

Electrocatalytic Determination of Sulfite at the Surface of a New Ferrocene Derivative-Modified Carbon Paste Electrode

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A chemically modified carbon paste electrode with 2, 7-bis (ferrocenyl ethyl) fluoren-9-one (2, 7-BFEFMCPE) was employed to study the electrocatalytic oxidation of sulfite in aqueous solution using cyclic voltammetry, differential pulse voltammetry and chronoamperometry. It has been found that under optimum condition (pH 8.00) in cyclic voltammetry, the oxidation of sulfite occurred at a potential about 420 mV less positive than that unmodified carbon paste electrode. The kinetic parameters such as electron transfer coefficient, α and catalytic reaction rate constant, K'_h were also determined using electrochemical approaches. The electrocatalytic oxidation peak current of sulfite shows a linear calibration curve were obtained in the range $8.7 \times 10^{-5} \text{ M} - 1.1 \times 10^{-2} \text{ M}$ and $4.0 \times 10^{-6} \text{ M} - 4.43 \times 10^{-4} \text{ M}$ of sulfite concentration with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods respectively. The detection limit (2δ) was determined as $5.3 \times 10^{-6} \text{ M}$ and $2.1 \times 10^{-7} \text{ M}$ by CV and DPV methods. This method was also examined as a selective, simple and precise new method for voltammetric determination of sulfite in real sample.

Keywords: 2, 7-bis (ferrocenyl ethyl) fluoren-9-one, sulfite, electrocatalysis, cyclic voltammetry, differential pulse voltammetry, chronoamperometry

1. INTRODUCTION

Sulfites are commonly used in the food and pharmaceutical industries as preservatives and antioxidants and brewing industry as an antibacterial agent. In large quantities, sulfite and its oxidation products are pollutants. In particular, sulfiting agents have received widespread attention, as a result of their allergenic effect on those individuals who are hypersensitive. Previous methods for determining sulfite have included titration [1], spectrophotometric [2-7], and chemiluminescence methods [8-12]. There has also been research in electrochemical techniques, as these can produce sensitive, selective, and simple methods of analysis. Voltammetric measurement can be used, based on sulfite oxidation at

platinum [13], and pre-treated glassy carbon electrodes [14]. Alternatively, enzyme electrodes using sulfite oxides have previously been reported [15, 16]. However, when using enzymes, the long-time stability at room temperature can sometimes be poor. Alternatively, it has been demonstrated that sulfite can undergo catalytic or mediated oxidation using some chemically modified electrodes (CMEs) [17-21]. One important group of is the ferrocene-derivative compounds.

In this paper, we describe the use of 2, 7-bis (ferrocenyl ethyl) fluoren-9-one as a mediator for the electrooxidation of sulfite in aqueous media. In addition, the suitability of the 2, 7-bis (ferrocenyl ethyl) fluoren-9-one modified carbon paste electrode in the electrocatalysis and determination of sulfite are discussed by cyclic voltammetry, double potential step chronoamperometry and differential pulse voltammetry.

2. EXPERIMENTAL DETAILS

2.1. Regents and Material

The solvent used for the electrochemical studies was twice distilled water. Buffer solution were prepared from orthophosphoric acid and its salts in the pH ranges 3.00-10.00. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter = 0.1 mm) from Merck was used as the working electrode (WE) substrate. The 2, 7-bis (ferrocenyl ethyl) fluoren-9-one was prepared by a reported procedure [22]. Sulfite was from Merck and was used as received. All other reagents were of analytical grade.

2.2. Working Electrode

A 1% (w/w) 2, 7-bis (ferrocenyl ethyl) fluoren-9-one spiked carbon powder was made by dissolving the given quantity of 2, 7-bis (ferrocenyl ethyl) fluoren-9-one in diethyl ether and hand mixing with 99 times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring a 1:1(w/w) mixture of 1% 2, 7-bis (ferrocenyl ethyl) fluoren-9-one spiked carbon powder and paraffin oil was blended by hand-mixing and the resulting paste was inserted in the bottom of a glass tube (with internal radius 3.0 mm). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without 2, 7-bis (ferrocenyl ethyl) fluoren-9-one was used as a blank to determine background current.

2.3 Apparatus

The electrochemical experiments were carried out using a Potentiostat/Galvanostat (BHP 2061-C Electrochemical Analysis System, Behpajoo, Iran) coupled with a Pentium III personal computer connected to a HP laser jet 6L printer, and experiments were performed in a three compartment cell. A platinum wire was used as the auxiliary electrode. The 2, 7-bis (ferrocenyl ethyl) fluoren-9-one modified carbon paste electrode (2, 7-BFEFMCPE) and $\text{Ag} | \text{AgCl} | \text{KCl}_{\text{sat}}$ (Metrohm) were used as the working and reference electrodes, respectively. A pH-meter (Ion Analyzer 250, Corning) was used to read the pH of the buffered solutions.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Properties of 2, 7-BFEFMCPE

We have recently constructed 2, 7-BFEFMCPE by incorporation of 2, 7-bis (ferrocenyl ethyl) fluoren-9-one into carbon paste matrix and studied its electrochemical properties in buffered aqueous solution by cyclic voltammetry and double step potential chronoamperometry. Its cyclic voltammograms exhibits an anodic ($E_{pa} = 0.35$ V) and corresponding cathodic peaks with $E_{pc} = 0.27$ V vs. Ag|AgCl|KCl_{sat} (Fig. 1) related to Fc/Fc⁺ redox couple with quasi-reversible behavior [23]. Also, the obtained result shows that the redox process of Fc/Fc⁺ in 2, 7-bis (ferrocenyl ethyl) fluoren-9-one is independent on the pH of aqueous solution.

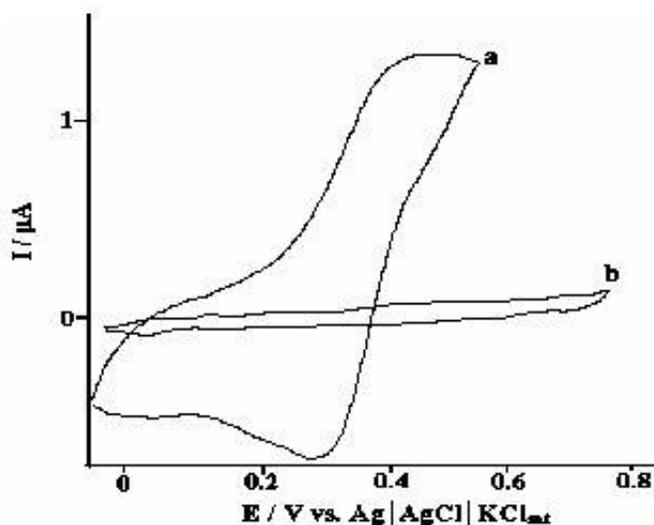


Figure 1 (a) Cyclic voltammogram of 2, 7-BFEFMCPE in 0.1 M phosphate buffer solution (pH 7.00) at scan rate 10 mV s^{-1} , (b) as a) at the surface of bare carbon paste electrode.

Double step potential chronoamperometry was employed for investigation the electrochemical processes of 2, 7-BFEFMCPE. Figure 2A shows the current- time curve of the 2, 7-BFEFMCPE obtaining by setting the working electrode potential at 0.6 V (at the first potential step) and 0.20 V (at the second potential step) vs. Ag|AgCl|KCl_{sat} in a buffered aqueous solution (pH 7.00). The results show very symmetrical chronoamperograms with an equal charge consumed for the oxidation and reduction of the redox couple in the CPE. The plot of net electrolysis current vs. $t^{-1/2}$ shows a straight line (Fig. 2B), which extrapolates close to the origin. Therefore, this type of near-Cottrellian behavior is not due to a linear semi-infinite diffusion process but may be caused by finite diffusion in a thin film, where the near-Cottrell equation behavior can be approximated over a short time period.

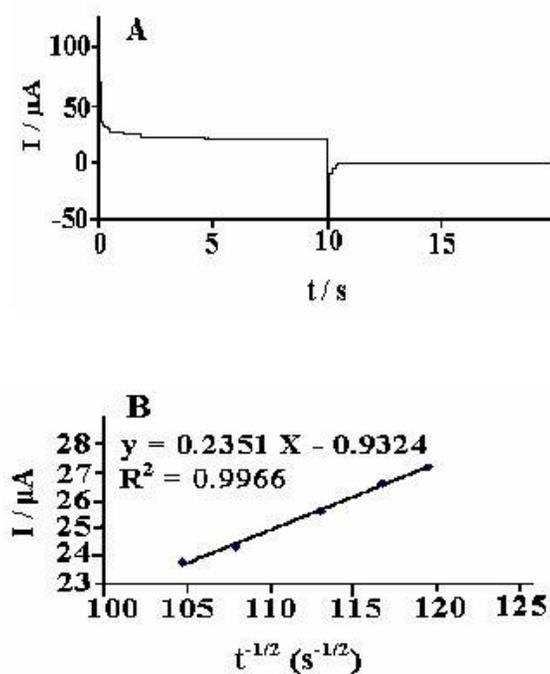


Figure 2 (A) Double step potential chronoamperogram obtained at the 2, 7-BFEFMCPE in absence of sulfite in 0.1 M phosphate buffer solution (pH 7.00). First and second potential step were 0.60 and 0.20 V vs. Ag| AgCl |KCl_{sat}. (B) Cottrell plot for curve (A)

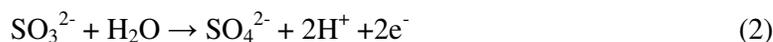
Consequently, we can assume diffusion controlled behavior for charge transfer at 2, 7-BFEFMCPE and use the potential-step chronoamperometric experiments to estimate the diffusion coefficient of 2, 7-bis (ferrocenyl ethyl) fluoren-9-one into the paraffin oil used for paste preparation. The slope of the linear region of the $I-t^{-1/2}$ plot in the short time region produces the apparent diffusion coefficient (D_{app}) of the spiked 2, 7-bis (ferrocenyl ethyl) fluoren-9-one into 2, 7-BFEFMCPE by using the Cottrell equation [24]:

$$I = n F A_g D_{app}^{1/2} c \pi^{-1/2} t^{-1/2} \quad (1)$$

Where c is the known concentration, D_{app} is the apparent diffusion coefficient of spiked 2, 7-bis (ferrocenyl ethyl) fluoren-9-one in paraffin oil and A_g is the geometric area of this electrode (the diameter (d) of the 2, 7-BFEFMCPE was measured and then the geometric area of the 2, 7-BFEFMCPE was calculated according to $(\pi (d/2)^2)$). Therefore, we calculated the apparent diffusion coefficient for 2, 7-bis (ferrocenyl ethyl) fluoren-9-one (Fig. 2B) in carbon paste matrix. It was found $2.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. While, in the equation $n=1$, $F=96485 \text{ C mol}^{-1}$, $A_g=0.091 \text{ cm}^2$ and corresponding c value was selected. This method has been used for estimation of D_{app} for 1, 4-naphthoquinone and some its derivatives [25].

3.2. pH Optimization of the Solution

It well known, the electrochemical behavior of sulfite is dependent on pH value of the aqueous solution, whereas the electrochemical properties of Fc/Fc⁺ redox couple are independent pH. Therefore, we studied the electrochemical behavior of sulfite in 0.1 M phosphate buffered solution with various pH (3.00 < pH < 10.00) at the surface of 2, 7-BFEFMCPE by cyclic voltammetry. Result shows that the catalytic current increases as pH increasing. This is probably due to a reaction mechanism involving proton transfer (see following equation):



Therefore, pH has effect on the kinetic of the catalytic reaction. Figure 3 shows the variation of I_{pa} versus the variation of pH. As can be seen, that maximum electrocatalytic current was obtained in pH 8.00. Therefore, pH 8.00 was chosen as the optimum pH for electrocatalysis of sulfite oxidation at the surface of 2, 7-BFEFMCPE. Hence, all electrochemical experiments were done at this pH.

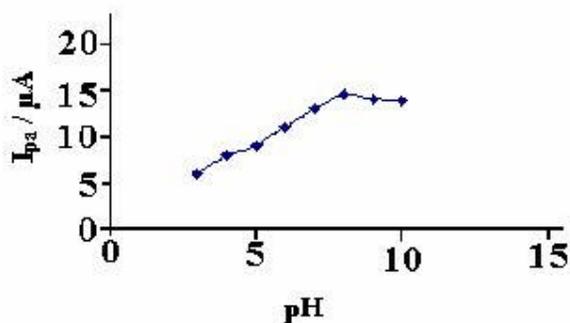


Figure 3 Current-pH curve for electrooxidation of 3 mM sulfite in 0.1 M phosphate buffer solution with various pH values: (a) 3.00, (b) 4.00, (c) 5.00, (d) 6.00, (e) 7.00, (f) 8.00, (h) 9.00 and (i) 10.00 at the surface of 2, 7-BFEFMCPE as scan rate 10 mV s⁻¹.

3.3. Mediated Oxidation of Sulfite

The cyclic voltammograms obtained for an unmodified carbon paste electrode and for 2, 7-BFEFMCPE in a phosphate buffer solution (0.1 M, pH 8.00) in the presence (0.1mM) and absence of sulfite are illustrated in Figure 4. At an unmodified CPE, the sulfite oxidation occurs irreversibly with a peak potential of nearly 0.88V versus Ag|AgCl|KCl_{sat} (Fig. 4b), in the absence of sulfite no peaks appears (Fig. 4a). In 0.1mM of sulfite solution, the anodic peak that is observed for 2, 7-BFEFMCPE in the absence of sulfite increases greatly, while the corresponding cathodic wave disappears on the reverse scan (Fig. 4c and d). This behavior is typical of that expected for electrocatalysis at chemically modified electrodes. The sulfite oxidation occurs at 0.46V vs. Ag|AgCl|KCl_{sat} at 2, 7-BFEFMCPE surface; therefore, it is shifted about 0.42 V toward less positive potential than that of a bare CPE. This value is comparable with values reported by other research groups for electrocatalytic oxidation of sulfite at the surface of chemically modified electrodes by other mediators (see Table 1).

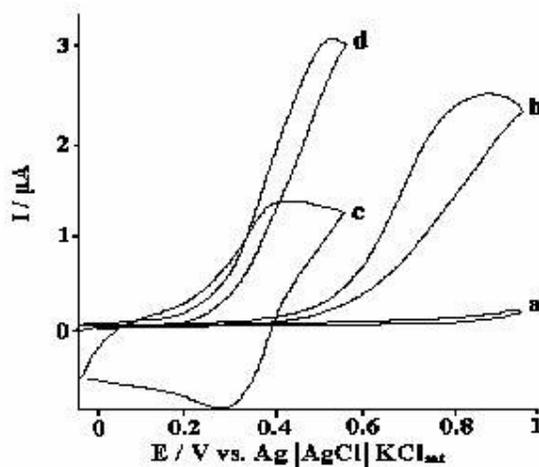


Figure 4 Cyclic voltammograms of (a) CPE in 0.2 M phosphate buffer solution (pH 8.00) at scan rate 10mV s^{-1} and (b) as (a) in the presence of 0.1 mM sulfite (c) as (a) and (d) as (b) at the surface of 2, 7-BFEFMCPE.

Table 1. Values of catalytic effect on anodic peak potential of sulfite by different catalysts.

Electrode	Use catalyst	Catalytic effect(mV)	pH	References
GC	NiHCF	350	7	[25]
GC	$[(\text{Fe}(\text{phen})_3)]^{2+}$	100	4	[26]
GC	$[(\text{Fe}(4,7\text{-Me}_2\text{phen})_3)]^{2+}$	150	5.5	[26]
GC	$[(\text{Fe}(3,4,7,8\text{-Me}_4\text{phen})_3)]^{2+}$	340	4	[26]
GC	Poly $[\text{Fe-NH}_2\text{-phen}]_3^{2+}$	200	2	[27]
GC	$[(\text{Fe}(\text{bpy})_3)]^{2+}$	160	4	[26]
GC	Fc	400	8	[21]
Carbon past	(2, 7-BFEFMCPE)	420	8	This work

NiHCF: nickel hexacyanoferrate; phen: phenanthroline, bpy: bipyridine; Me: methyl, FC: ferrocenecarboxylic acid, (2, 7-BFEFMCPE): 2, 7-bis (ferrocenyl ethyl) fluoren-9-one.

The above results show the oxidation of sulfite is facilitated and catalyzed by the presence of 2, 7-bis (ferrocenyl ethyl) fluoren-9-one spiked in to carbon paste electrode. The presence of 2, 7-bis (ferrocenyl ethyl) fluoren-9-one as a mediator on the surface electrode provides an alternative reaction site to carbon paste for electron transfer process of sulfite. Therefore, current due to the oxidation of sulfite is increased when a 2, 7-BFEFMCPE was used.

The effect of the potential scan rate on the electrocatalytic property of 2, 7-BFEFMCPE toward sulfite was studied by cyclic voltammetry. Figure 5A shows the cyclic voltammograms of the 2, 7-BFEFMCPE at various scan rates (10-350 mV/s). These results show that the catalytic effect of the mediator appeared at scan rates up to 25 mV s^{-1} . It can also be noted from Fig. 5A that with an increasing scan rate, the peak potential for the electrooxidation of sulfite shifts to more positive

potentials, suggesting a kinetic limitation in the reaction between the redox sites of 2, 7-BFEFMCPE and sulfite. In addition the cathodic current would increase with increasing scan rate, because in short time-scale experiments, there is not enough time for catalytic reaction to take place completely. However, the oxidation current of sulfite increased linearly with the square root of the scan rate of potentials (Fig. 5B), which demonstrates a diffusion controlled electrochemical process.

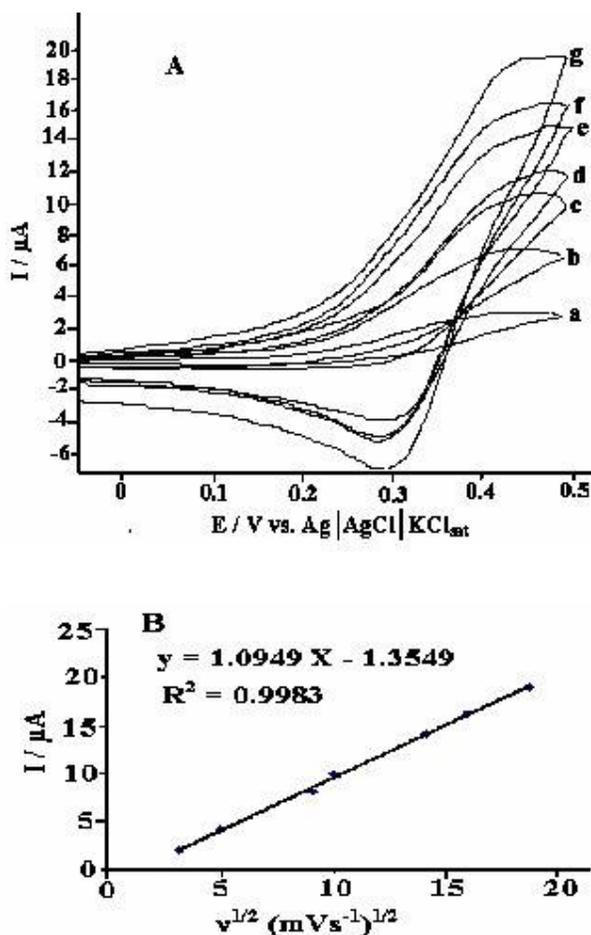


Figure 5 (A) Cyclic voltammograms of 0.2 mM sulfite at various scan rates: (a) 10; (b) 25; (c) 83; (d) 100; (e) 200, (f) 250 and (g) 350 mV s^{-1} in 0.1 M phosphate buffer solution (pH 8.000). (B) Plot of I_{pa} versus $v^{1/2}$ for the oxidation of sulfite at the surface of 2, 7-BFEFMCPE.

In order to get the information on the rate determining step, Tafel slope (b) determines using the following equation for a totally irreversible diffusion controlled process [29]:

$$E_p = b/2 \log v + \text{constant} \quad (3)$$

Based on Equation 1, the slope of E_p versus $\log v$ is $b/2$, where b indicates the Tafel slope. The slope of E_p versus $\log v$ plot was found to be 0.0291 V in this work, thus $b = 2 \times 0.0291 = 0.0582$ V. This slope value

indicated an electron transfer process, which is the rate limiting step by assumption of a transfer coefficient (α) equal to 0.507. Also, The values of αn_{α} (where α is the transfer coefficient and n_{α} is the number of electrons involved in the rate determining step) were calculated for the oxidation of sulfite at pH 8.00 at both modified and unmodified CPEs according to the following equation [30]:

$$\alpha n_{\alpha} = 0.048 / (E_p - E_{p/2}) \quad (4)$$

Where, $E_{p/2}$ is the potential corresponding to $I_{p/2}$. The values for αn_{α} were found to be 0.51 and 0.24 for the oxidation of sulfite at the surface of the 2, 7-BFEFMCPE and CPE, respectively. These values clearly show that not only the overpotential for sulfite oxidation is reduced at the surface of 2, 7-BFEFMCPE, but also the rate of the electron transfer process is greatly enhanced, this phenomenon is thus confirmed by the larger I_{pa} values recorded during cyclic voltammetry at 2, 7-BFEFMCPE.

3.4. Chronoamperometric Studies

Double step potential chronoamperometry was also employed to investigation of electrochemical behavior of aqueous buffered solution (pH 8.00) containing of various concentration of sulfite at 2, 7-BFEFMCPE by setting the working electrode potential at 0.60 V (at the first potential step) and 0.20 V (at the second potential step) vs. Ag|AgCl|KCl_{sat} (Fig.6A). As can be seen, there is not any net cathodic current corresponding to the reduction of mediator in the presence of sulfite, when the potential is stepped from 0.60 V to 0.20V vs. Ag|AgCl|KCl_{sat}. However, in the presence of sulfite the charge value associated with forward chronoamperometry is signification greater than that observed for backward chronoamperometry (Fig. 6B(b')). However, in the presence of sulfite the charge value associated with forward chronoamperometry is signification greater than that observed for backward chronoamperometry. The linearity of electrocatalytic current vs. $v^{1/2}$ indicates that the current must be controlled by diffusion of sulfite from bulk solution toward surface of electrode. Therefore the slope of this linear plot can be used to estimate the diffusion coefficient, D of sulfite. The mean value of the D found to be $2.751 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Therefore, the results show that mediator at the surface of 2, 7-BFEFMCPE can catalyze the oxidation of sulfite.

The rate constant for the chemical reaction between sulfite and redox sites in 2, 7-BFEFMCPE, K_h can be evaluated by chronoamperometry according to the method described in [31]:

$$I_C/I_L = \gamma^{1/2} [\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma) / \gamma^{1/2}] \quad (5)$$

where I_C is the catalytic current of 2, 7-BFEFMCPE in the presence of sulfite and I_L is the limited current in the absence of sulfite and $\gamma = k_h C_b t$ (C_b is the bulk concentration of sulfite, mol cm^{-3}) is the argument of error function. In the cases where γ exceeds 2, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_C/I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (k_h C_b t)^{1/2} \quad (6)$$

Where k_h and t are the catalytic rate constant ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) and time elapsed (s) respectively. The above equation (6) can be used to calculate the rate constant of catalytic process, k_h . Having measured the catalytic current, i.e. I_C , it is possible to carry out the electrode process in identical condition, but in the absence of sulfite, in order to determine I_L .

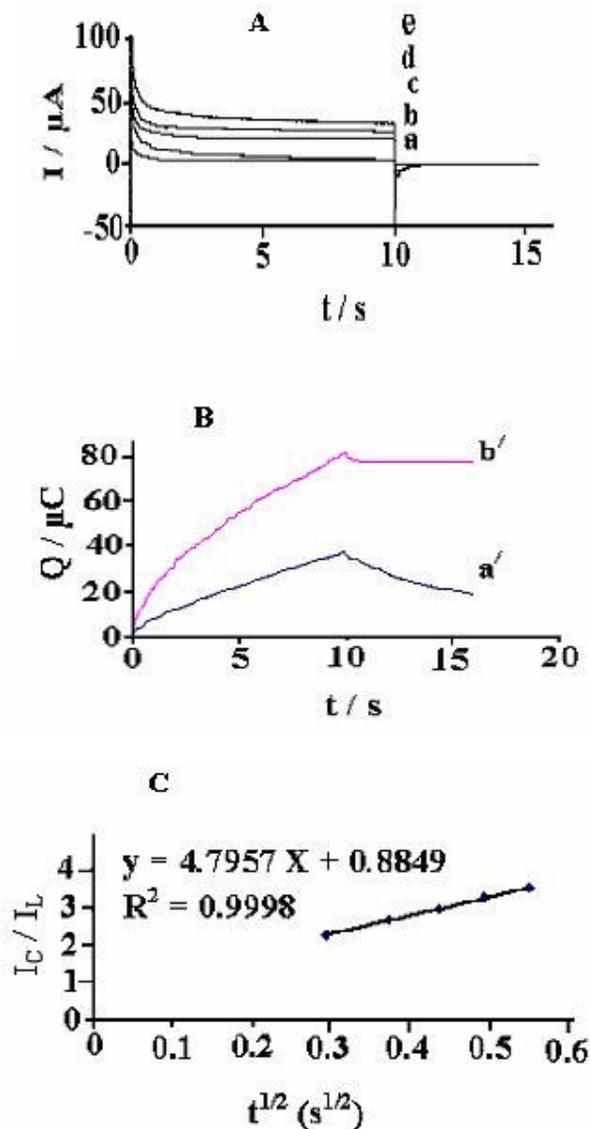


Figure 6 (A) Chronoamperograms obtained at the 2, 7-BFEFMCPE in the absence (a) and presence of (b) 1.0; (c) 3.0, (d) 4.0 and (e) 5.0 mM of sulfite in 0.1 M phosphate buffer solution (pH 8.00). First and second potential steps were 0.60 and 0.20 V. vs. Ag|AgCl|KCl_{sat}. (B) Shows the charge-time curves: (a) for curve (a) and (b) for curve (b). (C) Dependence of I_C/I_L on the $t^{1/2}$ driven from the chronoamperograms (A).

From the slope of I_C/I_L versus $t^{1/2}$ plot the value of k_h can be simply calculated for a given concentration of substrate. The calculated value of k_h is $7.32 \times 10^3 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ using the slope of I_C/I_L - $t^{1/2}$ plot (Fig. 7). This value of k_h explains as well as the sharp feature of the catalytic peak observed

for catalytic oxidation of sulfite at the surface of 2, 7-BFEFMCPE. On the other hand, the surface coverage (Γ) of a modified electrode prepared at optimum condition was obtained from the Equation $\Gamma=Q/nFA$, where Q is the charge obtained by integration the anodic peak under the background correction, A is the geometric area of electrode; and other symbols have their usual meanings. The calculated value of Γ was 6.5×10^{-7} mol cm^{-2} at pH 8.00. Using this value of coverage, the heterogeneous rate constant of catalytic reaction was calculated as $K'_h = 1.21 \times 10^{-3}$ cm s^{-1} .

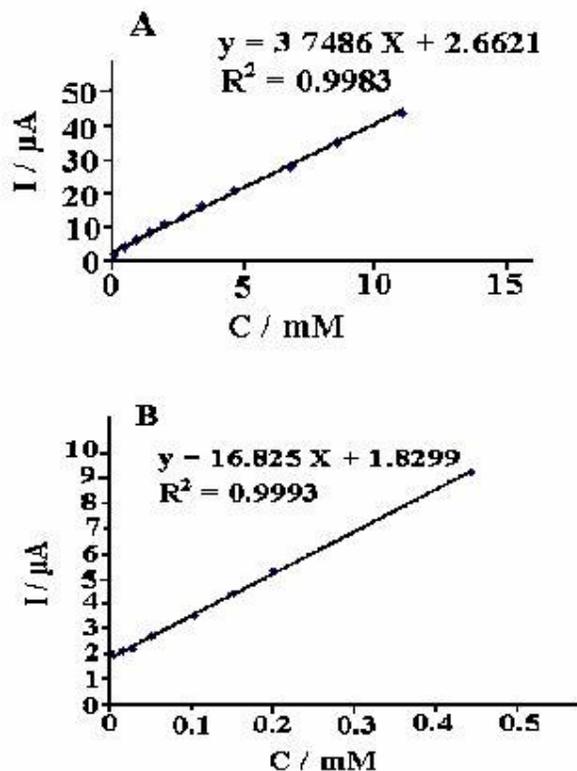


Figure 7 The Plot of electrocatalytic peak currents from (A) cyclic voltammograms of sulfite at the various concentrations (data points from left to right): 0.087, 0.50, 0.96, 1.47, 2.00, 2.76, 3.45, 4.7, 6.82, 8.57 and 11.10 mM. (B) Differential pulse voltammograms of sulfite at various concentrations (data points from left to right): 0.004, 0.0149, 0.0267, 0.05, 0.100, 0.150, 0.200 and 0.443 mM in 0.1 M phosphate buffer solution (pH 8.00) vs. sulfite concentrations at the surface of 2, 7-BFEFMCPE at a scan rate of 10 mV s^{-1} .

3.5. Electrocatalytic Determination of Sulfite

The electrocatalytic current of sulfite oxidation at the surface of 2, 7-BFEFMCPE can be used for determination of sulfite in solution. Therefore, cyclic voltammetry experiments were performed using 2, 7-BFEFMCPE in a phosphate buffer solution containing various concentration of sulfite. The results show that the electrocatalytic peak current of sulfite oxidation at the surface of 2, 7-BFEFMCPE was linearly dependent on sulfite concentration, and also the range of this linearity is dependent on the amount of the mediator in the electrode matrix. The mediated oxidation peak currents of sulfite at the surface of 1% 2, 7-BFEFMCPE were proportion to the concentration of sulfite within the range of 8.7×10^{-5} M - 1.1×10^{-2} M and 4.0×10^{-6} M - 4.43×10^{-4} M (with the correlation coefficient of 0.9981 and

0.9993) in the cyclic voltammetry and differential pulse voltammetry respectively (Fig. 8). The detection limits (2σ) were 5.3×10^{-6} M and 2.1×10^{-7} M, respectively.

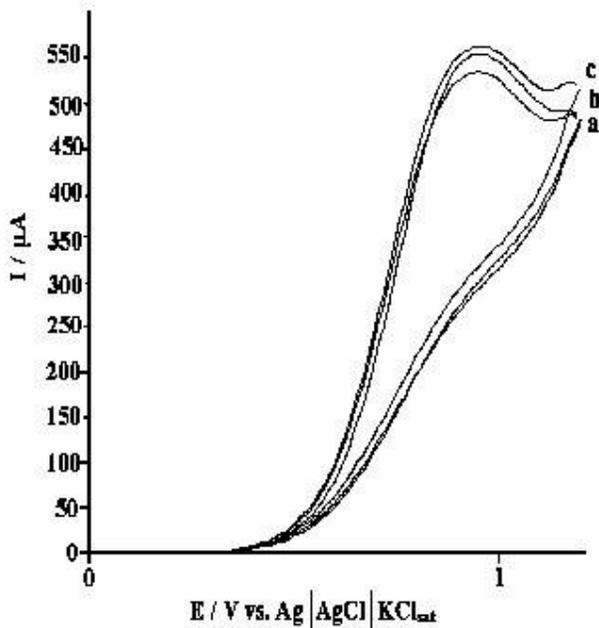


Figure 8 Cyclic voltammograms of a) solution of 5 order dilution of weak liquor from wood and paper factory in the presence of 0.1 M LiClO_4 and 0.1 M phosphate buffer at pH 8.00, b) and c) as a) after addition sodium sulfite 3.5 and 5 mM, respectively. $\nu = 10 \text{ mV s}^{-1}$.

3.6. Determination of Sulfite in Real Sample

In order to demonstrate the catalytic oxidation of sulfite in a real sample, we examined this ability in determining sulfite in weak liquor from the wood and paper industry. Figure 9 Shows the cyclic voltammograms recorded for the diluted weak liquor in the phosphate buffer 0.1 M and LiClO_4 0.1 M (curve a). As can be seen in this Figure, adding sulfite to the solution caused an increase in the oxidation peak height (curves b and c). Thus the peak was attributed to sulfite oxidation. This peak appeared about 960 mV which is 80 mV more than the 880 mV related to standard solutions of sulfite due to matrix effect. The determination of sulfite in a sample was carried out by the standard addition method for presentation of any matrix effect. By this method sulfite concentration in the weak liquor from the wood and paper factory of Mazandaran province in Iran was about 0.095 M. The relative standard deviation obtained from the line equation ($R^2 = 0.9973$) for the real sample was 5.4%. Accuracy was examined by comparison of data obtained from this method with a recognized common method [32] for determination of sulfite (oxidation-reduction titration in acid solution of KIO_3/KI in the presence of starch as indicator). The results from the statistical calculation indicate good agreement between the mean values (t-test) and precision (f-test) for the two methods.

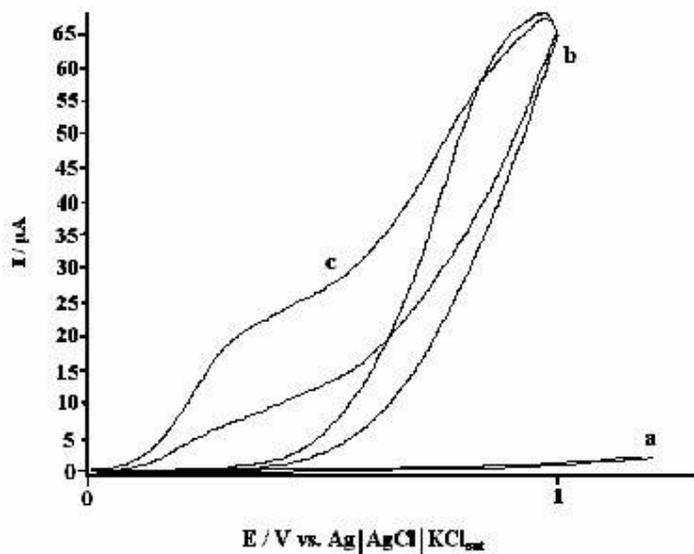


Figure 9 Cyclic voltammograms of (a) 0.1 M phosphate buffer + 0.1 M LiClO₄; (b) as (a) + 0.5 mL of weak liquor solution; (c) as (b) + 1 mM of gallic acid; $\nu = 10 \text{ mV s}^{-1}$ and pH 8.00.

3.7. Interference Study

A group of wood extractive materials is phenolic compounds which seem electroactive and exist in wood [33]. Therefore, the interference effect of some phenolic compounds such as gallic acid, ellagic acid and chrysin in the determination of sulfite in a weak liquor solution has been investigated. The cyclic voltammogram for the weak liquor (Fig. 10 curve b) shows that in the range of the sweep potential only the sulfite oxidation peak is observed, while after addition of gallic acid from its standard solution to the same weak liquor a new oxidation peak (Fig. 10, curve c) appears at 0.250 V that is related to gallic acid oxidation. Other phenolic compounds show similar effects.

Thus, trace phenolic compounds do not interfere with this electrocatalytic method for sulfite determination in weak liquor solution.

4. CONCLUSIONS

This work describes the construction of chemically modified carbon paste electrode by the incorporation of 2, 7-bis (ferrocenyl-ethyl) fluoren-9-one as a modifying species. The value of the peak separation potential obtained for 2, 7-bis (ferrocenyl-ethyl) fluoren-9-one / 2, 7-bis (ferricenium-ethyl) fluoren-9-one couple suggests that the couple can act as a quasireversible system in the carbon paste matrix. Electrochemical studies show that the oxidation of sulfite is catalyzed at the pH 8.00, whereas, the peak potential of sulfite is shifted by 420 mV to less positive potential at the surface of 2, 7-BFEFMCPE. The kinetic parameter of the electrocatalytic process, the diffusion coefficients of sulfite in an aqueous solution and 2, 7-bis (ferrocenyl-ethyl) fluoren-9-one in carbon paste matrix were determined. Finally, the electrocatalytic oxidation currents of sulfite at the surface of 2, 7-BFEFMCPE

was linear to concentration of sulfite. In addition, results show some phenolic compounds such as gallic acid, ellagic acid and chrysin have not any interference effect in the determination of sulfite in a weak liquor solution.

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