Performance Optimization of Electrochemical Sensor based on Iron Oxide-reduced Graphene Oxide Nanocomposite: Application for Environmental Monitoring

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Abstract _In this work, an electrochemical sensor based on iron oxide-reduced graphene oxide nanococmposite modified screen printed graphite electrode (Fe₃O₄-rGO/SPGE) has been developed for selective detection of nitrite ions in drinking water using differential pulse voltammetry (DPV). The proposed nitrite electrochemical sensor exhibited a relative standard deviation of 4.37% for three replicate analysis of 10^{-3} M L^{-1} NO_2. In addition, it displays high electrochemical stability for nitrite oxidation over the pH 6.5, high sensitivity and low limit of detection of 1.2×10^{-5} ML^{-1} with good selectivity in the concentration range 10^{-4} - 10^{-3} which is the range where the rate of nitrite is maximum. These results prove that the metal oxide-rGO nanocomposite modified SPGE has good applications for the determination of nitrite in water.

Keywords__Iron Oxide-reduced graphene oxide nanocomposites, Electrochemical detection ,Nitrite sensor.

I. INTRODUCTION:

The rapid increasing pollution of groundwater resources for human consumption nitrite is receiving worldwide attention and quantitative analysis and detection of nitrite (NO_2) have attracted tremendous attention in the last decades, because of its potential in environmental and human health implications [1]. Several work have been realized to improve the performance of the sensors using metal nanoparticles such as Cu [2-4], Pd [5-7], Pt [8-10] Ag, Ni, and Au.

Since the electrochemical methods are normally based on the oxidation of nitrite on the cathode surface and the choice of electrode materials is essential to the performances of fabricated sensors. iron oxide – reduced graphene oxide nanocomposite was chosen because it is considered as the most efficient and non-toxic electrocatalyst for NO_2.

Therefore, the aim of the present work, is to develop a simple, sensitive, direct, low-cost test kit for routine analysis to evaluate water quality and to determine ultra-trace amount of nitrites using nanotechnology.

II. EXPERIMENTAL

A. Chemicals and apparatus

All chemicals were purchased with analytic grade and used without further purification and a distlled water was used throughout. Iron oxide - reduced graphene oxide nanocomposite was purchased from Brazil laboratory.

Cyclic voltammetric (CV), differential pulse voltammetric (DPV) and electrochemical impedance spectroscopy (EIS) measurements were performed using the potentiostat/galvanostat PalmSens system. The acquisition and treatment of data were carried out by means of a PSTrace software, version 5.5 with a personal computer.

A commercial electrochemical cell based on a three-electrode system was used in all the experiments which were purchased from Palmsens(Austin, Germany) and consisted of graphite as working electrode, 2.65 mm of diameter , carbon wire was used as counter electrode and Ag/AgCl as reference electrode, and all electrochemical measurements were carried out at room temperature (20 °C) without oxygen removal. A scanning electron microscope (SEM) was used to characterize the working electrode.

B. Preparation of the Fe₃O₄-rGO modified electrode:

In this work, a simple approach to the chemical synthesis of iron oxide/reduced graphene oxide (Fe₃O₄/rGO)

nanocomposite is reported. 80ml of GO was dispersed in deionized water (DI) by stirring and underwent sonication, which is essential to obtain a well dispersed solution. Then, 28% NH_4OH solution was added dropwise to the GO solution until the pH reached 10. Added NH_3 to the GO solution, added slowly the $FeSO_4$ solution to the GO solution under magnetic stirring and left overnight at room temperature. The next day, the black solution was centrifuged and washed three times with DI water for 90 min to remove the extra ammonium.

The obtained product were exfoliated with ultrasonication for 2-3 hours.

III. RESULTS AND DISCUSSION

A. Characterization of Fe₃O₄-rGO nanocomposites :

The nanocomposite used for the functionalization of SPGE was deposited by the drop casting method, Furthermore, the quantitative analysis of modified electrode and the surface morphologies were studied EDX and SEM respectively, which was carried out to study the changes of the surface of the WE.
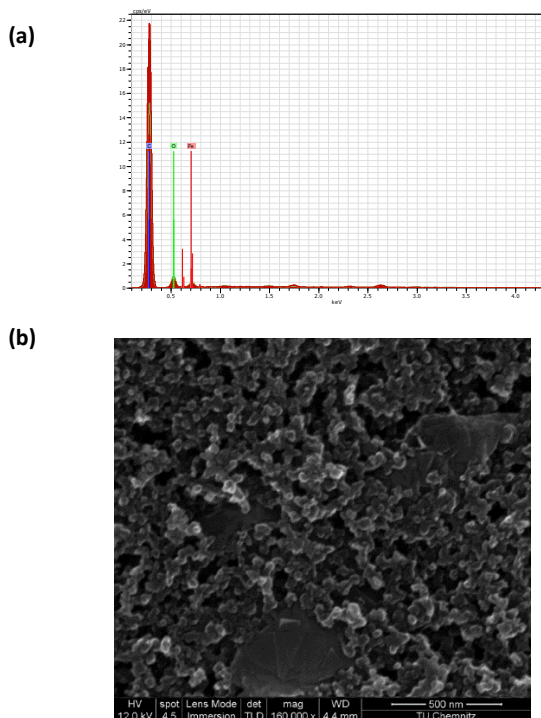
(a)

(b)

Figure 1 EDX spectra (a) and SEM image (b) of Fe_3O_4-rGO/SPGE.

The EDX spectra reveals the percentages of the constituent elements the sensitive layer, 94.6% for carbon, 4.78% for oxygene, 0.63% for iron. But on the SEM image (Figure 1-b) no free Fe_3O_4 nanoparticle was observed outside of rGO, indicating a strong interaction between Fe_3O_4 nanoparticles

and rGO, it was observed that Fe_3O_4-rGO / SPGE had good morphology and dispersability which improves the electrochemical performance.

B. Parametric study:Effect of nanocomposite volume and concentrations on sensor performance:

Following the results of the parametric study of the relationship between WE area and sensor performance, a study was performed to examine the relationship between the current generated and nitrite volume and concentration. As can be seen by the graphs, Figure 2 that the optimal values were found to be: Volume= 4μL and concentraion= $0.58 gL^{-1}$ of Fe_3O_4-rGO.

Under these optimal conditions, it has found that the electroactive surface area has obviously increased after modification with the nanocomposite Fe_3O_4-rGO, indicating that the introduction of nanocomposite provides more conduction pathways for electronic transfer due to the availability of more active surface and higher conductivity.
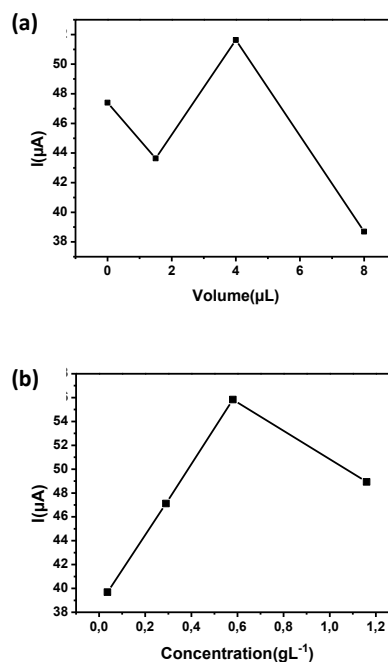
(a)

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Figure 2 Effect of volume (a) and concentration (b) of Fe_3O_4-rGO on the recoveries of Nitrite

C. Electrochemical measurements

Cyclic Voltammetry and electrochemical impedance spectroscopy (EIS) was with 5 mM of $K_3Fe (CN)_6$ / $K_4Fe (CN)_6$ mixture with 0.1M KCl (pH6.5) The current potential set as 0.3 V (Fig 2 a-b) .

The peak currents of the voltammograms for the rGO-Fe_3O_4/SPGE electrode were higher than the bare electrode, due to the availability of more active surface area and hence,

higher conductivity, after modification. Based on these results, it is clear that the best electrochemical behavior among the studied electrodes was observed at Fe_3O_4/rGO/SPGE.
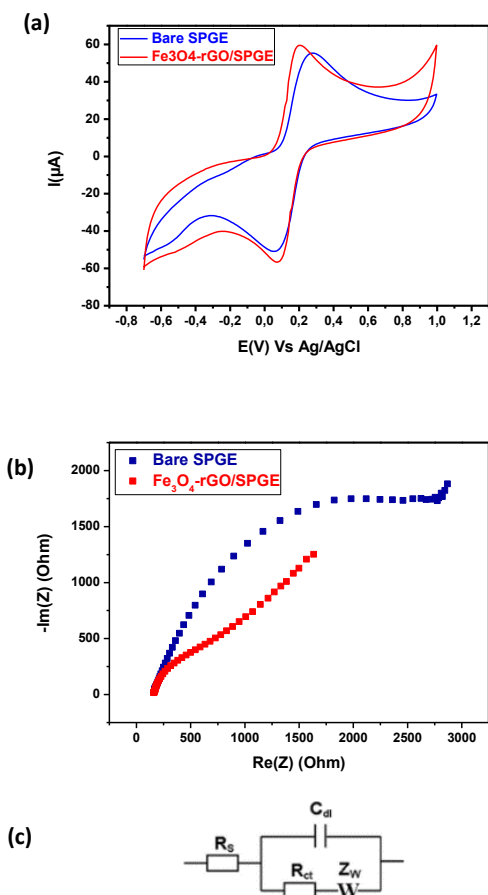
(a)

(b)

(c)

Figure 2 Cyclic voltammograms (a) obtained in 0.1 M KCL containing 5 mM $[Fe(CN)_6]^{3-/4}$ at scan rate 50 mV s^{-1} at bare SPGE and Fe_3O_4-rGO/SPGE. The Nyquist plots (b) obtained in the same solution at bare and modified SPGE and Randles circuit (c).

The Randles equivalent circuit is one of the simplest possible models describing the processes at the electrochemical interface, it composed of a solution R_S in series with the combination in parallel of the double layer capacity C_{dl} and an impedance of a faradic reaction Z_W and a charge transfer resistance R_{ct} .

After the fitting, the semicircle or charge transfer resistance nearly disappeared which the Rct value is ca. 482.2 Ω, indicates that Fe_3O_4-rGO nanocomposite have been successfully modified on the SPGE surface and the charge transfer becomes easier with the modified SPGE electrode.

D. Optimization of pH

It was noted from figure 3 that the current responses and the peak potential of NO_2 significantly change with increasing pH from 3.5 to 6.5. Until pH 6.5 the response of NO_2 decreased revealed that the detection of NO_2 is feasible only in the acidic with the modified screen printed graphite electrode. Based on the peak response, pH 6.5 was selected for the identification of nitrite in the aqueous medium.
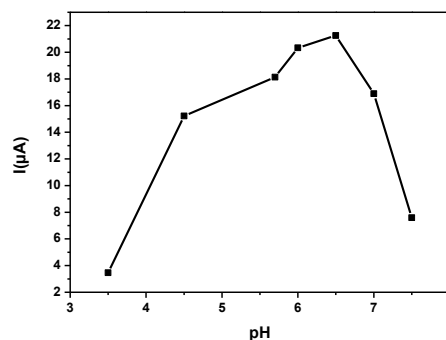
Figure 3 Cyclic voltammetry of Fe_3O_4-rGO/SPGE in different pH of Pbs (0.1M) at a scan rate 50 mVs^{-1}

E. Optimization of DPV parameters:

The current response for NO_2 were greatly affected by varying the parameters of differetiel pulse voltammetric; the scan rates, the pulse potential and pulse time values. The optimization of these parameters with modified screen printed graphite electrodes, was carried out.
Thus, the optimal values of differential pulse voltammetric parameters were found to be: 10 mV for pulse potential; 0.03 s for pulse time and 4 mVs-1 for scan rate.

F. Electrochemical determination of nitrite:

Under The calibration plot between the current recorded and the various concentrations of nitrite is represented in figure 5. Linear dependency of the recorded current was observed vs. NO_2 concentration but the sensitivity is lost at a further lower concentrations.
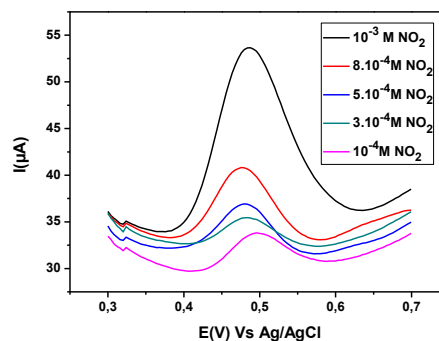
Figure 5 the Differentiel pulse voltammetry of Fe_3O_4-rGO/SPGE at diffrents concentration of NO_2.

G. Reproducibility, limit of detection and stability measurements

In order to investigate the stability of the nanocomposite, Fe_3O_4/rGO modified electrode, the DPVs for 10^{-3} M nitrite in a 0.1 M PBS. It was found that the oxidation peak current conserved the same value with a relative standard deviation of 4.37% for 3 repetitive measurements, after we put the electrode in a PBS at room temperature, we observed that the current response decreased about 0.10%, these results indicate that the Fe_3O_4-rGO modified electrode has a good stability.

To ascertain the reproducibility of the results, three different SPGE were modified with the Fe_3O_4/rGO and their response toward the oxidation of 3×10^{-4} M of NO_2 was tested. The peak current obtained in the measurements of thoose independent electrodes showed a relative standard deviation (RSD%) of 14.02%, confirming that the results are reproducible. However, to see the efficacy of the method, the detection limit was calculated and found to be, LOD = 12 μM L^{-1}, the Proposed sensors exhibits low LOD compared to the concentration compared to the concentration mentioned by the World Health Organization.

IV. CONCLUSION

In this work, an electrochemical nitrite sensor was fabricated based on iron oxide nanoparticles and reduced graphene oxide nanocomposite modified screen printed graphite electrode. The modified electrode shows a high current response that exhibits more excellent sensitivity and faster response to NO_2. It has also demonstrated good selectivity and stability, and detection limit has proven 1.2 10^{-5} M L^{-1}.

All these advantageous features have proved that the modified electrode could be a promising candidate for the detection of nitrite in real samples.

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