Int. J. Electrochem. Sci., 3 (**2008**) 1236 - 1247

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrocatalytic Oxidation of Sulfite by Quinizarine at Carbon Paste Electrode

Mohammad Mazloum Ardakani[1,*], *Fahime Habibollahi*[1], *Hamid Reza Zare*[1], *Hossein Naeimi*[2]

[1] Department of Chemistry, Faculty of Science, Yazd University, Yazd, 89195-741, I.R. Iran
[2] Departemant of Chemistry, Faculty of Science, University of Kashan, Kashan, 87317, I.R. Iran
[*]E-mail: mazloum@yazduni.ac.ir

Received: 1 August 2008 / *Accepted:* 29 August 2008 / *Published:* 4 October 2008

A chemically modified carbon paste electrode with quinizarine (Q-MCPE) was employed to study the electrocatalytic oxidation of sulfite in aqueous solution using cyclic voltammetry, chronocoulometry and differential pulse voltammetry. It has been found that under optimum condition (pH 7.0) in cyclic voltammetry, the oxidation of sulfite occurred at less positive potential than that unmodified carbon paste electrode. The electrocatalytic process was highly dependent on the pH of supporting electrolyte. The kinetics parameters of this process were calculated, the apparent electron transfer rate constant k_s and electron transfer coefficient, α were 2.88 s^{-1} and 0.59, respectively. The experimental parameters were optimized and the mechanism of the catalytic process was discussed. Using differential pulse voltammetry, the calibration curve for sulfite was obtained and detection limit of sulfite was 4.0×10^{-5} M. With good selectivity and sensitivity, this method was also examined as a selective, simple and precise new method for voltammetric determination of sulfite in real sample.

Keywords: Sulfite; Quinizarine; Carbon paste electrode; Electrocatalytic oxidation

1. INTRODUCTION

During the last years great attention has been drawn to the development of methods for sulfite determination. Sulfites is used as a preservative in the food industry because its addition to several products (vegetables, fruits, and several beverages) prevents oxidation, inhibits bacterial growth and assists in preserving vitamin C[1]. Despite these great advantages, the sulfite content in foods and beverages should be strictly limited due to its potential toxicity. Therefore, the existence of methods allowing an accurate measurement of sulfite is very important for food industry in order to control product quality. Among the methods available for the measurement of this sulfite we can highlight titration [2], spectrofluorometry [3], chemiluminiscence [4,5], phosphorimetry [6], spectrophotometry [7], flow injection analysis (FIA) [8]. However, the majority of these methods need extensive sample pre-treatment and reagent preparation. There has also been research in electrochemical techniques, as these can produce sensitive and simple methods of analysis. Voltammetric measurement can be used, based on sulfite oxidation at platinum [9] and pre-treated glassy carbon electrodes [10]. Alternatively, enzyme electrodes using sulfite oxides have previously been reported [11,12]. However when using enzymes, the long-time stability at room temperature can sometimes be poor. In the recent years several chemically modified electrodes for sulfite sensing based on polyaniline [13], poly[Ni-(protoporphyrinIX)] [14], Ru(bpy)(tpy)Cl]PF_6 [15], metal pentacyanonitrosyl ferrate [16,17] and copper hydroxide [18], new ferrocene derivative [19].

In this work, we described the use of quinizarine as a mediator for the electrooxidation of sulfite in aqueous media. The electrochemical properties and electrocatalytic activity of the modified electrode toward the oxidation of sulfite were studied using various electrochemical procedures. In order to demonstrate the catalytic ability of this modified electrode in the oxidation of sulfite in real sample, we examined this ability in determining sulfite in wastewater.

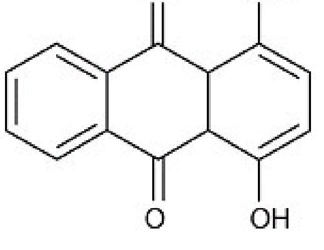
2. EXPERIMENTAL PART

2.1. Electrochemical measurement

All electrochemical experiments were carried out using a μAutolab potentiostat (Eco Chemie B. V., Type III) equipped with GPES 4.9 software. The cell used was equipped with a modified carbon paste electrode as the working electrode, a saturated Ag/AgCl reference electrode, and a platinum wire counter electrode. All potentials were measured and reported versus the Ag/AgCl reference electrode.

2.2. Reagents

Quinizarine (1,4-dihydroxyanthraquinone) (scheme.1) has been synthesized from hydroquinone and phthalic anhydride in our laboratory and characterized by physical and spectroscopic data. Sodium sulfite, graphite fine powder and viscous paraffin were obtained from Merck and used as received. All solutions were prepared with twice distilled water. Buffer solutions were prepared from orthophosphoric acid and its salts. All chemicals were of the highest purity available from Merck and were used without further purification.



Scheme 1.

2.3. Preparation of working electrode

A 1% (w/w) quinizarine spiked carbon powder was made by dissolving a given quantity of quinizarine in methanol 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% quinizarine spiked carbon powder and paraffin oil was blended by hand mixing and the resulting paste was then inserted in the bottom of a glass tube(quinizarine modified carbon paste electrode, Q-MCPE). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without quinizarine was used as a blank to determine background current.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of quinizarine

According to our knowledge, there is no report on a study of the electrochemical properties and especially the electrocatalytic activity, of Q-MCPE in aqueous media. Because this compound is insoluble in aqueous media, we prepared Q-MCPE. Therefore, we studied the electrochemical behavior of Q-MCPE in a pure buffered aqueous solution by cyclic voltammetry. Fig. 1A shows cyclic voltammograms of Q-MCPE for various scan rates (2-150 mV s^{-1}) in a 0.1 M phosphate buffered aqueous solution (pH 7.0). As can be seen, the peak separation potential, ΔE_p (= $E_{p.a} - E_{p.c}$), is about 150 mV at low scan rate (10 mV s^{-1}). That is greater than the (59/n) mV expected for a reversible system. This result suggests that a quinizarine/quinizarine$_{ox}$ redox in Q-MCPE shows a quasi-reversible behavior in an aqueous medium. In addition, the formal potential [$E^{0'} = (E_{p.a} + E_{p.c})/2$] is almost independent of the potential scan rate for sweep rates suggesting facile charge transfer kinetics over this range of scan rate. However, for scan rates above 600 mV s^{-1}, the peak separation being to increase, indicating the limitation arising from charge transfer kinetics. Also, the electrochemical responses of the Q-MCPE were those anticipated for a bulk-confined redox couple, because the peak currents were directly proportional to the scan rate (Fig. 1, inset B), as predicated for a diffusionless system. The apparent charge transfer rate constant, k_s, and the charge transfer coefficient, α, of a bulk-confined redox couple can be evaluated from cyclic voltammetric experiments and using the variation of anodic and cathodic peak potential with scan rate, according to the procedure of Laviron [20]. Inset C of Fig. 1 shows the variations of cathodic peak potentials ($E_{p.c}$) as a function of the potential scan rate. We found that the E_p values are proportional to the logarithm of the scan rate, for scan rates higher than 600 mV s^{-1} (Fig. 1 inset D) under these conditions, the following equation can be used to determine the electron transfer rate constant between quinizarine and carbon paste electrode (CPE) [20]:

$$\log k_s = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log (RT/nF\nu) - \alpha (1-\alpha) nF\Delta Ep/2.3RT \qquad (1)$$

Where $(1-\alpha)n_\alpha = 0.41$, n=2, $\Delta E_p = E_{p.a} - E_{p.c}$, υ is the sweep rate and all other symbols have their conventional meanings. From the values of ΔE_p corresponding to different sweep rates, an average value of k_s was found to be 2.88 ± 0.07 s^{-1}. Also the value obtained for the charge transfer coefficient, from the slopes of the inset D plot, was found to be 0.59. Generally**,** the electrode process of quinizarine involves the participation of protons. The effect of pH on the Q-MCPE signal was investigated by cyclic voltammetry using 0.1 M buffer solution with various pH values, ranging from 2.0 to 10.0. As can be seen in Fig. 2, the formal potential, $E^{0'} = E_{p.a} - 0.59(E_{p.a} - E_{p.c})$, of Q-MCPE was pH dependent. Two linear segments were found with slope values of -56.3 mV/pH and -30.0 mV/pH in the ranges of pH < pK_{a1} and pH > pK_{a1}, respectively. The intersection of these two linear segments should therefore correspond to the pK_{a1} of quinizarine. The value obtained for pK_{a1} of quinizarine is 9.0. The total number of protons that also participates in the redox process of quinizarine may vary in accordance with the pH range. Depending on the number of protons taking part in the redox process with two electron transfer, $E^{0'}$ will shift by -56.3 mV/pH ($2H^+$) and -30.0 mV/pH ($1H^+$) [21]. So there are two protons transferred in the redox reaction in the pH range of 2.0-9.0 and one proton in the pH range above 9.0.

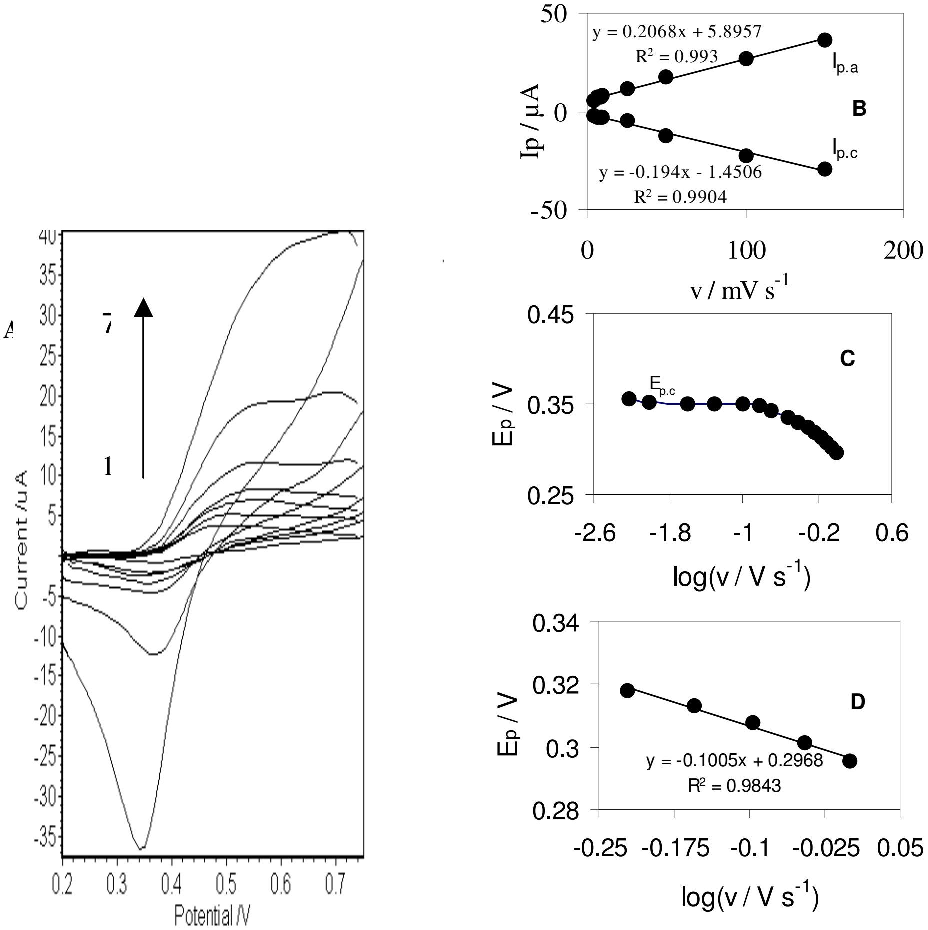


Figure 1. (A) Cyclic voltammograms of Q-MCPE in 0.1 M phosphate buffer (pH 7.0) at various scan rates: The numbers 1-7 correspond to 2, 4, 6, 10, 25, 50 and 150 mV s^{-1} scan rates, respectively. (B) Variation of I_p versus scan rates. (C) Variation of $E_{p.c}$ versus the logarithm of the scan rate. (D) Magnification of the same plot for high scan rates.

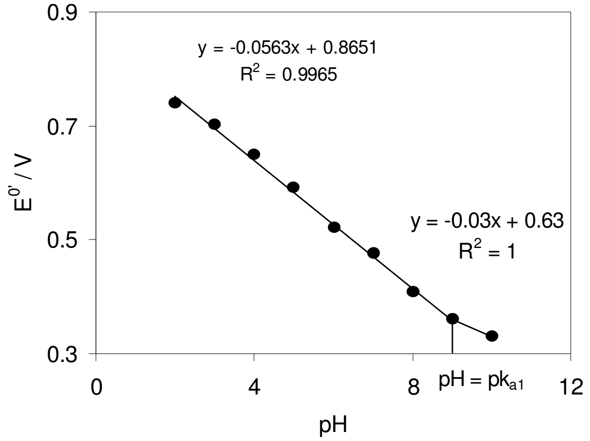


Figure 2. Dependence on pH of the formal potential, E0', for the Q-MCPE in 0.1 M phosphate buffer solution.

3.2. Electrochemistry of sulfite at Q-MCPE

It well known, the electrochemical behavior of sulfite is dependent on pH value of the aqueous solution. Therefore we studied the electrochemical behavior of sulfite in 0.1 M phosphate buffered solution with various pH (4.0 < pH < 9.0) at the surface of Q-MCPE by cyclic voltammetry. Fig. 3 shows the variation of $I_{p.a}$ versus the variation of pH. As can be seen, that maximum electrocatalytic current was obtained in pH 7.0. Therefore, pH 7.0 was chosen as the optimum pH for electrocatalysis of sulfite oxidation at the surface of Q-MCPE. Hence, all electrochemical experiments were done at this pH.

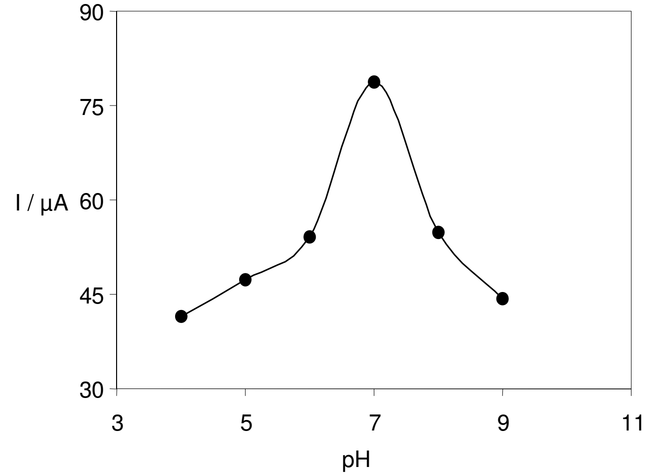


Figure 3. Current-pH curve for electrooxidation of 2.5 mM sulfite in 0.1 M phosphate buffer solution with various pH values: (a) 4.0, (b) 5.0, (c) 6.0, (d) 7, (e) 8 and (f) 9 at the surface of Q-MCPE as scan rate 10 mV s^{-1}.

The cyclic voltammograms obtained for an unmodified carbon paste electrode and for Q-MCPE in a phosphate buffer solution (0.1 M, pH 7.0) in presence (2.5 mM) and absence of sulfite are illustrated in Fig. 4. At an unmodified CPE, the sulfite oxidation occurs irreversibly with a peak potential of nearly 900 mV versus Ag/AgCl/KCl $_{sat}$ (Fig. 4c). In 2.5 mM of sulfite solution, the anodic peak that is observed for Q-MCPE in the absence of sulfite increases greatly, while the corresponding cathodic wave disappears on the reverse scan (Fig. 4b and a). This behavior is typical of that expected for electrocatalysis at chemically modified electrodes. The sulfite oxidation occurs at 609 mV vs. Ag/AgCl/KCl $_{sat}$ at Q-MCPE surface; therefore, it is shifted about 291 mV toward less positive potential than that of a bare CPE.

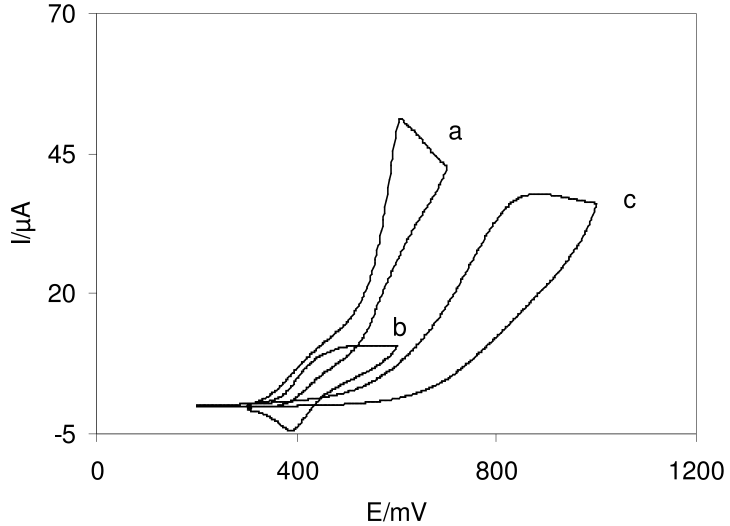


Figure 4. Cyclic voltammograms of quinizarine modified carbon paste electrode in 0.1 M phosphate buffer solution of pH 7.0 at scan rate 25 mV s^{-1}, (a) in 2.5 mM of sulfite, (b) in absence of sulfite, (c) as (a) for an unmodified CPE.

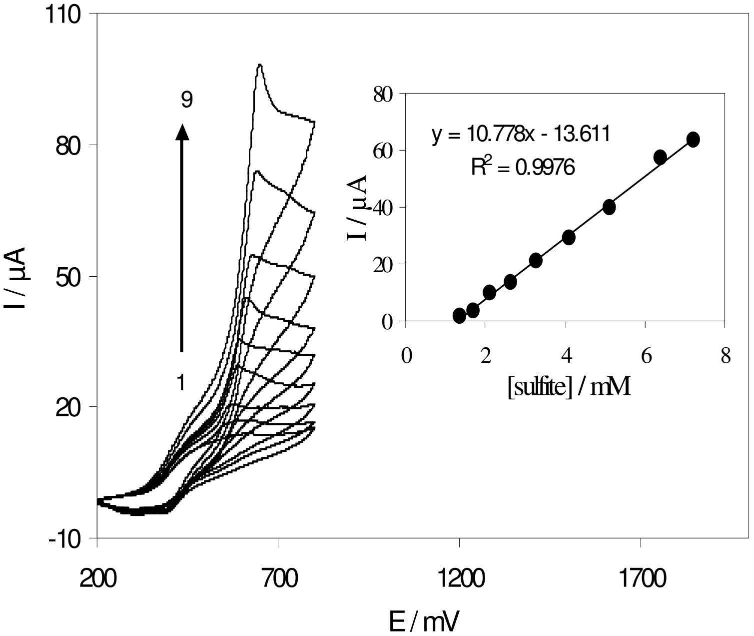


Figure 5. Cyclic voltammograms of different concentration of sulfite at quinizarine modified carbon paste electrode in (0.1) M phosphate buffer (pH 7): The numbers 1-9 correspond to, 1.3, 1.7, 2.1, 2.6, 3.3, 4.1, 5.1, 6.4, 7.2 mM, respectively. Inset: represents the variations of peak currents vs. sulfite concentration.

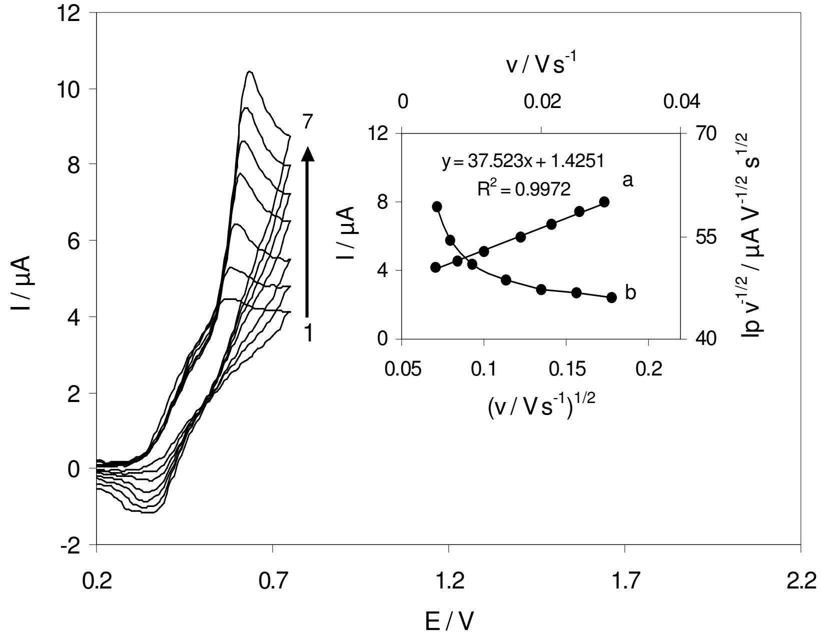


Figure 6. Cyclic voltammograms of the Q-MCPE in 0.1 M phosphate buffer (pH 7.0) containing 0.4 mM sulfite at different scan rates. The numbers of 1 to 7 correspond to 5, 7, 10, 15, 20, 25 and 30 mV s^{-1}, respectively. Inset: (a) variation of the electrocatalytic peak currents (I_p) versus the square root of scan rate and (b) variation of the scan rate-normalized current ($I_p/v^{1/2}$) with the scan rate, derived from cyclic voltammograms data of a Q-MCPE in 0.1 M phosphate buffer (pH 7.0) containing 0.4 mM sulfite.

Fig. 5 shows the dependence of the voltammetric response of Q-MCPE on the sulfite concentration. With the addition of sulfite, there was an increase in the anodic current. The plot of electrocatalytic current versus sulfite concentration is shown in inset of Fig. 5. The oxidation peak currents of sulfite at the surface of Q-MCPE were proportion to the concentration of sulfite within the range of 1.3 mM – 7.2 mM.

The cyclic voltammogram of Q-MCPE at various scan rate (5-30 mV s^{-1}) in the presence of 0.4 mM sulfite was studied (Fig. 6). The oxidation current for sulfite increased linearly with the square root of scan rate (inset, curve a), suggesting that at sufficient overpotential the reaction is diffusion limited. A plot of the sweep rate-normalized current ($Ip/\upsilon^{1/2}$) versus sweep (inset, curve b) exhibits the characteristic shape typical of an EC catalytic process. Andrieux and Saveant [22], developed a theoretical model for such a mechanism and derived a relation between the peak current and concentration of the substrate for the case of a slow rate, υ, and a catalytic rate constant, k'_h:

$$I_{cat} = 0.496(\alpha n')^{1/2} nFAC_s(F\nu D / RT)^{1/2} \qquad (2)$$

Where D and C_s are the diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration ($mol\ cm^{-3}$) of the substrate (sulfite in this case), respectively. Low values of k'_h result in values lower than 0.496 for the constant. Based on extensive computations, a working curve showing the relationship between numerical values of the constant, $I_{cat}/nFAC_s(DnF\upsilon/RT)^{1/2}$, log $[k\Gamma/(DnF\upsilon/RT)^{1/2}]$ (Fig. 1 of reference

[22]) is given. The value of k'_h can thus be calculated from such a working curve. For low scan rates (5-30 mVs^{-1}), we find the value coverage of $\Gamma = 6.1 \times 10^{-10}$ mol cm^{-2}, surface coverage (Γ) of a modified electrode prepared at optimum condition was obtained from the equation $\Gamma = Q/nFA$, where Q is the charge from the area under the quinizarine anodic peak corrected for the baseline; n the number of electrons exchanged per reactant molecule (n = 2), a geometric area (A) of 0.09 cm^2 and considering $D = 8.2 \times 10^{-6}$ cm^2 s^{-1} (this is obtained by chronocoulometry as below), in the presence of 0.4 mM sulfite. Using this value and Fig. 1 from the theoretical paper by Andrieux and Saveant [22], the value of k'_h was found to be 2.0×10^{-4} cm s^{-1} for low scan rates (5-30 mV s^{-1}).

The number of electrons in the overall reaction can also be obtained from the slope of the I_p versus $\upsilon^{1/2}$ plot (inset, curve a). Using the slope of this plot and according to the following equation for a totally irreversible diffusion-controlled process [23]:

$$n = I_p/v^{1/2} / \{3.01\times10^5 \, [(1-\alpha)n]^{1/2} \, AD^{1/2}C_s\} \qquad (3)$$

and considering $(1-\alpha)n_\alpha = 0.33$ (see below), it is estimated that the total number of electrons involved in the anodic oxidation of sulfite is n = 2.00.

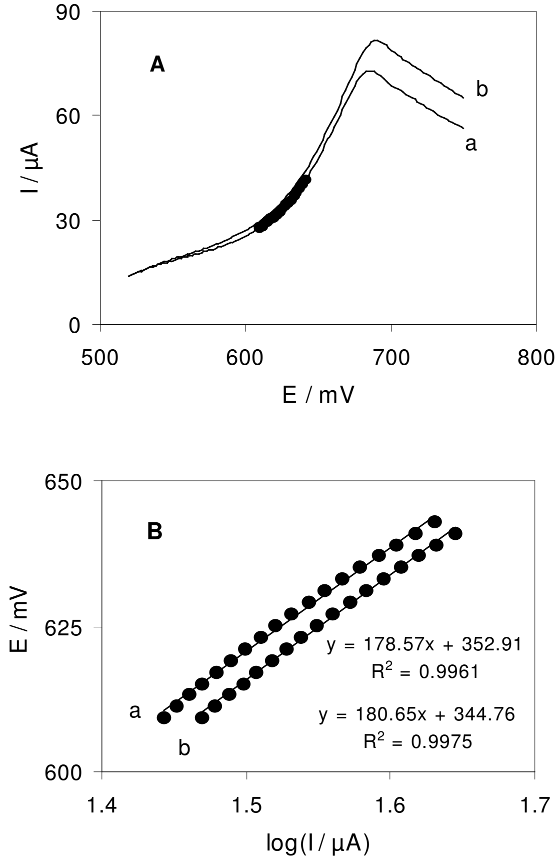


Figure 7. (A) Linear sweep voltammograms of the Q-MCPE in 0.1 M phosphate buffer (pH 7.0) containing 2.0 mM sulfite at scan rate of (a) 25, (b) 30 mV s^{-1}. The points are the data used in the (B) Tafel plots derived from linear sweep voltammograms shown in (A).

3.3. Linear sweep voltammetry measuerements

Fig. 7A shows the linear sweep voltammograms, at 25 mV s^{-1} and 30 mV s^{-1} of a Q-MCPE in 0.1 M phosphate buffer solution (pH 7.0) containing 2 mM sulfite. The points show the rising part of volammograms which is known as Tafel region and is affected by electron transfer kinetics between sulfite and Q-MCPE, assuming the deprotonation of sulfite as a sufficiently fast step. In this condition, the number of electrons involved in the rate determining step can be estimated from the slope of Tafel plot. Fig. 7B shows Tafel plots that were drawn from points of the Tafel regions of the linear sweep voltammograms. Average value of Tafel slope of 179.61 mV $decade^{-1}$, obtained from two Tafel plots in this case, agrees well with the involvement of one electron in the rate determine step of the electrode process, assuming a charge transfer coefficient of $\alpha = 0.67$ [21]. In addition, the exchange current density, j_o, is obviously readily accessible from intercept of the Tafel plot [21]. The value obtained for the exchange current density for sulfite at the Q-MCPE was found to be 0.13 μA cm^{-2}.

3.4. Chronocoulometry investigations

Chronocoulometry was also employed to investigation of electrochemical behavior of aqueous buffered solution (pH 7.0) containing of various concentration of sulfite at Q-MCPE. Chronocoulograms obtained at a potential step 800 mV. Fig. 8 (inset A) shows chronocoulometric measurements of sulfite at Q-MCPE. Inset B in Figure 8 shows the plots of slope μC $s^{-1/2}$ as a function of sulfite concentration. From whose slope and using the Cottrell equation [21], we calculated a diffusion coefficient of 8.2×10^{-6} cm^2 s^{-1} for sulfite.

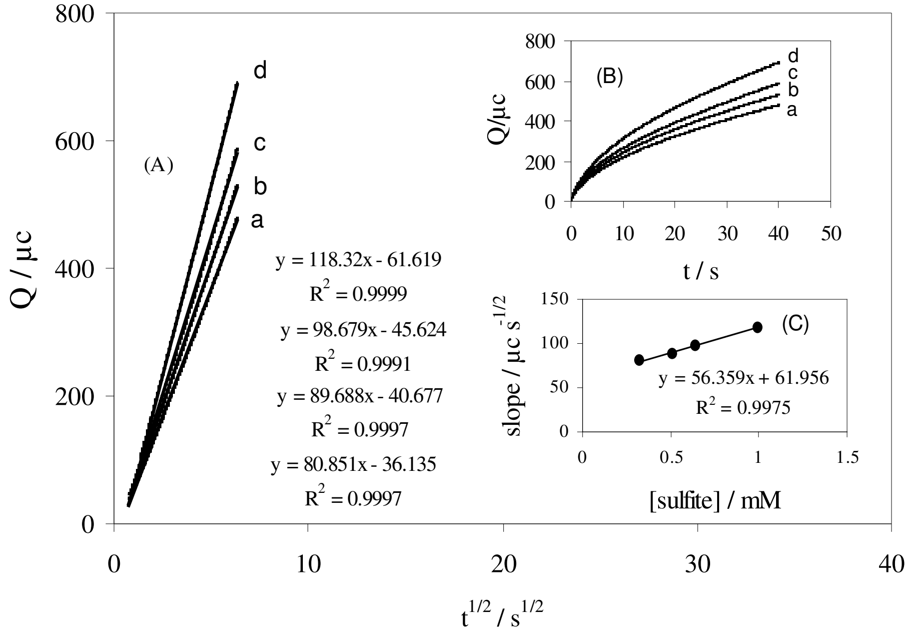


Figure 8. (A) Plot of Q vs. $t^{1/2}$ obtained from chronocoulometry experiments for a quinizarine modified carbon paste electrode in 0.1 M phosphate buffer solution (pH 7.0) containing sulfite at concentration of (a) 0.33 (b) 0.51 (c) 0.64 (d) 1.0 mM sulfite (B) Chronocoulmetric response at quinizarine modified carbon paste electrode in 0.1 M phosphate buffer solution containing (a) 0.33, (b) 0.51, (c) 0.64, (d) 1.0 mM sulfite. (C) The slopes of the resulting straight line of inset B vs. the sulfite concentration.

3.5. Electrocatalytic determination of sulfite

Sensitivities in differential pulse voltammerty (DPV) are better than other techniques of voltammetry. Since, the improvement comes from a reduced contribution from background currents. Fig. 9 shows the DPVs obtained for the oxidation of different concentrations of sulfite at the Q-MCPE. The dependence of the peak current on the sulfite concentration is shown in inset A of Fig. 9. Inset B and C of this figure clearly show that the plot of peak current versus sulfite concentration is constituted of two linear segments with different slopes, corresponding to two different ranges of substrate concentration. The detection limit (kσ, k = 2) was 4.0×10^{-5} M.

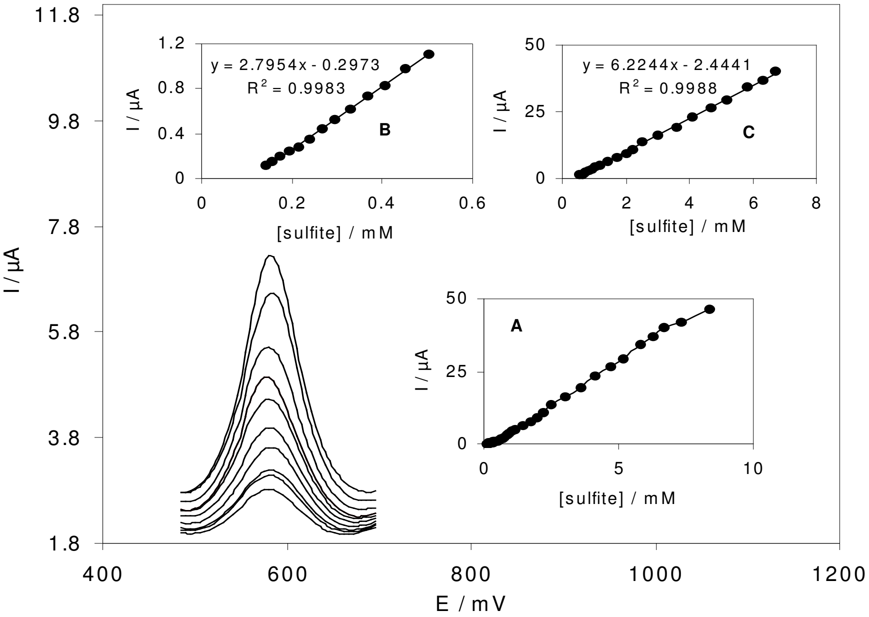


Figure 9. Differential pulse voltammograms of Q-MCPE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of sulfite (from inner to outer): 0.4, 0.45, 0.5, 0.55, 0.6, 0.68, 0.76, 0.85, 0.94 and 1.0 mM. Insets show the plots of the electrocatalytic peak current as a function of sulfite concentration in the range of: (A) 0.14 to 8.4 mM, (B) 0.14 to 0.5 mM and (c) 0.5 to 6.7 mM**.**

3.6. Determination of sulfite in real sample

In order to demonstrate the catalytic oxidation of sulfite in the real sample, we examined this ability in determining sulfite in wastewater from the wood and paper industry. Fig. 10 shows the differential pulse voltammograms recorded for the diluted wastewater in the phosphate buffer 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, c and d). Thus the peak was attributed to sulfite oxidation. 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 wastewater from wood and paper factory was about 1.0 M. Accuracy was examined by comparison of data obtained from this method with a recognized common method [24], for determination of sulfite (Table 1).

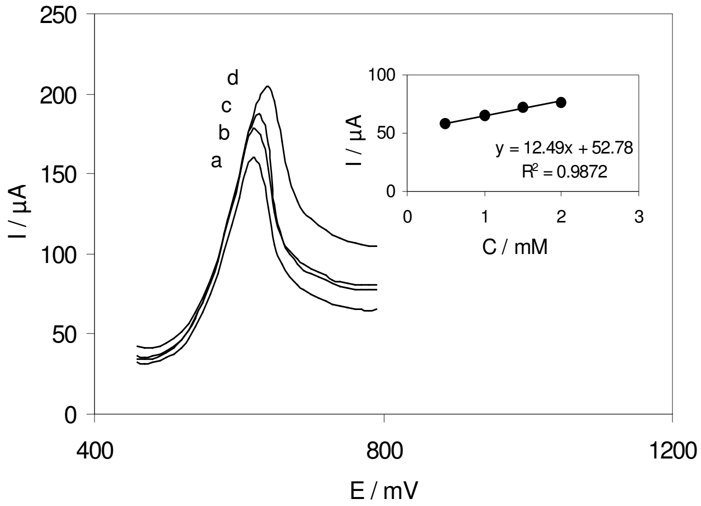


Figure 10. Differential pulse voltammograms of (a) 250 order dilution of weak liquor from wood and paper factory in the presence of 0.1 M phosphate buffer at pH 7.0. (b) to (d) after adding solution sulfite 1.0, 1.5 and 2.0 mM, respectively; υ was 10 mV s^{-1}. Inset shows plot of $I_{p.a}$ as a function of added sulfite concentration.

Table 1. Determination of sulfite in real sample

Proposed method (M)	Reference method (M)	t_{exp}
1.06 ± 0.05	1.10 ± 0.07	0.81

n = 3, Theoretical value for t = 2.78

4. CONCLUSIONS

This work demonstrates the construction of a chemically modified carbon paste electrode by the incorporation of quinizarine as modifying species. The carbon paste electrode modified with quinizarine was considerably stable. This electrode is simple, ease to prepare and renew is surface. The electrochemical behavior of the quinizarine has been studied by cyclic voltammetry and chronocoulometry in both the absence and presence of sulfite. The results show that the oxidation of sulfite is catalyzed at pH 7.0, whereas the peak potential of sulfite is shifted by 291 mV to a less positive potential at the surface of the Q-MCPE.

ACKNOWLEDGEMENTS
The authors wish to thankful the Yazd University Research Council, IUT Research Council and Excellence in Sensors for financial support of this research.

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