

Full Paper

Electrocatalytic Oxidation of Hydroxylamine on Graphite Screen Printed Electrode Modified with Iron Oxide Nanoparticles

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Abstract- A graphite screen printed electrode was modified with iron oxide nanoparticles (Fe₃O₄ NPs). This modified electrode is proposed for electrochemical detection of hydroxylamine. Nanoparticles act as catalysts and also increase the surface area. Under optimized conditions, the oxidation peak currents, obtained by differential pulse voltammetry, of hydroxylamine increased linearly with increases in this concentration in the range of 1.0–125.0 μM. In this analysis, the detection limit was 0.4 μM. The developed electrochemical sensor was successfully applied to determine hydroxylamine in water samples.

Keywords- Hydroxylamine, Iron oxide nanoparticles, Voltammetric sensor, Screen printed electrode, Real samples

1. INTRODUCTION

Hydroxylamine is an important intermediate in the ammonium oxidation and nitrification processes. Hydroxylamine is frequently used as pharmaceutical intermediates, nuclear fuel reprocessing, and in the manufacturing of semiconductors. Most of the bicyclic hydroxamates are still used as a drug for the treatment of inflammatory disorders [1-4]. Recently, the

potential of hydroxylamine exposure were being awaked due to the occurrence of two major accidents in USA and Japan in the year 1999 and 2000 respectively, which killed nine people [5]. In addition to that, it is identified as a mutagen, moderately toxic and its exposure is very harmful to mammals, humans and even to plants which can produce irreversible and reversible physiological changes [6]. It was reported that a mill molar concentration of hydroxylamine could be stable for some hours at pH 4, but in air at pH 7.8, it remain stable for only one hour. Thus, it is difficult for the direct determination of hydroxylamine in environmental and biological aspects due to its instability [7].

Therefore, from the industrial, environmental and health viewpoints, development of a sensitive analytical method for the determination of low levels of hydroxylamine is of significant importance. The reported methods of the hydroxylamine determination include spectrophotometry [8], high performance liquid chromatography [9], gas chromatography [10], potentiometry [11], polarography [12] and biamperometry [13]. However, the processes involved in many of these methods are extremely complex, and the linear ranges are relatively narrow and have low precision [14-19].

Fortunately, electrochemical techniques offer the opportunity for portable, cheap and rapid methodologies [20-27]. However, hydroxylamine 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 [28-35]. Recently, various chemically modified electrodes (CMEs) have been prepared and applied in the determination of analyte, which can significantly lower the overpotentials and increase the oxidation current response [36-48].

In the recent years, various nanoparticles have been used to construct electrochemical sensors [49-51]. Fe_3O_4 NPs are a type of magnetic materials with high attention due to their low toxicity, paramagnetic property, good biocompatibility and easy preparation [52-54]. In addition, Fe_3O_4 NPs have been widely used for the modification of electrodes because they increase the electrode surface and electrical conductivity as well as enhancing electron transfer kinetics between the electrode surface and wide range of electroactive species [55,56].

In this work, a screen printed electrode modified with the Fe_3O_4 nanoparticles was used for sensitive voltammetric determination of hydroxylamine and the modified electrode exhibited excellent electrocatalytic activity to hydroxylamine.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a

general purpose electrochemical system software. The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode and an unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Hydroxylamine and all other reagents were analytical grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

2.2. Synthesis of Fe₃O₄ nanoparticles

Fe₃O₄ nanoparticles were synthesized in the presence of urea using a solvothermal method. Solution of urea was dissolved in 100 ml of ethylene glycol (EG). Then 10 mL FeCl₃.6H₂O (16 mmol) and 10 mL FeCl₂.6H₂O (8 mmol) were added into the above solution, respectively. The mixed solutions, with stoichiometric 30 molar ratio of urea/Fe³⁺ (with excess urea that form sufficient precipitating ions for metal oxides formation), were magnetically stirred until all the starting materials were totally dissolved at 25 °C. These solutions were further homogenized in an ultrasonic water bath for 15 min and then respectively transferred into Teflon-lined stainless steel autoclave with a capacity of 200 ml in order to keep them at 200 °C for 24 h in an oven. Subsequently, the autoclaves were air cooled to room temperature. The as-obtained precipitates were centrifuged, and then washed with DI water and absolute ethanol for several times to remove the impurities in the products. The resulting products were dried in a vacuum oven at 100 °C for 12 h.

2.3. Preparation of the electrode

The bare screen-printed electrode was coated with Fe₃O₄ nanoparticles according to the following simple procedure. 1 mg Fe₃O₄ nanoparticles were dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

3. RESULT AND DISCUSSION

3.2. Electrochemical profile of the hydroxylamine on the Fe₃O₄/SPE

To study the electrochemical behaviour of hydroxylamine which is pH-dependent, it is necessary to obtain the optimized pH value in order to achieve the accurate results. By performing the experiments by use of modified electrodes at various pH values ranging from 2.0–9.0, it was revealed that the best results for electro-oxidation of hydroxylamine occur at pH=7.0. The obtained cyclic voltammograms in the presence of 125.0 µM hydroxylamine using the Fe₃O₄/SPE (Curve a) and bare SPE (Curve b) are shown in Fig. 1. According to CV

results the maximum oxidation of hydroxylamine on the $\text{Fe}_3\text{O}_4/\text{SPE}$ occurs at 870 mV which is about 130 mV more negative compared with unmodified SPE.

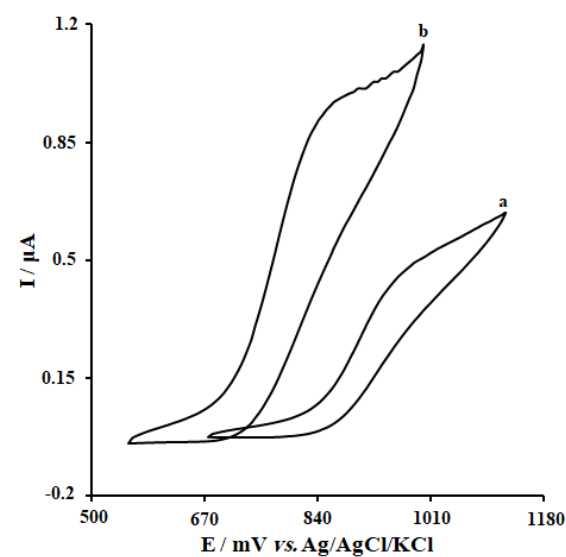


Fig. 1. Cyclic voltammograms of (a) $\text{Fe}_3\text{O}_4/\text{SPE}$ and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 125.0 μM at the scan rate 50 mVs^{-1}

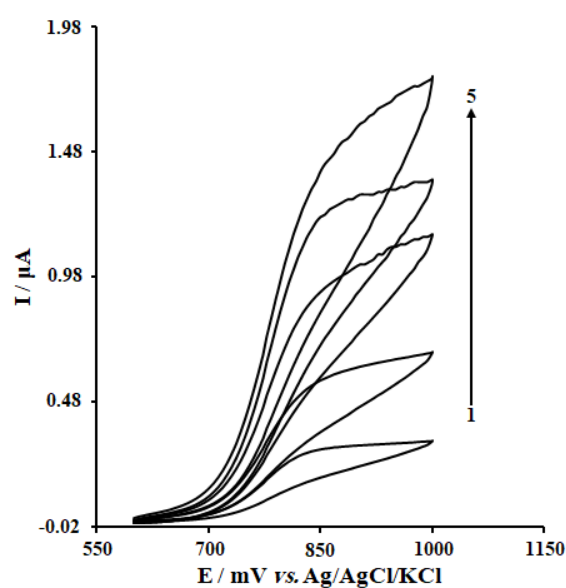


Fig. 2. CVs of $\text{Fe}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) containing 125.0 μM hydroxylamine at various scan rates; numbers 1-5 correspond to 10, 25, 50, 75 and 100 mV s^{-1} , respectively

3.2. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of hydroxylamine, Fig. 2. In addition, there is a linear relationship between I_p and the square root of the potential scan rate ($v^{1/2}$) that demonstrates that the oxidation procedure of analyst is in control of diffusion (Fig. 3).

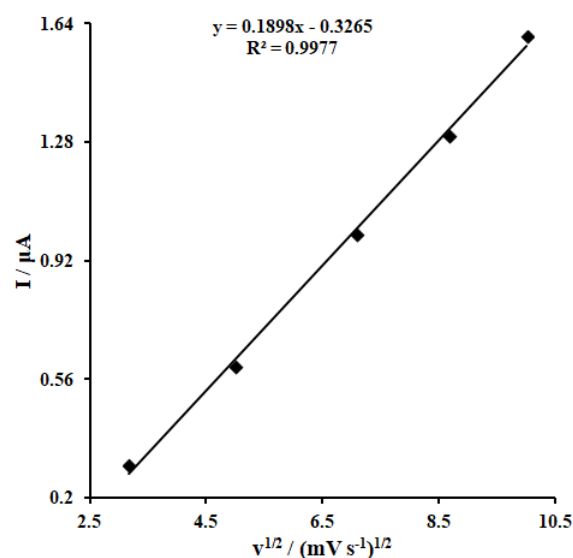


Fig. 3. Variation of anodic peak current vs. $v^{1/2}$ obtained from CVs in Fig. 2

3.3. Chronoamperometric analysis

The analysis of chronoamperometry for hydroxylamine samples was performed by use of $\text{Fe}_3\text{O}_4/\text{SPE}$ vs. $\text{Ag}/\text{AgCl}/\text{KCl}$ (3.0 M) at 0.92 V. The Chronoamperometric results of different concentration of hydroxylamine sample in PBS (pH 7.0) are demonstrated in Fig. 4. The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follow [57]:

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

Where D represents the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), and C_b is the applied bulk concentration (mol cm^{-3}). Experimental results of I vs. $t^{-1/2}$ were plotted in Fig. 5A, with the best fits for different concentrations of hydroxylamine. The resulted slopes corresponding to straight lines in Fig. 5A, were then plotted against the concentration of hydroxylamine (Fig. 5B). The mean value of D was determined to be $1.2 \times 10^{-6} \text{ cm}^2/\text{s}$ according to the resulting slope and Cottrell equation.

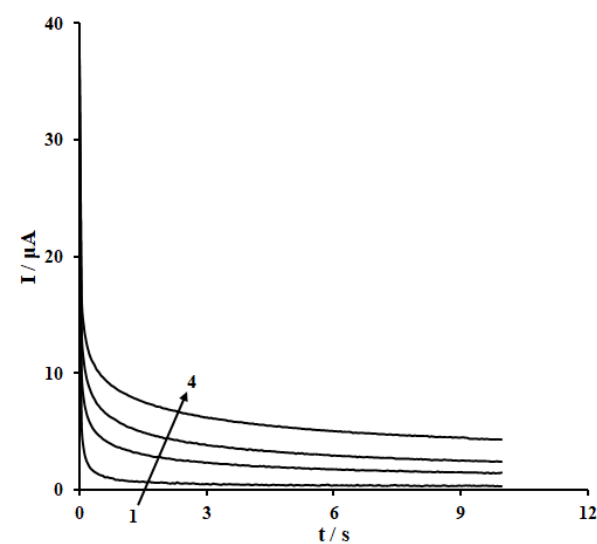


Fig. 4. Chronoamperograms obtained at $\text{Fe}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) for different concentration of hydroxylamine. The numbers 1–4 correspond to 0.1, 0.4, 0.6, and 0.75 mM of hydroxylamine.

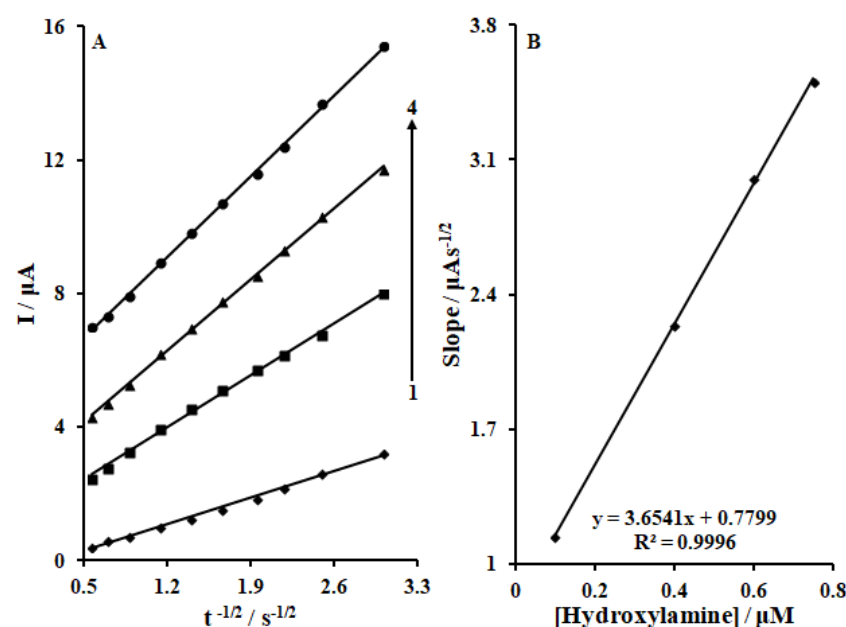


Fig. 5. (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–4; (B) Plot of the slope of the straight lines against hydroxylamine concentration

3.4. Calibration curves

Based on the resulting peak currents of hydroxylamine by use of $\text{Fe}_3\text{O}_4/\text{SPE}$, the quantitative analysis of hydroxylamine was done in water solutions. The modified electrode ($\text{Fe}_3\text{O}_4/\text{SPE}$) as working electrode in the range of hydroxylamine concentration in 0.1 M PBS

was used in differential pulse voltammetry (DPV) due to the advantages of DPV including the improved sensitivity and better performance in analytical applications (Fig. 6).

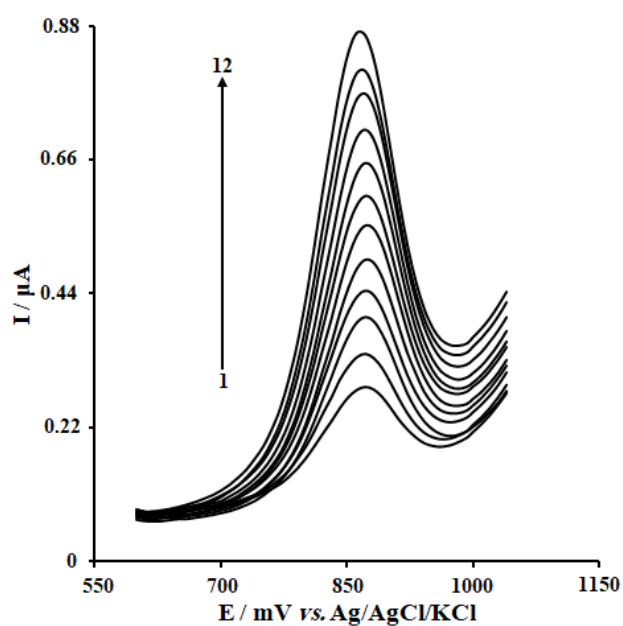


Fig. 6. DPVs of Fe₃O₄/SPE in 0.1 M (pH 7.0) containing different concentrations of hydroxylamine. Numbers 1–12 correspond to 1.0, 5.0, 20.0, 30.0, 40.0, 50.0, 60.0, 75.0, 90.0, 100.0, 110.0 and 125.0 μM of hydroxylamine

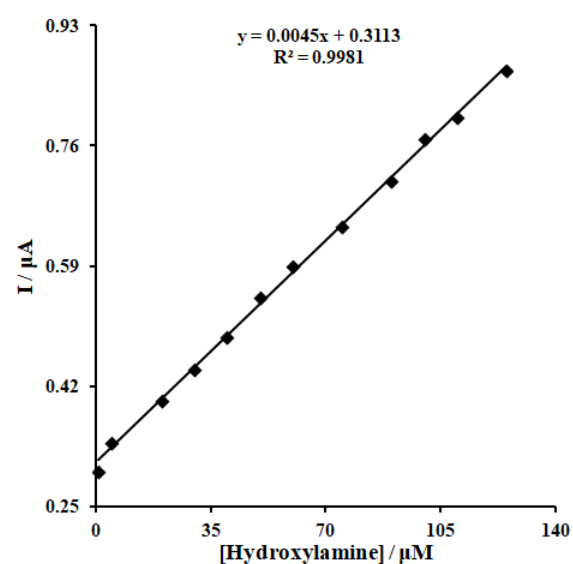


Fig. 7. Plot of the electrocatalytic peak current as a function of hydroxylamine concentration in the range of 1.0-125.0 μM

According to the results, a linear relationship exists between the peak currents and concentrations of hydroxylamine within the concentration range of 1.0-125.0 μM with the correlation coefficient of 0.9981 (Fig. 7). The detection limit was obtained 0.4 μM .

3.5. Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of hydroxylamine in water sample using the described method. In order to perform this analysis, standard addition method was employed and the results are listed in Table 1. Accordingly, the results of hydroxylamine recovery are satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

Table 1. The application of $\text{Fe}_3\text{O}_4/\text{SPE}$ for determination of hydroxylamine in water samples (n=5). All concentrations are in μM

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Well water	0	-	-	-
	5.0	4.9	98.0	1.3
	10.0	10.2	102.0	3.3
	15.0	15.5	103.3	2.1
	20.0	19.8	99.0	2.8
River water	0	-	-	-
	7.5	7.7	102.6	2.5
	12.5	12.3	98.4	1.7
	17.5	17.8	101.7	3.1
	22.5	22.6	100.4	1.4

4. CONCLUSION

In conclusion, Fe_3O_4 nanoparticles was synthesized using solvothermal method and it was applied as a new sensor material for hydroxylamine sensing. The electrochemical characterization of the prepared material was done using cyclic voltammetry and chronoamperometry and differential pulse voltammetry. CV studies of Fe_3O_4 nanoparticles modified electrode showed that the electro oxidation of hydroxylamine took place at lesser potential with drastic enhancement in the anodic oxidation current in comparison with bare electrode. The electro catalytic activity of the modified electrode is explored and is suitable for real sample analysis.

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