be 0.47 and 0.12 at the surface of DED/NiO/NPs/CPE and CPE, respectively. This result was also confirmed by the larger I_{pa} values recorded during linear seep voltammetry at DED/NiO/NPs/CPE.

Chronoamperometric measurements of HX at DED/NiO/NPs/CPE were carried out for various concentrations of HX in buffered aqueous solutions (pH 8.0) by setting the working electrode potentials at 0.0 mV and 400 mV *vs.* Ag/AgCl/KCl$_{sat}$ (Figure 5A). For an electroactive material (HX, in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition was described using the Cottrell equation. Experimental plots of I *vs.* $t^{-1/2}$ were employed, with the best fits for 300 µM of HX (Figure 5B). The slope of the resulting straight line was then plotted against HX concentration (Figure 5B). From the resulting slope and Cottrell equation, the mean value of the D was found to be 2.1×10^{-6} cm^2 s^{-1} [24].

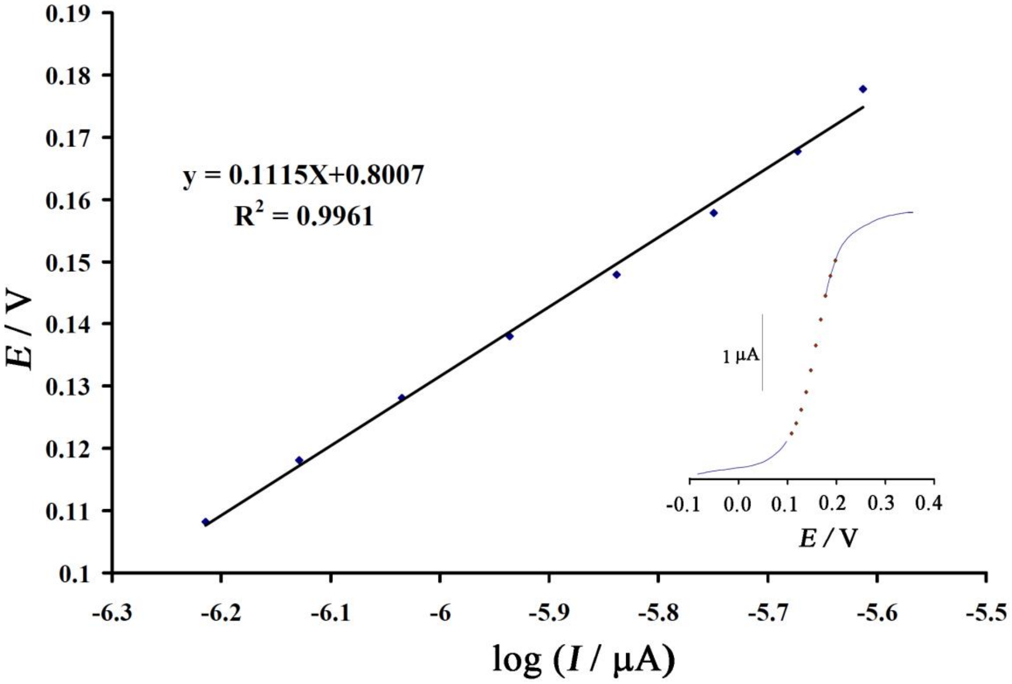

***Figure 4.** Tafel plot for DED/NiO/NPs/CPE in 0.1 mol L^{-1} PBS (pH 8.0) with a scan rate of 8 in the presence of 100.0 µM HX.*

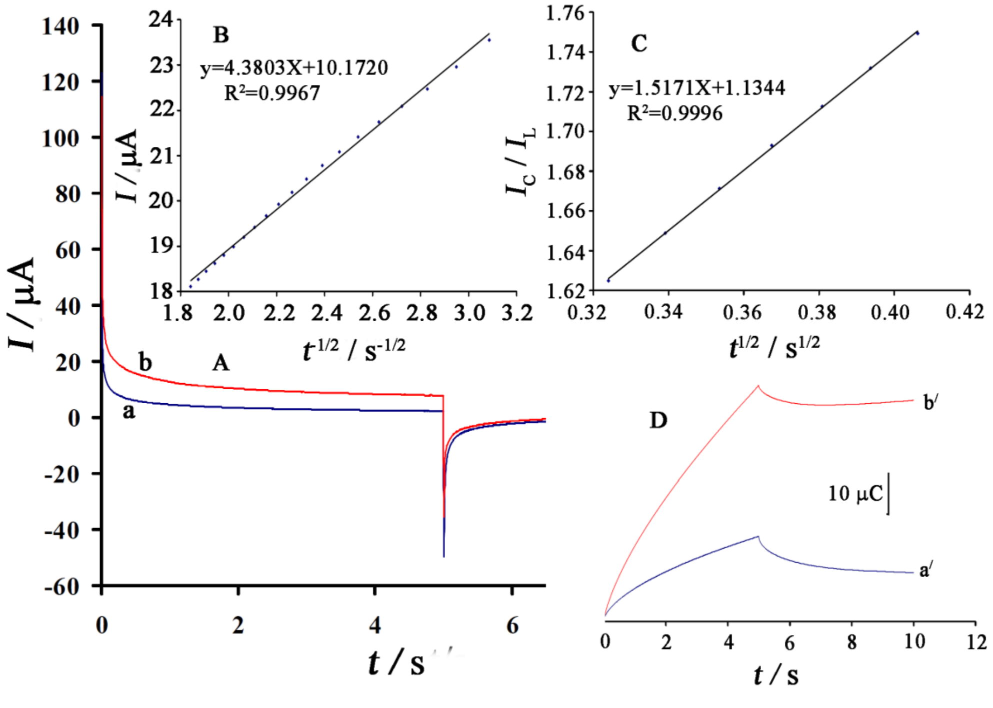

***Figure 5. A** – Chronoamperograms obtained at DED/NiO/NPs/CPE (a) in the absence and in the presence of (b) 300 µM HX at pH 8.0; **B** – Cottrell's plot for the data from the chronoamperograms; **C** – Dependence of IC/IL on t$^{1/2}$ derived from the chronoamperogram data; **D** – The charge-time curves (a') for curve (a) and (b') for curve (b).*

The rate constant for the chemical reaction between HX and redox sites in DED/NiO/NPs/CPE, k_h, can be evaluated by chronoamperometry according to the method set out by Galus [25]:

$$I_C/I_L = \pi^{1/2}\gamma^{1/2} = \pi^{1/2}(kC_bt)^{1/2} \tag{2}$$

Where I_C is the catalytic current of HX at DED/NiO/NPs/CPE, I_L the limited current in the absence of HX and t is the time elapsed (s). The above equation can be used to calculate the rate constant of the catalytic process k_h. Based on the slope of the I_C/I_L versus $t^{1/2}$ plots (Figure 5C), k_h can be obtained for a given HX concentration. From the values of the slopes, an average value of k_h was found to be k_h = 2.454×10^3 M^{-1} s^{-1}. The value of k_h also explains the sharp feature of the catalytic peak observed for catalytic oxidation of HX at the surface of DED/NiO/NPs/CPE.

Double potential step chronocoulometry, as well as other electrochemical methods, was in addition employed for the investigation of the electrode processes at DED/NiO/NPs/CPE. Forward and backward potential step chronocoulometry on the modified electrode in a blank buffer solution showed very symmetrical chronocoulograms. These had about an equal charge consumed for both oxidation and reduction of the DED_{Red}/DED_{Ox} redox system in DED/NiO/NPs/CPE. However, in the presence of HX, the charge value associated with forward chronocoulometry was significantly greater than that observed for the backward chronocoulometry (Figure 5D). This behaviour is typical of that expected for electrocatalysis at a chemically modified electrode [26].

Stability and reproducibility

The repeatability and stability of modified electrode was investigated using CV measurements of 400.0 µM HX in a buffer solution. The relative standard deviation (RSD) for five successive assays was 1.4 %. When seven different DED/NiO/NPs/CPEs were used, the RSD for ten measurements was 2.1 %. When the electrode was stored in the laboratory, the modified electrode retained 95 % of its initial response after a week and 92 % after 30 days (see Figure 6). These results indicate that DED/NiO/NPs/CPE has good stability and reproducibility, and could be used for HX measurements.

Determination of HX individually

Square wave voltammetry (SWV) was used to determine the concentration of HX. Since square wave voltammetry has a much higher current sensitivity and better resolution than cyclic voltammetry, the SWV was used for the determination of HX (Figure 7 inset). The plot of peak current vs. the HX concentration consisted of two linear segments with slopes of 5.9035 and 0.1498 µA/µM at the concentration ranges of 0.1-2.0 µM and 2.0-400.0 µM, respectively (Fig. 7).

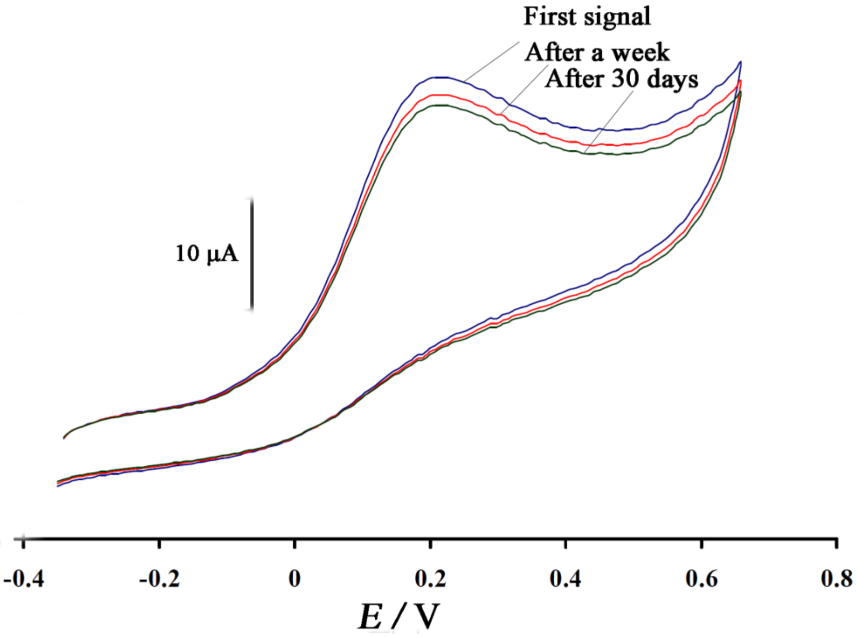

Figure 6. *Cyclic voltammograms of 300 µM HX at a surface of DED/NiO/NPs/CPE in a 0.1 mol L^{-1} phosphate buffer solution (pH 8.0) at different times.*

The decreasing of sensitivity (slope) of the second linear segment was likely due to kinetic limitation. The detection limit was determined as 0.07 μM for HX based on $Y_{LOD} = Y_B+3\sigma$.

Interference study and real sample studies

Analytical selectivity was one of the important parameters that affected the accuracy of the analysis. In order to evaluate the selectivity of the proposed method for the determination of HX, the influence of various substances as potentially interfering compounds, which can be present in the water and waste water samples with the determination of HX, were studied under optimum conditions with 1.0 μM HX at pH 8.0. The tolerance limit was taken as the maximum concentration of the foreign substances, which caused an approximate 3% relative error (in potential or current) in the determination. The result of interfering studied for some of the various substances in oxidation current and oxidation peak potential of HX showed that 1000-fold of Ni^{2+}, CN^{-}, Ca^{2+}, Mg^{2+}, Mn^{+2}, K^{+}, Na^{+}, Cl^{-} and SCN^{-}, 800-fold of glucose, sucrose, lactose and fructose did not affect the selectivity.

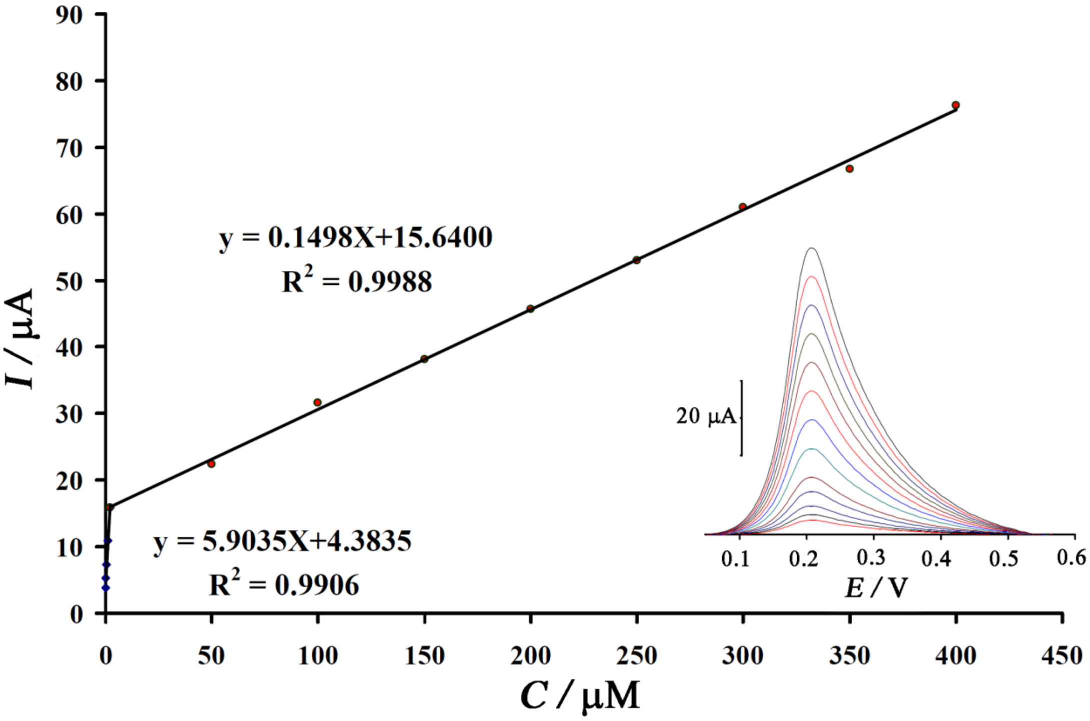

Figure 7. *The plots of the electrocatalytic peak current as a function of HX concentration. Inset shows the SWVs of DED/NiO/NPs/CPE in a 0.1 mol L*$^{-1}$ *phosphate buffer solution (pH 8.0) containing different concentrations of HX. From bottom-up corresponds to 0.0, 0.1, 0.5, 1.0, 2.0, 50.0, 100.0, 150.0, 200.0, 250.0, 300.0, 350.0 and 400.0 μM of HX.*

In order to demonstrate the applicability of the new sensor in determining HX in real samples, we used the new sensor in determining HX in tap water, river water, wastewater and well water. The determinations of HX in samples were carried out using the standard addition method (Table 1). The accuracy of the method was examined by comparing the results obtained from this method with published methods for the determination of HX [2]. The results from the statistical calculation indicated good agreement between them for the mean values (t-test) and the precision (F-test) in the determination of HX in real samples for the three analyses. It was clear that a modified electrode was capable of voltammetric determination of HX, with high selectivity and good reproducibility.

Table 1: *Determination of HX in water samples (n=3).*

Sample	Added, µM	Founded, µM	Published method, µM	F_{ex}	F_{tab}	t_{ex}	t_{tab}
Tap water	1.00	1.05±0.10	0.98±0.11	6.3	19.0	1.2	3.8
Well water	5.0	4.85±0.16	5.22±0.32	7.8	19.0	1.5	3.8
River water[a]	10.0	10.45±0.65	10.55±0.76	9.6	19.0	2.1	3.8
Waste water	30.0	29.73±0.75	30.75±1.2	13.5	19.0	3.2	3.8

[a] *Tejan River, Sari, Iran*

F_{ex} - calculated F value; F_{tab} - reported F value from F-test table with 95 % confidence level and 2/2 degree of freedom; t_{ex} - calculated t; t_{tab} - reported t value from student t-test table with 98 % confidence level.

Conclusion

A carbon paste electrode modified with NiO/NPs and DED was used for electrocatalytic determination of HX. The results showed that the oxidation of HX was catalysed at pH 8.0, whereas the peak potential of hydrazine was shifted by 800 mV to a less positive potential at the surface of DED/NiO/NPs/CPE. In addition, it was shown that HX can be determined using the square wave voltammetry technique. The detection limit (3σ) was 0.07 according to the SWV method. The kinetic parameters, such as electron transfer coefficient, α (0.47) and a rate constant for the chemical reaction between HX and redox sites in DED/NiO/NPs/CPE, k_h (2.454×10^3 M^{-1} s^{-1}) were also determined using electrochemical approaches. Finally, the electrocatalytic oxidation of HX at the surface of this modified electrode can be employed as a new method for the voltammetric determination of HX in real samples such as tap water, river water, wastewater and well water.

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