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Nanostructured Base Electrochemical Sensor for Determination of Sulfite

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A novel carbon paste electrode modified with carbon nanotube and benzoylferrocene (BF) was fabricated. The electrochemical study of the modified electrode, as well as its efficiency for electrocatalytic oxidation of sulfite is described. Cyclic voltammetry was used to investigate the redox properties of this modified electrode. The electrode was also employed to study the electrocatalytic oxidation of sulfite, using cyclic voltammetry, chronoamperometry and square wave voltammetry as diagnostic techniques. It has been found that the oxidation of sulfite at the surface of modified electrode occurs at a potential of about 240 mV less positive than that of an unmodified CPE. The diffusion coefficient, electron transfer coefficient, and heterogeneous rate constant, for oxidation of sulfite at the modified electrode surface were also determined. Square wave voltammetry exhibits a linear dynamic range from 1.0×10^{-7} to 4.0×10^{-4} M and a detection limit of 90.0 nM for sulfite. Finally this modified electrode was used for determination of sulfite in real samples.

Keywords: Sulfite Determination, Carbon Nanotubes; Modified electrode, Voltammetry

1. INTRODUCTION

Sulfite is an anion of major importance and its determination is important particularly from biological and industrial point of view [1]. Technically, sulfite is important as a reducing agent and in bleaching. It is usually used in boilers and boiler-feed waters for dissolved oxygen control and found in natural or wastewaters as a result of industrial pollution. The presence of excess sulfite in boiler waters lowers the pH and promotes corrosion. Thus, control of sulfite ion in wastewater is environmentally important, principally because of its toxicity to aquatic life. Sulfite is also widely used as additive in food and beverages to prevent oxidation and bacterial growth and to control enzymatic reactions during production and storage.

The level of sulfite in food has been the subject of legislation since it was discovered that certain concentration level causes allergic reactions in some individuals. Thus, to assure the quality control of manufactured products, a sensitive and selective method for sulfite determination is required. Various analytical methods have been used for the determination of sulfite, including simple titrimetry [2], spectrophotometry [3–7], chemiluminescence [8–10] and electrochemical methods [11-15].

Investigation of electrochemical behavior of sulfite in aqueous media is performed at common metal electrodes [15–19], but the kinetics of electron transfer are quite sluggish. A number of chemically modified electrodes (CMEs) have been designed for the determination of sulfite utilizing different modification procedures and sensing materials [20,21]. The electrocatalysis of slow electron transfer reactions is perhaps the most important feature of CMEs. The chief problem for the determination of sulfite with many of these electrodes is the interference from other matrix constituents such as the oxidation of polyphenolics and ascorbate. The electrochemical reduction of aqueous solutions of sulfite in acidic media has been the subject of some investigations [22,23]. The advantage of this method over the oxidative route is that the analytical peak lies in a region where there are few competing electrode processes. However, the need for acidic media limits the use of this approach.

The electrochemical methods using chemically modified electrodes (CMEs) have been widely used as sensitive and selective analytical methods for the detection of the trace amounts of biologically important compounds [24-36]. One of the most important properties of CMEs has been their ability to catalyze the electrode process via significant decreasing of overpotential respect to unmodified electrode. With respect to relatively selective interaction of the electron mediator with the target analyte in a coordination fashion, these electrodes are capable to considerably enhance the selectivity in the electroanalytical methods [36-56].

Carbon paste electrode (CPE) is a special kind of heterogeneous carbon electrode consisting of mixture prepared from carbon powder (as graphite, glassy carbon and others carbonaceous materials) and a suitable water-immiscible or non-conducting binder [57-95]. The use of carbon paste as an electrode was initially reported in 1958 by Adams. In afterward researches a wide variety of modifiers including enzymes [96-110], polymers (nafion, chitosan, etc.) [11-116] and nanomaterials [117-125] have been used with these versatile electrodes. CPEs are widely applicable in both electrochemical studies and electroanalysis thank to their advantages such as very low background current (compared to solid graphite or noble metal electrodes), facility to prepare, low cost, large potential window, simple surface renewal process and easiness of miniaturization[125-128]. Besides the advantageous properties and characteristics listed before, the feasibility of incorporation different substances during the paste preparation (which resulting in the so-called modified carbon paste electrode), allow the fabrication of electrodes with desired composition, and hence, with pre-determined properties [129-139].

Since the discovery of carbon nanotubes (CNTs) in 1991 [140-150], numerous investigations were focused on the studies of their properties and applications [151-153]. Because of the special tube structure, CNTs possess several unique properties such as good electrical conductivity, high chemical stability and extremely high mechanical strength [154-155]. In addition, the subtle electronic behavior of CNTs reveals that they have the ability to promote electron-transfer reaction and have a high electrocatalytic effect when used as electrode materials [156-160]. All these fascinating properties make CNTs as a suitable candidate for the modification of electrodes [161-165].

In the present work, we describe the preparation of a new electrode composed of CNPE modified with benzoylferrocene (BFCNPE) and investigate its performance for the electrocatalytic determination of sulfite in aqueous solutions.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, The Netherlands) and Metrohm 797 VA Computrace Model. 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, a platinum wire, and the BFCNPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 691 pH/Ion Meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. Sulfite and all other reagents were of analytical grade from Merck (Darmstadt, Germany). Graphite powder and paraffin oil (DC 350, density = 0.88 g cm^{-3}) as the binding agent (both from Merck) were used for preparing the pastes. Multiwalled carbon nanotubes (purity more than 95%) with o.d. between 10 and 20 nm, i.d. between 5 and 10 nm, and tube length from 10 to 30 μm were prepared from Nanostructured & Amorphous Materials, Inc. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-11.0.

2.2. Preparation of the electrode

The BFCNPEs were prepared by hand mixing 0.01 g of BF with 0.89 g graphite powder and 0.1 g CNTs with a mortar and pestle. Then, ~ 0.7 mL of paraffin was added to the above mixture and mixed for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 10 cm long). 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.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of BFCNPE

BFCNPE was constructed and its electrochemical properties were studied in a 0.1 M PBS (pH 7.0) using CV (Fig. 1).

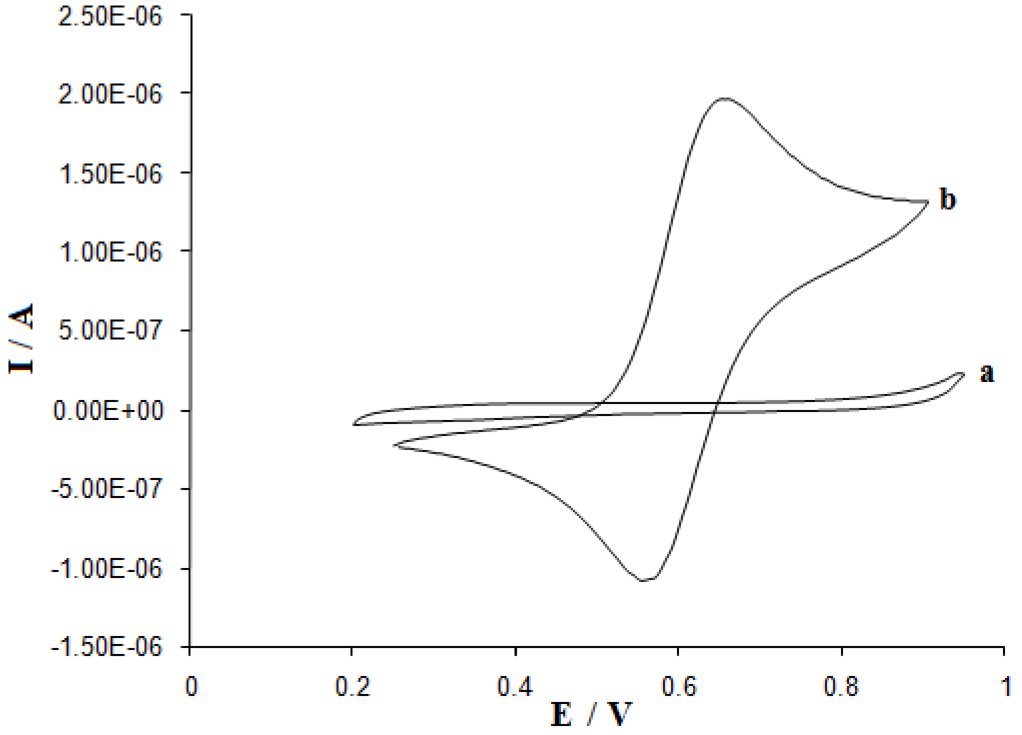

Figure 1. (a) Cyclic voltammograms of unmodified carbon paste electrode in 0.1M phosphate buffer (pH 7.0) and (b) as (a) at the surface of BFCNPE. In all cases scan rate is 100 mVs^{-1}.

The experimental results show well-defined and reproducible anodic and cathodic peaks related to Fc/Fc$^+$ redox system, which show a quasireversible behavior in an aqueous medium [50]. 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 BFCNPE. 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 [50]. However we regenerated the surface of BFCNPE before each experiment according to our previous results [50].

3.2. Electrocatalytic oxidation of sulfite at a BFCNPE

The utility of the modified electrode for oxidation of sulfite was evaluated by cyclic voltammetry. The cyclic voltammetric responses of a bare carbon-paste electrode in 0.1M phosphate buffer (pH 7.0), without and with sulfite, are shown in Fig. 2 (curves a and b, respectively). Figures 2c shows cyclic voltammograms of modified electrode in the buffer solution with 200.0 µM of sulfite. The results show that the sensor produces a large anodic peak current in the presence of sulfite without a cathodic counterpart (Fig. 1, curve b).

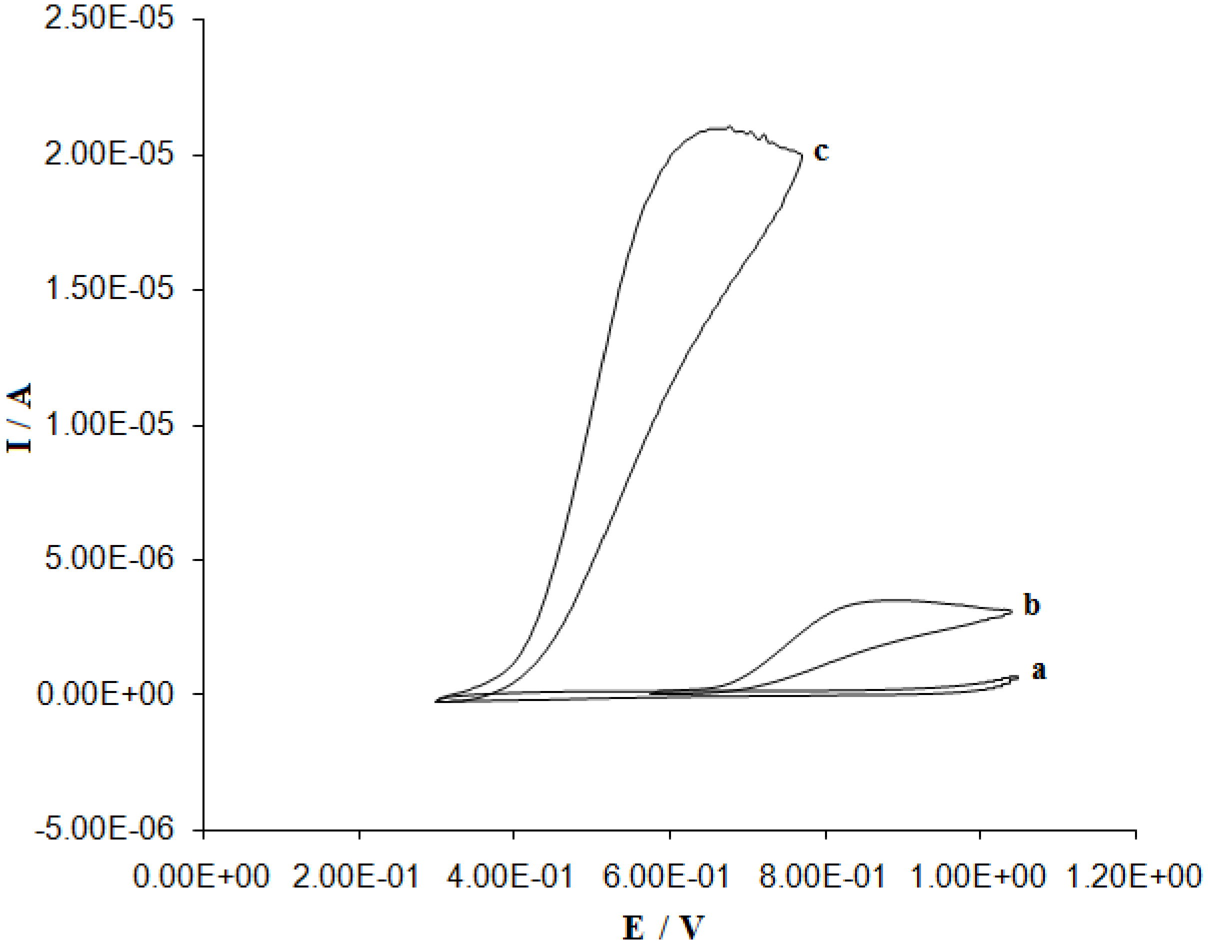

Figure 2. (a) Cyclic voltammogram of unmodified carbon paste electrode in 0.1M phosphate buffer (pH 7.0) (b) as (a) in the presence of 200.0 µM sulfite and (c) cyclic voltammogram of BFCNPE in the presence of 200.0 µM sulfite. In all cases scan rate is 10 mVs^{-1}.

That the current observed is associated with sulfite oxidation and not the oxidation of modifier is demonstrated by comparing the current in Fig. 1 (curve b, without sulfite) with the one in the presence of sulfite in Fig. 2 (curve c). It is apparent that the anodic current associated with the surface-attached materials is significantly less than that obtained in the solution containing sulfite. At the surface of a bare electrode, sulfite was oxidized around 890 mV. As can be seen, the electroactivity of sulfite on the modified electrode was significant (Figs. 2 curve c), with strongly defined peak potential, around 650 mV *vs.* Ag/AgCl/KCl (3.0 M) electrode. Thus, a decrease in overpotential and enhancement of peak current for sulfite oxidation are achieved with the modified electrode. Such a behavior is indicative of an EC′ mechanism [167].

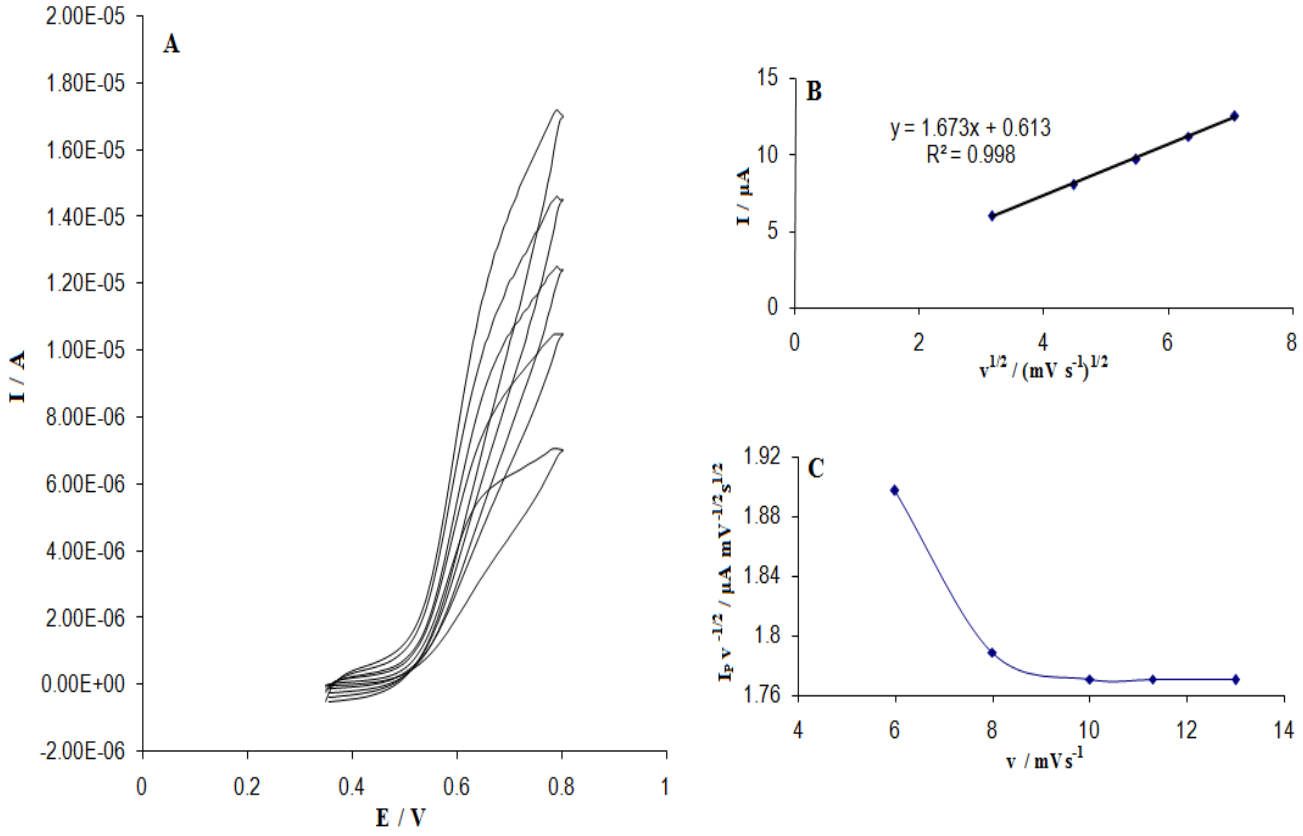

Figure 3. (A) CVs of BFCNPE in 0.1 M phosphate buffer solution (pH 7.0) containing 50.0 µM sulfite at various scan rates; From inner to outer scan rates of 10, 20, 30, 40 and 50 and mV s^{-1}, respectively. (B) Variation of anodic peak current vs. $\nu^{1/2}$ and (C) normalized current ($I_p/\nu^{1/2}$) vs. ν.

The effect of scan rate on the electrocatalytic oxidation of sulfite at the BFCNPE was investigated by cyclic voltammetry (Fig. 3A). As can be observed in Fig. 3A, 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 ($\nu^{1/2}$) was found to be linear in the range of 10–50 mV s^{-1}, suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 3B). A plot of the scan rate-normalized current ($I_p/\nu^{1/2}$) vs. scan rate (Fig. 3C) exhibits the characteristic shape typical of an EC'process [167].

Fig. 4A shows the cyclic voltammogram of a BFCNPE obtained in 0.1 M phosphate buffer solution (pH 7.0) containing 50.0 µM sulfite, 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 sulfite and BFCNPE. If deprotonation of sulfite 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. Fig. 4B shows a Tafel plot that was drawn from points of the Tafel region of the cyclic voltammogram. The Tafel slope of 0.1 V obtained in this case agreeswell with the involvement of one electron in the rate determining step of the electrode process, assuming a charge transfer coefficient of α=0.41.

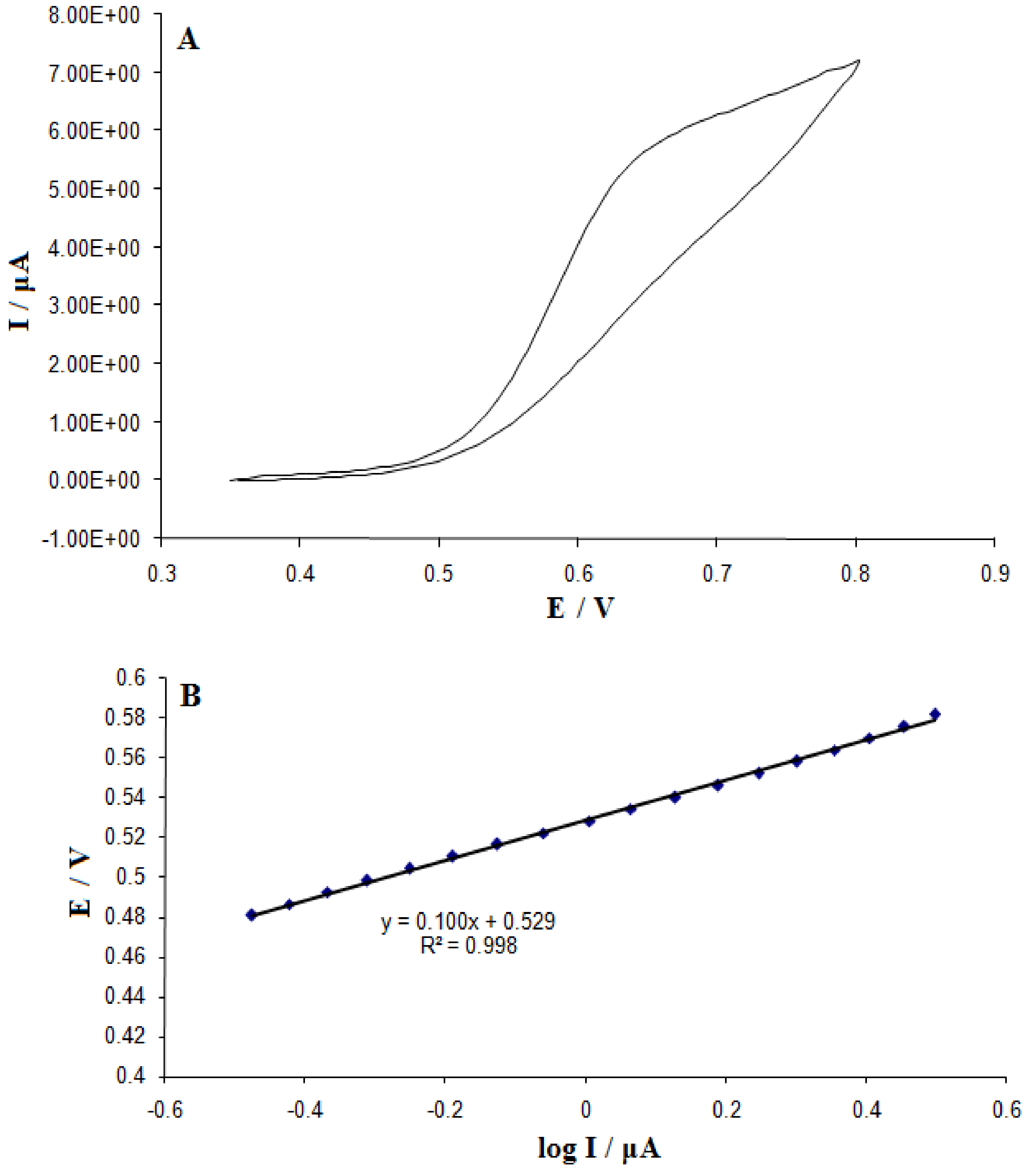

Figure 4. (A) Cyclic voltammogram (at 10 mV s^{-1}) of an BFCNPE in 0.1 M phosphate buffer (pH 7.0) containing 50.0 µM sulfite. (B) Tafel plot derived from the cyclic voltammogram.

3.3. Chronoamperometric measurements

Chronoamperometric measurements of sulfite at BFCNPE were carried out by setting the working electrode potential at 0.7 V *vs.* Ag/AgCl/KCl (3.0 M) for the various concentration of sulfite in buffered aqueous solutions (pH 7.0) (Not shown). For an electroactive material (sulfite 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 [167]. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of sulfite.

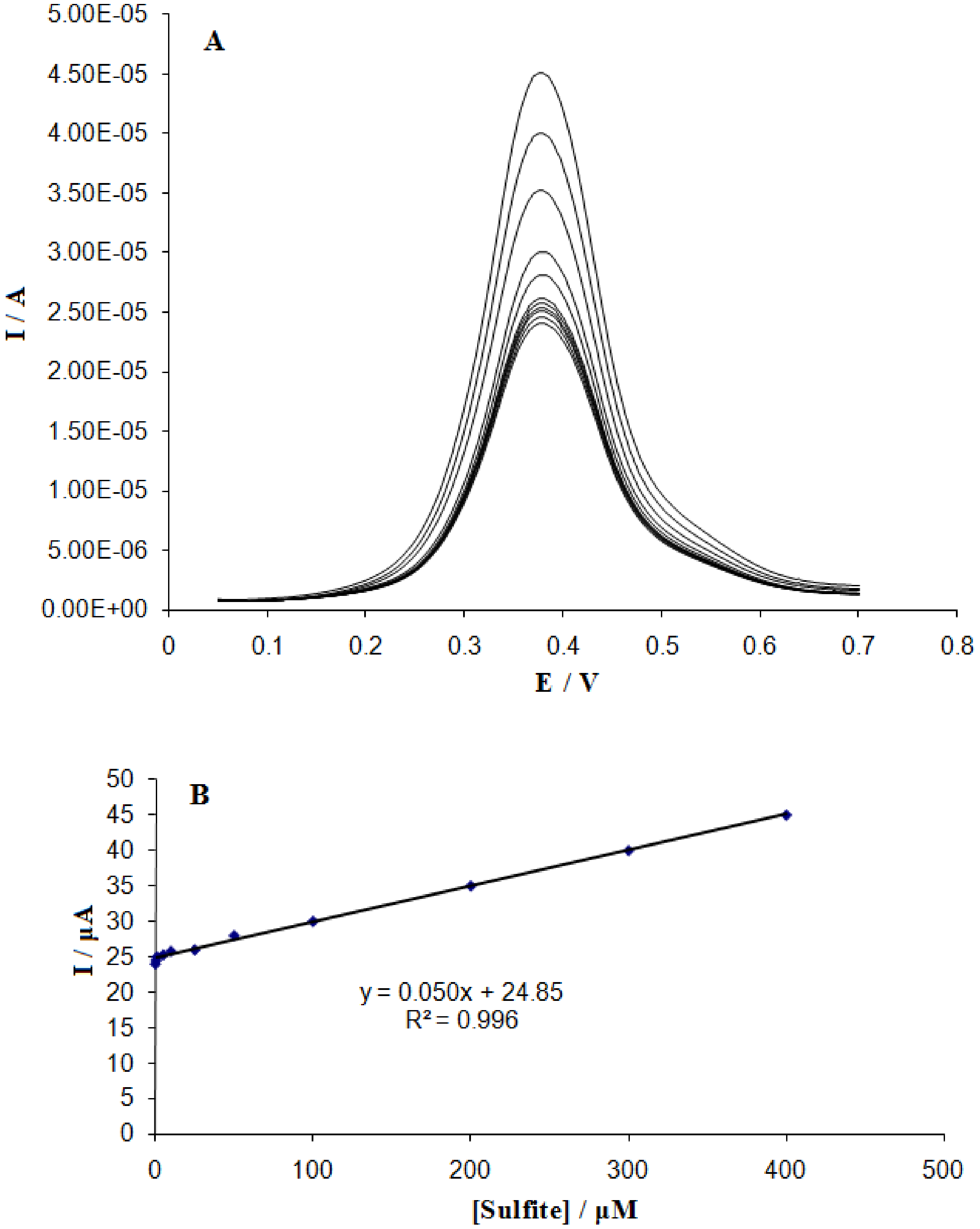

Figure 5. (A) Differential pulse voltammograms of BFCNPE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of sulfite. From inner to outer correspond to 0.1, 0.5, 1.0, 5.0, 10.0, 25.0, 50.0, 100.0, 200.0, 300.0 and 400.0 µM of sulfite. (B) Plots of the electrocatalytic peak current as a function of sulfite concentration in the range of 0.1 to 400.0 M.

The slopes of the resulting straight lines were then plotted vs. sulfite concentration. From the resulting slope and Cottrell equation the mean value of the D was found to be $1.7 \times 10^{-6} cm^2/s$.

Chronoamperometry can also be employed to evaluate the catalytic rate constant, k, for the reaction between sulfite and the BFCNPE according to the method of Galus [168]:

$$I_C / I_L = \gamma^{1/2}[\pi^{1/2} \operatorname{erf}(\gamma^{1/2}) + \exp(-\gamma) / \gamma^{1/2}] \qquad (1)$$

where I_C is the catalytic current of sulfite at the BFCNPE, I_L is the limited current in the absence of sulfite and $\gamma = kC_bt$ is the argument of the error function (C_b is the bulk concentration of sulfite). In cases where γ exceeds the value of 2, the error function is almost equal to 1 and therefore, the above equation can be reduced to:

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

where t is the time elapsed. The above equation can be used to calculate the rate constant, k, of the catalytic process from the slope of I_C/I_L vs. $t^{1/2}$ at a given sulfite concentration. From the values of the slopes, the average value of k was found to be $3.5 \times 10^{4} M^{-1} s^{-1}$.

3.4. Calibration plot and limit of detection

The electrocatalytic peak current of sulfite oxidation at the surface of the modified electrode can be used for determination of sulfite in solution. Therefore, square wave voltammetry (SWV) experiments were performed using modified electrode in phosphate buffer solution containing various concentration of sulfite. The results show the electrocatalytic peak current of sulfite oxidation at the surface of modified electrode was linearly dependent on the sulfite concentrations. The mediated oxidation peak currents of sulfite at the surface of a modified electrode were proportional to the concentration of the sulfite within the ranges 0.1-400.0 μM in the SWV. The detection limits (3σ) wad 90.0 nM.

3.5. Determination of sulfite in water samples

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of sulfite in water samples. Based on the repeated square wave voltammetric responses (n=5) of the diluted analytes and the samples that were spiked with specified concentration of sulfite, measurements were made for determination of sulfite concentrations in the water samples. The results are listed in table1.

Table 1. The application of BFCNPE for determination of sulfite in water samples (n=5)

Sample	Added (μM)	Expected (μM)	Found (μM)	Recovery (%)	RSD (%)
Drinking Water					
	5.0	5.0	4.9	98.0	3.1
	10.0	10.0	10.3	103.0	2.9
	15.0	15.0	15.3	102.0	1.6
	20.0	20.0	19.8	99.0	2.2
River Water					
	4.0	4.0	4.1	102.5	1.8
	9.0	9.0	8.8	97.8	2.9
	14.0	14.0	13.6	97.1	2.1
	19.0	19.0	19.2	101.0	3.4

4. CONCLUSIONS

This work demonstrates the construction of a carbon carbon electrode chemically modified with carbon nanotubes and benzoylferrocene (BF). This modified electrode was used for electrocatalytic determination of sulfite. The results demonstrated that the electrooxidation of sulfite at the surface of the modified electrode. Finally, this method was used for the determination of sulfite in water samples.

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