Electrocatalytic oxidation of sulfite ion at the surface carbon ceramic modified electrode with prussian blue

Sohrab Ershad*, Razieh Mofidi Rasi

Department of Chemistry, College of sciences, Payam Noor University, 19395-4697 Tehran, Iran

Abstract

The redox properties of sulfite ion have been examind using cyclic voltammetry in acetonitrile solvent at the surface of gold, pelatin and glassy carbon electrodes. It has been found that, sulfite ion exhibits two electron oxidation peak with EC' mechanism. A novel and chemically modified electrode containing Prussian blue complex and multi wall carbon nanotubes (MWCNs) was achieved on the surface of glassy carbon electrode using sol-gel technique. The obtained film electrode was very stable and exhibited electrocatalytic response for oxidation of sulfite. Results showed that at bare GC electrode, a small oxidation peak current was observed at about 0.663mV and a well-formed sharp catalytic oxidation peak was observed at Prussian blue complex modified electrode. The transfer coefficient (α) for electrocatalytic oxidation of sulfite and the diffusion coefficient of this substance under the experimental conditions were also investigated.

Keywords: Prussian blue complex; cyclic voltammetry; sulfite; electrocatalytic oxidation.

Introduction

Sulfites are commonly used as preservatives in the food industry due to their addition to some products, such as vegetables, fruits and several beverages to prevent oxidation, inhibit bacterial growth and assist preserving vitamin C [1-4]. Despite these advantages, sulfite should be applied in strictly limited amounts due to its potential toxicity. The level of sulfite in food has been subjected to legislation since it was discovered that at a certain concentration level sulfite causes allergic reactions in some individuals [5].

Therefore, the existence of methods allowing an accurate measurement of sulfite ion is very important for food industry in order to control product quality. Among the methods available for the measurement of this analyte we can highlight spectro flourimetry [6], chemiluminiscence[7,8], phosphorimetry [9], spectrophotometry [10], flow injection analysis [11] and enzymatic techniques [12].

However, the majority of these methods need extensive sample pre-treatment and reagent preparation. In this sense, the development of sensors for sulfite determination is of considerable interest because its use involves several advantages such as

*Corresponding author: Sohrab Ershad

Tel: +98 (41) 42236978, Fax: +98 (41) 42233370
E-mail: sohrabsd@yahoo.com

rapid response, high specifity, low cost and no need of sample preparation.

Oxidation studies of sulfite using a number of modified electrodes have been used for the determinartion of sulfite [13-22].

The use of bare electrodes such as carbon, platinum and gold for the oxidation of sulfite requires high potentials and these electrodes tend to be poisoned by the species formed during the electrochemical process. A good way of lowering potentials is by modification of the electrodes [23]. One promising approach for minimizing this effect is the use of chemically modified electrodes (CMEs). Many different strategies have been employed for the electrode modification, such as electrochemical polymerization [24-25], covalent bonding [26-27] and mixing with carbon paste [28-29].

Nowadays, a graet deal of interest in the development of new materials capable to be incorporated to electrode surface in order to obtain electrochemical sulfite sensors with better analytical properties has been invested. In this sense, electrodes modified films derived from inorganic polymeric nanostructure have been extensively investigated.

The sol-gel process is very well adopted for coating of thin films on complex shapes.

The porosity and pore size of these films can be controlled to maximize the specific surface area and to ensure that permeability of the film remain high. Furthermore, the sol-gel process involves low-temperature hydrolysis and condensation of appropriate monomeric precursors and is suitable inclusion of organic moieties that cannot withstand high temperatures [30].

Prussian blue (PB) is one of the well-studied materials and has been extensively studied with well-known eletrochromic, electrochemical [31], magnetic properties [32], photophysical [33] and potential analytical applications [34-35].

But up to now, only a few chemically modified electrodes [36] containing prussian blue complex were fabricated. In the present work, described here is the investigation the electrochemical response of sulfite ion at the surface of unmodified Au, Pt and GC electrodes. Then the response of sulfite ion at the MWCNT-PB composite film modified GCE and the development of a convenient and sensitive method for the determination of sulfite based on the MWCNT and PB properties will be noted.

Experimental
Reagents and solutions
Sodium sulfite, Methyl trimethoxy silane (MTMOS), methanol and HCl were of analytical grade supplied by Merck. Deionized water was used for the preparation of all solutions. Multi-walled carbon nanotubes (OD=10-30 nm, ID=5-10nm, length=0.5-500 μm, 95%) were purchased from Aldrich. The background electrolyte solution was prepared from potassium chloride. The pH of solutions was adjusted to 7 with phosphate buffer. The Prussian blue complex was synthesized, purified and characterized as reported [37].

Instrumentation
Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands) and a system was run on a pc using GPES 4.9 software. The morphology of CCEs modified with PB-complex and MWCNTs surface was observed using a scanning electron microscope (SEM) from SERON technology AIS-2100. An GC electrode was used as a working electrode. A

platinum wire was employed as counter electrode and a saturated Ag/AgCl (saturated KCl) served as the reference electrode and all potentials in the text refer to it (all electrode obtained from Azar Electrode Co., Urmia, Iran).

Preparation of MWCNT-PB composite film modified electrode

The method of immobilizing Prussian blue on GC electrode is described briefly as follows. The GC electrode was polished with emery paper (p 2000) and then by 0.05 µm alumina powder. Then electrode was rinsed by distilled water and sonicated in water and absolute ethanol, respectively (each for 5 min), and then allowed to dry at room temperature. At first 5 mg Prussian blue was dissolved in 1ml Methanol and homogenized thoroughly by sonication for 5 min until a clear solution was obtained. Then, 0.9 ml of this solution was mixed with 0.6 mL

(MTMOS), and 0.1 mL hydrochloric acid (0.1 M) and stirred for 5 min until a homogeneous gel solution resulted. The resulting clear solution was aged for 30 min, and then 10 µl of the freshly prepared mixed solution was pipetted onto the surface of GC electrode. The gel films were dried in an air for 24 h and were ready for use. A few I-E runs were needed at the beginning to stabilize the electrode and obtain reproducible results.

Results and discussion

In order to investigate the surface effect on the electrochemical behavior of sulfite ion, their cyclic voltammograms were recorded at the surface of different unmodified(Bare) solid electrodes such as pelatin (Pt), gold (Au) and glassy carbon (GC). The typical results of diferent electrodes in the absence or presence for 0.001 M of sulfite ion are shown in Figures 1-3.
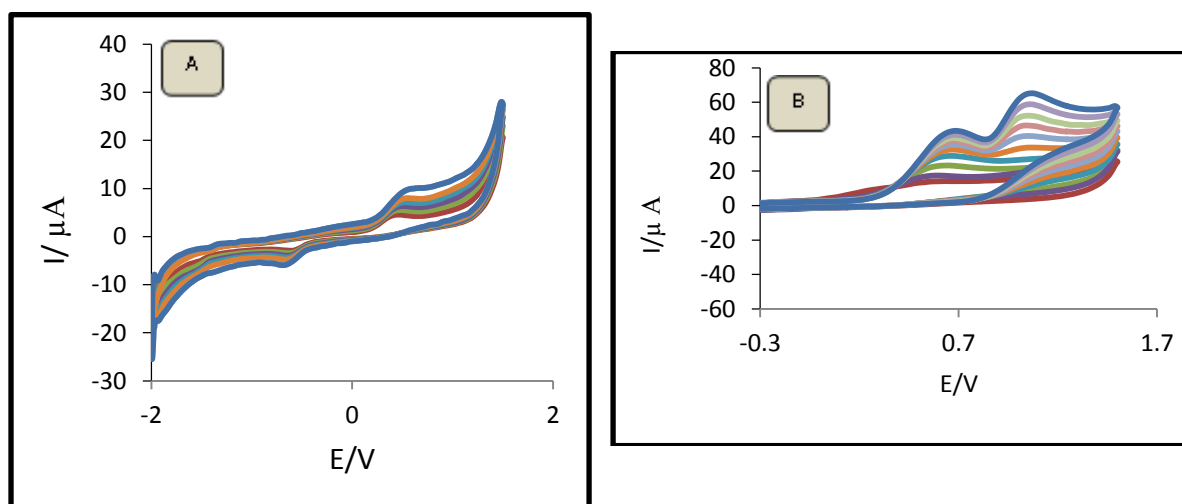

Figure 1. Cyclic voltammograms for 1.0 mM sulfite at (A) GC electrode in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rates 10, 15,20, 25, 30,40, 50 mV s^{-1} .(B) different concentration of sulfite ion 1, 2, 3, 4, 5, 6, 7, 8, 9,10 mM
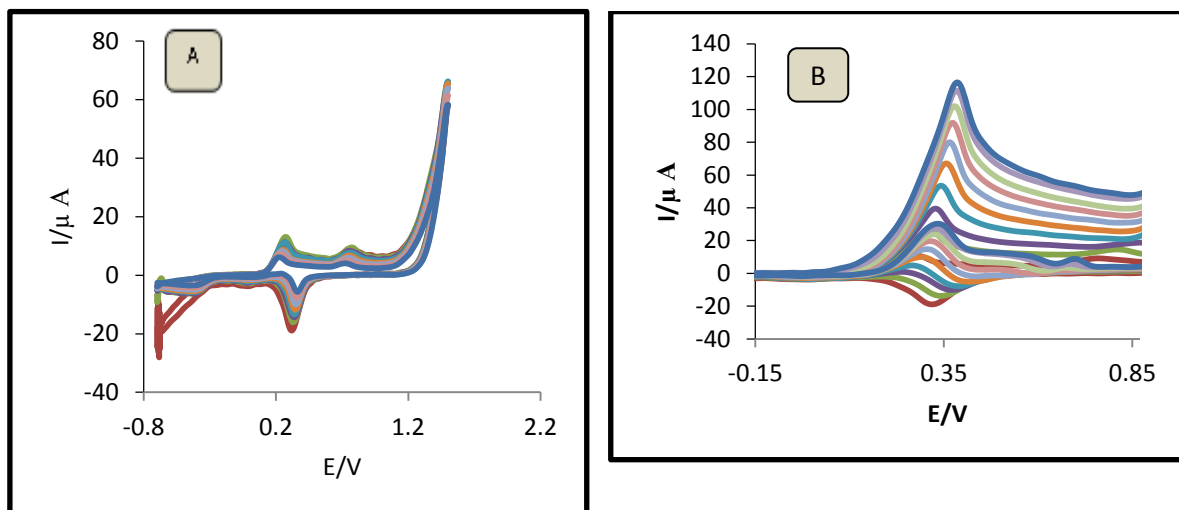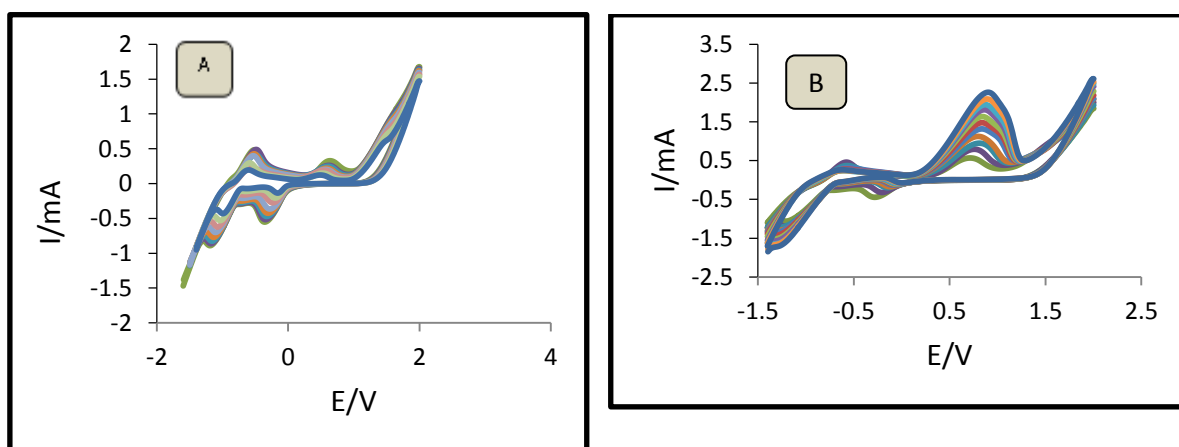
Figure 2. Cyclic voltammograms for 1.0 mM sulfite at (A) Au electrode in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rates 10, 15,20, 25, 30,40, 50 mV s^{-1} .(B) different concentration of sulfite ion 1, 2, 3, 4, 5, 6, 7, 8, 9,10 mM

Figure 3. Cyclic voltammograms for 1.0 mM sulfite at (A) Pt electrode in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rates 10, 15,20, 25, 30,40, 50 mV s^{-1} .(B) different concentration of sulfite ion 1, 2, 3, 4, 5, 6, 7, 8, 9,10, 11,12 mM

The comparing results for different elcetrodes are showen in the Table. 1. The comparison of linear range of the three electrodes shows: 1-9 mM (Au), 2-12 mM(Pt) and 2-5 mm for GC electrode.

Table 1. Comparison results for different electrodes

E$_P$(V)	I$_P$(μA)	(pH=7)
0.2838	10.7μA	Au
0.6679	0.337mA	Pt
0.6636	14.2μA	GC

At the second step, the modified electrode with Prussian blue complex was prepared by sol-gel technique at the surface of GC electrode. The Prussian blue -complex modified carbon ceramic electrode was first characterized by SEM. Scanning electron microscopy (SEM) has been an essential tool for characterizing the surface morphology and fundamental physical properties of the absorbent. A typical scanning electron micrograph image of the carbon ceramic electrode, are shown in Figure 4. The structure of the composite showed a homogeneous film on the surface of GCE. It can be seen clearly at magnification of three times that MWCNT was shown as thin fibers which merged to form bundles, entwined together.
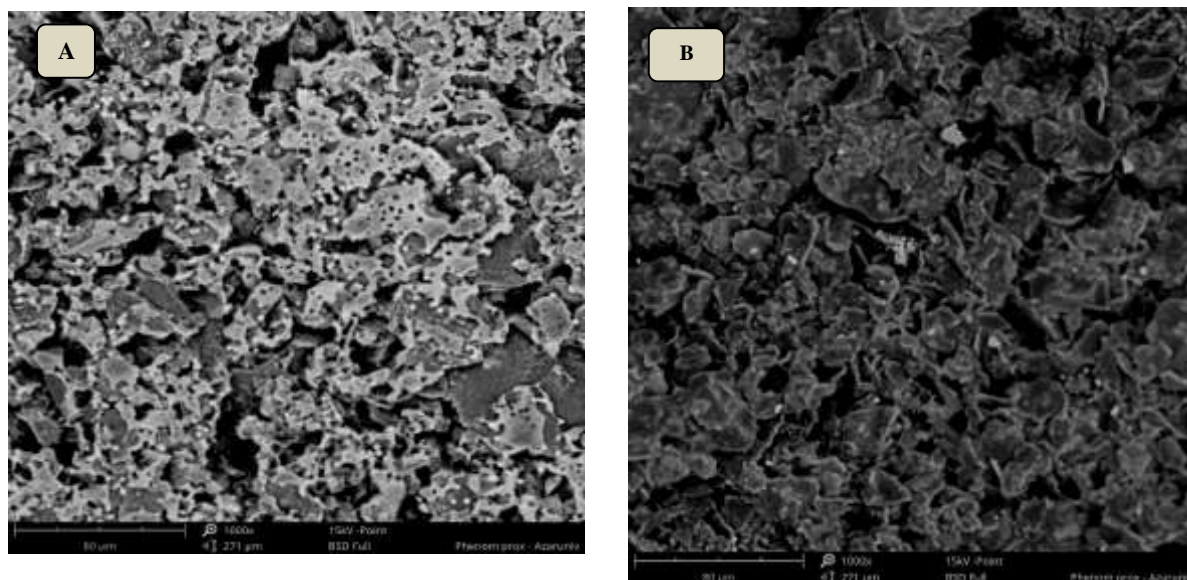

Figure 4. SEM image of (A) bare carbon ceramic electrode (B) Prussian blue modified CCE with MWCNT

The electrochemical properties of the Prussian blue modified GC electrode with sol-gel technique were studied, using cyclic voltammetry. Figure 5 shows typical cyclic voltammograms of the bare and Prussian blue modified GC electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rate 10 mV s^{-1}. It shows that the oxidation peak areas of Prussian blue modified GC electrodes are much larger than the bare GC electrode.
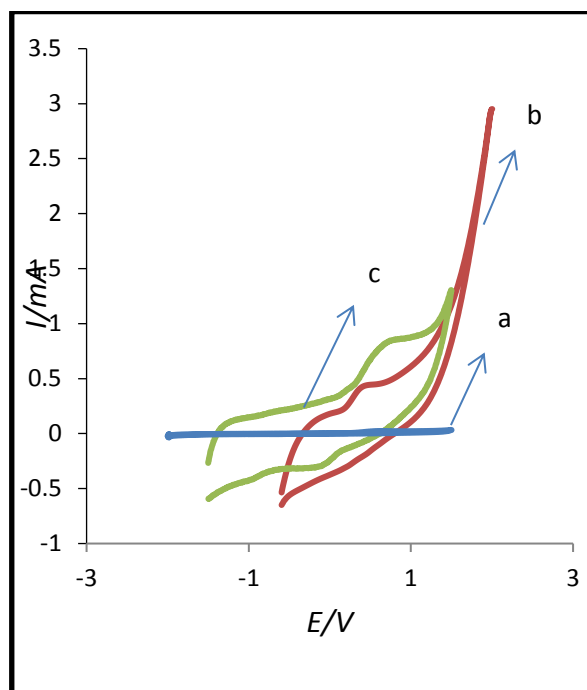
Figure 5. Cyclic voltammograms for 1.0 mM sulfite at (A) bare GC electrode (B) modified GC electrodes by carbon nanotube (C) Prussian blue modified GC electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) at scan rate 10 mV s^{-1}

There was an irreversible oxidation peak at …V on bare GCE, which was corresponding to the conversion SO_3^{2-} to SO_4^{2-} through a two-electron oxidation process [38].

The nature of the oxidation process was found to be diffusion controlled in the buffer system studied, as evidenced from the linear plots of the peak current (i_p) versus square root of the scan rate ($v^{1/2}$) for sulfite.
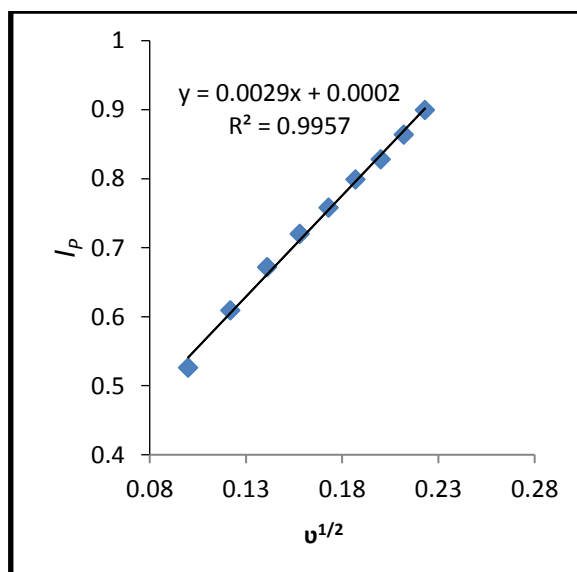

Figure 6. Ip versus $v^{1/2}$ for modified GC electrodes by carbon nanotube with Prussian blue modified GC electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7.0) ion at scan rates: 10, 20, 30, 40, 50, 60, 70, 80 and 90 mVs^{-1}

It can be noted from Figure 6 that the anodic currents increase and the peak potential shifts as the scan rate increases. When peak current values were plotted against $v^{1/2}$, the following linear relationship was obtained:

$$I_p = 2.9 \times 10^{-3} v^{1/2} - 2 \times 10^{-4} \text{ (mV / s)}^{1/2}, \quad R^2 = 0.9957 \quad (1)$$

This behavior suggests that the oxidation process is controlled by diffusion.

Thus, according to the following equation for a totally irreversible diffusive process:

$$I_p = 3.01 \times 10^5 n \, [(1-\alpha) \, n_\alpha]^{1/2} A C D^{1/2} v^{1/2} \quad (2)$$

and considering $(1-\alpha)n_\alpha = 0.1985$ (see below), $D = 2.40 \times 10^{-5}$ cm^2 s^{-1} (see chronoamperometric studies), $A = 0.123$ cm^2, it is estimated that the total number of electrons involved in the anodic oxidation of sulfite is $n = 1.94 \approx 2$.
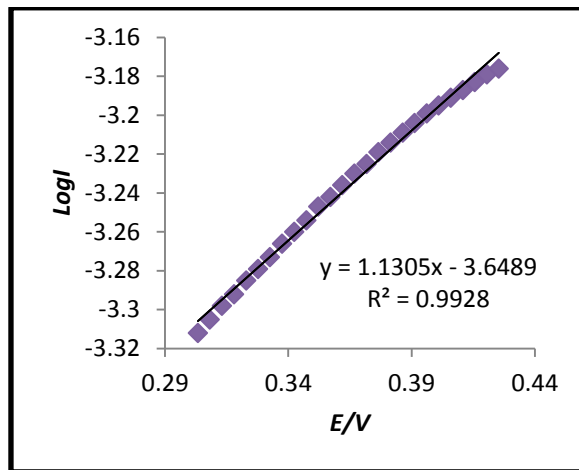

Figure 7. Tafel plot derived from data of the rising part of the E *vs.* log *I* curve at a scan rate of 10 mV s^{-1}

In order to get information on the rate determining step, the peak potential, E_p is proportional to log v, can be used in this step. The slope of E_p *vs.* log v is 0.1985 mV. The tafel slope may be estimated according to the equation for the totally irreversible diffusion-controlled process [39] :

$E_{pa} = b/2(\log v) + $ constant (4)

This slope indicates a one electron transfer to be rate limiting assuming a transfer coefficient of $\alpha = 0.80$ for sulfite at pH=7.0. The minimum value should be 0.5 indicated that there was an equal probability that the reaction activated transition state can form either products or reactants [40]. Thus the value larger than 0.5 indicates a more

favored reaction mechanism [41], which may explain why the electrocatalytic oxidation of sulfite to its oxidation product was more favored on the PB modified electrode compared with the bare GCE.

The tafel slope, b, can be obtained by another method. A tafel plot was drawn (Figure 7). Derived from data of the rising part of the current-voltage curve at a scan rate of 10 mV s^{-1}, B slope of 1.1305 V^{-1} is obtained which indicates that the rate limiting step is one electron transfer (assuming a transfer coefficient of $\alpha = 0.5$) using the following equation:

$$E/\log I = \text{Slope} = 0.059/(1 - \alpha)n_\alpha \quad (3)$$

The electrocatalytic oxidation of sulfite at the Prussian blue modified electrode was studied by chronoamperometry. The chronoamperograms obtained for a series of sulfite solutions with vaious concentrations was illustrated in Figure 8.
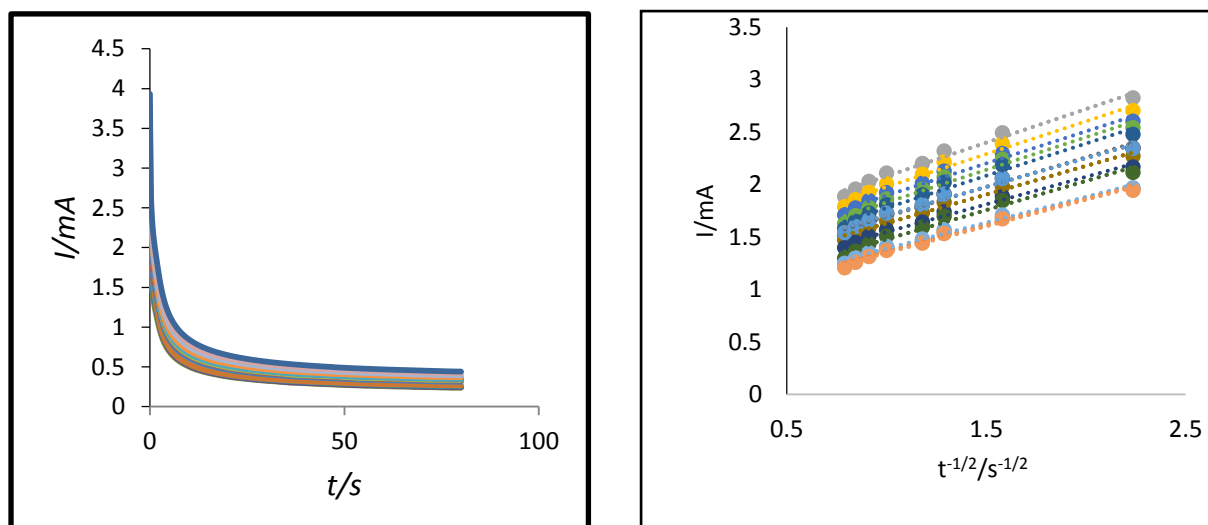

Figure 8. (A) Chronoamprometric response of a prussian blue modified electrode in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of sulfite ion for a potential step of 530 mV vs. Ag/AgCl in the range of 1 to 20 mM (B) Plot of plot of *I* versus $t^{-1/2}$ obtained from chronoamprometric experiments.

An increase in concentration of sulfite was accompanied by an increase in anodic currents obtained for a potential step of 530 mV versus Ag/AgCl reference electrode. In addition, the level of the Cottrell current, which was measured for 70 s, increases with increasing concentration of sulfite in the range of 1 to 20 mM. In chronoamperometric studies, in the diffusion coefficient of sulfite, the modified electrode can be determined. The relationship between current and time can be described by the Cottrell equation [42]:

$$I = nFAD^{1/2}C/\pi^{1/2}t^{1/2} \qquad (5)$$

where *D* is the diffusion coefficient (cm^2 s^{-1}) and *C* is the bulk concentration (mol cm^{-3}). The plot of *I* versus $t^{-1/2}$ will be linear, and from the slope, the value of *D* can be obtained. Figure 8B shows the experimental condition which we calculated a diffusion coefficient of 2.4×10^{-5} cm^2 s^{-1} for sulfite.

A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 9 to16 mM sulfite ion.

Conclusion

GC electrode coated with a thin film of sol-gel doped with Prussian blue act as an electrocatalyst for oxidation of sulfite. This film exhibits excellent electrocatalytic behavior toward sulfite oxidation in aqueous phosphate buffer solution. The overall number of electrons involved in the oxidation of sulfite, the number of electrons involved in the rate-determining step and the diffusion coefficient of sulfite were calculated.

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