

Full Paper

Tetrachloro-ortho-Benzoquinone as Catalyst for Electrocatalytic Oxidation of Sulfite in Acidic Media and its Analytical Application

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Abstract- A chemically modified carbon paste electrode (MCPE) with tetrachloro-ortho-benzoquinone (TOB) was employed to study the electrocatalytic oxidation of sulfite in aqueous solution using cyclic voltammetry (CV) and double-potential step chronoamperometry. It has been found that under an optimum condition (pH 2.0), the oxidation of sulfite at the surface of MCPE occurs at a potential of about 700 mV less positive than that of an unmodified CPE. The diffusion coefficient (D) for sulfite was found as $8.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ by chronoamperometry. The electron transfer coefficient, α , was estimated to be 0.4 and 0.24 for the oxidation of sulfite at the surface of MCPE and unmodified CPE, respectively. The electrocatalytic oxidation peak currents showed a linear dependence on the sulfite concentration in the range of $1 \times 10^{-4} \text{ M}$ - $4.2 \times 10^{-3} \text{ M}$ with detection limit (3σ) $5.7 \times 10^{-5} \text{ M}$ by CV. This method was also used for selective determination of sulfite in weak liquor.

Keywords- Sulfite, Tetrachloro-ortho-benzoquinone, Carbon paste electrode, Electrocatalysis, Cyclic voltammetry

Abbreviations- MCPE: modified carbon paste electrode, TOB: tetrachloro-ortho-benzoquinone, CV: cyclic voltammetry, CMEs: Chemically modified electrodes

1. INTRODUCTION

Sulfite (SO_3^{2-}) is commonly used in foodstuffs, beverage and pharmaceutical industries as antioxidant and inhibitor of bacterial and yeast growth. In the particular case of wine industries, stability is highly dependent on the presence of sulfites. The sulfite content prevents oxidation and undesirables flavors, taste and color generated by yeast and bacterial [1-4]. Sulfite emitted by chemical industries such as paper manufactures and refineries plays an important role in air pollution and leads to acidic rain and acidification of soils, lakes and damages agriculture crops, building and aquatic life. It can produce harmful effect towards hypersensitive people [5,6]. For these reasons the determination of sulfite concentration in the food, water and other material is of great important and it needs rapid, precise and simple methods.

Up to now several methods for determination of sulfite concentration have been developed, such as iodometric [7], colorometric [8], conductimetric [9], electrochemical [10-14], fluorometric [15,16], spectrophotometric [17], chemiluminescence [18,19], Electrochemiluminescence [20], and chromatographic [21,22] methods. Among these, electrochemical methods find widespread use due to their simplicity, easy modification and easy adoptability. Chemically modified electrodes (CMEs) have become significant ones in recent years due to their tailoring made properties which imparts selectivity as well as analyte specificity.

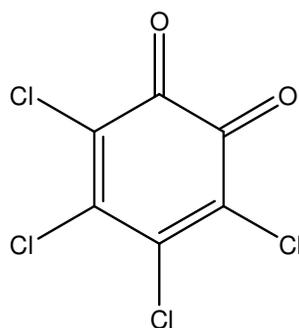
Pouranghi-Azar et al. applied a nickel pentacyanonitrosylferrate film modified/Al electrode [10], N. Rea et al. constructed a porphyrins bound to $\text{Ru}(\text{bpy})_2$ clusters coated on glassy carbon electrode (GCE) [23], G. Shi et al. constructed a pvp/Pd/ IrO_2 on Pt electrode [24], M. Lucero reported a glassy carbon electrode coated with a polymeric film of Fe-tetra-4-aminopolyenylporphyrin [25], A. A. Ensafi and H. Karimi-Maleh used a ferrocenedicarboxylic acid modified carbon nanotubes paste electrode [26], S. Devaramani, and P. Malingappa reported cobalt nitroprusside nanoparticles MCPE for sulfite sensing in food and water samples [27], and P.-Y. Chen et al. a phenothiazine drop-coated screen printed carbon electrode in couple with flow injection analysis [28].

Since the introduction of CMEs, a variety of modification procedures have been developed, including: chemisorptions, covalent bonding, composite, self-assembly, carbon paste, sol-gel and screen printing [10,12,23-29]. The electrocatalysis of slow electron transfer reactions by CME, is complicated and strongly dependent on the mediator. Such modified electrodes enhance the rate of electron transfer by reducing the overpotential due to using a chemical reaction. Therefore, such electrocatalysis enables a high current density (i.e, increased sensitivity) to be obtained for a slow kinetic reaction at a potential close to the equilibrium potential.

Previously, we have demonstrated that some ferrocene derivatives can catalyze the oxidation of sulfite in both homogeneous [30] and heterogeneous [31] cases. Previously, we

have shown that the para chloranil (tetrachloro-para-benzoquinone) chemically MCPE show a good electrocatalytic effect toward the oxidation of ascorbic acid [32].

In this work, we decided to examine the electrocatalytic ability of para and ortho derivatives chloranil MCPE toward the oxidation of sulfite. According to our experiments no observed any electrocatalytic effect by para derivative of chloranil. But, our electrocatalytic experiments performed in the second part by use of ortho derivative of chloranil (i.e. tetrachloro-ortho-benzoquinone, TOB,) (Scheme 1) showed very good electrocatalytic ability (700 mV) for this catalyst. We report a simple and precise electrocatalytic method for determination of sulfite by the TOB modified carbon paste electrode (TOBMCPE).



Scheme 1. Structure of tetrachloro-ortho-benzoquinone (TOB)

2. EXPERIMENTAL

2.1. Reagents and Materials

All chemicals used were of analytical reagent grade. Doubly distilled water was used throughout. Potassium chloride from Fluka was used as the supporting electrolyte. Tetrachloro-ortho-benzoquinone was used from Fluka and sodium sulfite from Merck, all used without further purification. Buffer solutions were prepared from orthophosphoric acid and its salts in the pH range 2.0-7.0 and the pH was adjusted with 0.1 M H_3PO_4 and NaOH. High viscosity paraffin (density 0.87 g cm^{-3}) from Fluka was used as the pasting liquid for the CPE. Pure graphite powder (particle diameter=0.1 mm) from Merck was used as the substrate for the preparation of the CPE as a working electrode.

2.2. Apparatus

The electrochemical experiments were carried out by using a potentiostat/ galvanostat (BHP 2061-C Electrochemical Analysis system, Behpajoo, Iran) coupled with a Pentium II personal computer. A conventional three electrode cell was used, with a platinum wire as the auxiliary electrode. A MCPE and a double-junction $\text{Ag|AgCl|KCl}_{\text{sat}}$ electrode 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.

2.3. Preparation of TOBMCPE

A 1% (w/w) TOB spiked carbon paste powder was made by dissolving a given quantity of TOB 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. Then liquid oil was added and mixed by hand until obtaining a uniformly wetted paste. Portions of the resulting composite material were packed in the end of a polypropylene tube (i.d.=0.3 mm). Electrical contact to the carbon paste was made with a copper wire. A fresh surface was polished on filter paper until it had a shiny surface. A CPE without TOB was used as a blank to determine the background current.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of TOBMCPE

At first we prepared TOBMCPE and then studied the electrochemical behavior of it in a pure buffered aqueous solution by CV. Fig. 1b shows cyclic voltammograms of TOBMCPE in a 0.1 M phosphate buffered aqueous solution (pH=2.0) with 0.1 M KCl as the supporting electrolyte. As can be seen, the cyclic voltammogram exhibits an anodic peak current at catalyst scan of the potential related to the oxidation of the reduced form of (H_2Q) to oxidized form of catalyst (Q), whereas at a reverse scan of the potential, a cathodic peak current appears related to the reduction of Q to H_2Q . The cyclic voltammogram of unmodified CPE (UMCPE) in the buffered solution shows no anodic or cathodic peak (Fig. 1a). The experimental results show reproducible anodic and cathodic peaks related to H_2Q/Q couple. The H_2Q/Q redox system has been used as a mediator for the electrocatalysis of some important biological compounds with slow electron transfer rates [32,33]. As can be seen in voltammogram of Fig. 1b, the peak separation potential ($\Delta E_p = E_{pa} - E_{pc}$) is greater than the 59/n mV, expected for a reversible system. These results demonstrate that a H_2Q/Q redox system in TOBMCPE shows a quasi-reversible behavior in a aqueous media.

In addition, the effect of the potential scan rate on the electrochemical properties of the H_2Q/Q redox couple in TOBMCPE was studied in an acidic aqueous solution (pH 2.0) by CV (Fig. 2A). As can be seen, the plots of the anodic and cathodic peak currents at scan rate up to 80 $mV s^{-1}$ show that the I_p values are linearly dependent on v with a correlation coefficient of 0.99 (Fig. 2B). This behavior indicates that the nature of redox process is not diffusion controlled, so reaction happens on the surface of electrode. However, at scan rate between 100-800 $mV s^{-1}$ the I_p values are linearly dependent on $v^{1/2}$ with a correlation coefficient of 0.99 (not shown). This behavior indicates that the nature of redox process is diffusion controlled in higher scan rates. Such behavior was reported for anthraquinones on the carbon paste electrode [35]. On the other hand, the behavior of TOBMCPE was studied by CV in aqueous buffered solution at a wide range of pH. The half-wave potentials ($E_{1/2}$) calculating

as the average of the anodic and cathodic potentials of cyclic voltammograms ($E_{1/2} = (E_{pa} + E_{pc})/2$) recorded at different pHs, exhibits to decrease of $E_{1/2}$ as a function of pH increase (not shown). This result is similar to our previous work about para-derivative [32]. For this reason, we do not discuss as detail here.

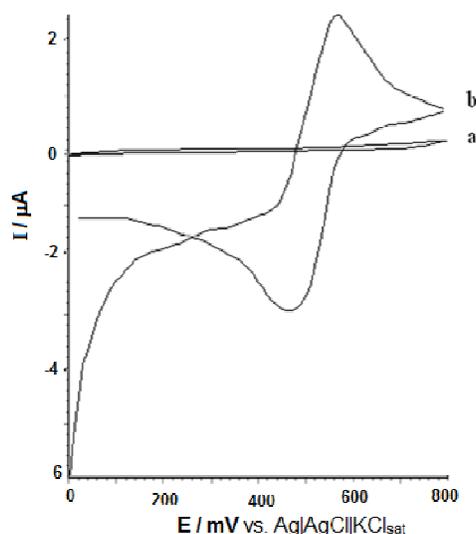


Fig. 1. Cyclic voltammograms of (a) UMCPE and (b) TOBMCPE in 0.1 M phosphate buffer solution (pH=2.0) with 0.1 M KCl as supporting electrolyte, scan rate is 10 mV s^{-1}

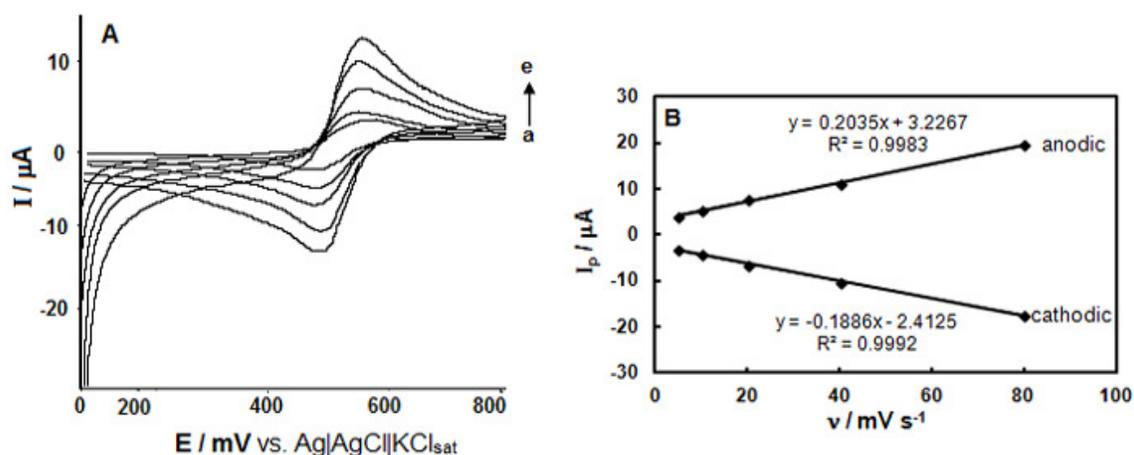


Fig. 2. (A) Cyclic voltammograms of the TOBMCPE in 0.1 M phosphate buffer solution (pH=2.0) with 0.1 M KCl as supporting electrolyte, at various scan rates: a) 5, b) 10, c) 20, d) 40, e) 80 mV s^{-1} . (B) plots of anodic (a) and cathodic (b) peak currents of TOBMCPE vs. v from cyclic voltammograms of (A)

The effect of the aqueous solution pH on the electrochemical behavior of the H₂Q/Q redox couple has been studied. The obtained result shows that the H₂Q/Q redox couple dependent to the solution pH. Therefore the redox process of H₂Q/Q is dependent on the pH.

3.2. Stability of TOBMCPE

In the case of stability this mediator for the electrocatalytic oxidation of sulfite, the rate loss of electrochemical activity for this electrode was investigated. This rate was evaluated by noting any decrease in the exchanged charge in consecutive potential scan cycle. The results showed that the anodic and cathodic peak current of the H₂Q/Q redox couple decreased, consequently the electrochemical activity of MCPE was reduced during successive scans, without any change in the half-wave potential ($E_{1/2}$). The decrease in the electrochemical activity may be due to decomposition of the hydroquinone produced at the electrode by dissolution into the aqueous solution. According to the above results, surface renewal of the TOBMCPE before each experimental is necessary. Therefore the effects of the supporting electrolyte and the nature of the oil were also demonstrated. The results show that the rate of loss of the electrochemical activity in the case of paraffin oil and KCl (0.1 M) was minimum.

3.3. Effect of pH on the Sulfite Electrocatalytic Oxidation

The experimental investigation showed that the catalytic peak current of sulfite is influenced by the electrolyte solution pH. The current response was obtained with 1.5 mM sulfite in 0.1 M phosphate buffer and 0.1 M KCl solution in the pH range between 0.5-7.0. The obtained results show that MCPE just can catalyze the electro-oxidation of sulfite in strong acidic solution.

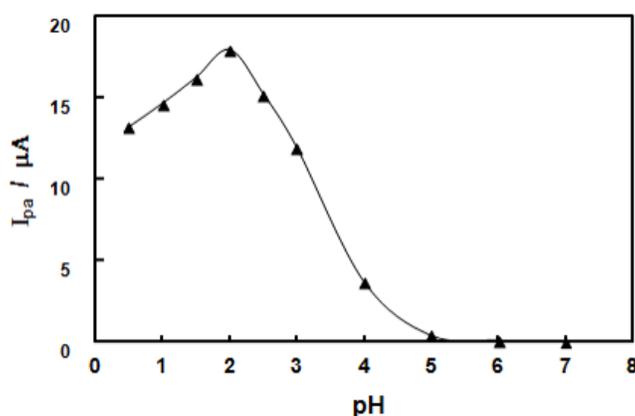
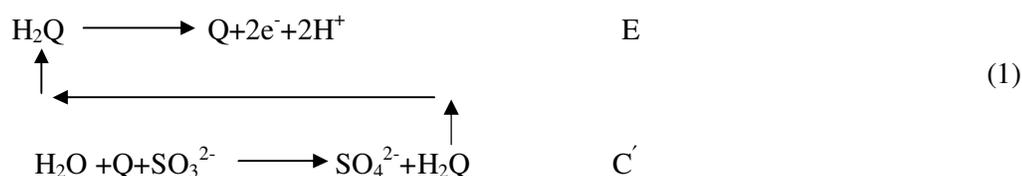


Fig. 3. Variations of the anodic peak current I_{pa} for the catalytic oxidation of 1.5 mM sulfite solution at TOBMCPE vs. pH of electrolyte solution. 0.1 M KCl as supporting electrolyte with 0.1 M phosphate buffer of different pH values, scan rate is 10 mV s^{-1}

As seen in Fig. 3, a maximum peak current is obtained at phosphate buffer solution of pH 2.0. Thus a pH 2.0 was chosen during the electrocatalytic studies for sulfite oxidation.

3.4. Electrocatalytic Ability of TOBMCPE at Optimum pH

Fig. 4 shows the cyclic voltammograms of the TOBMCPE in the absence (curve a) and presence of 1.5 mM sulfite (curve b). An increase in the anodic peak current is observed, whereas the cathodic peak is depressed. This behavior is typical of that expected for catalytic oxidation of sulfite at the formal potential of $\text{H}_2\text{Q}/\text{Q}$ (≈ 500 mV) (EC' mechanism).



But under the same conditions at a UCPE, oxidation of sulfite is observed as irreversible (curve d, $E \approx 1200$ mV) with highly overpotential. The reduction in the overpotential and the enhanced current response observed at the TOBMCPE in presence of sulfite is due to the catalytic oxidation of sulfite to sulfate by the quinone formed during the anodic scan.

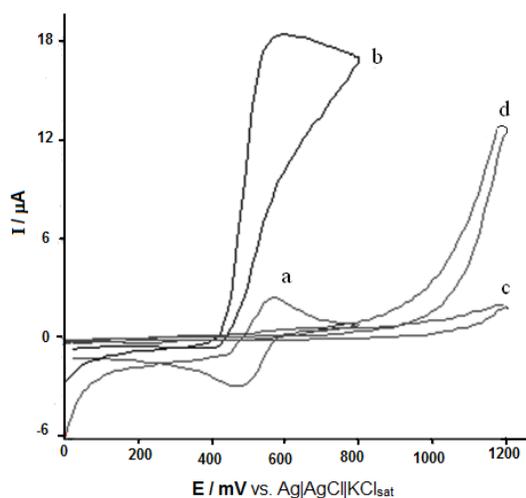


Fig. 4. Cyclic voltammograms of (a) TOBMCPE in 0.1 M phosphate buffer solution (pH=2.0) with 0.1 M KCl as supporting electrolyte, scan rate is 10 mV s^{-1} ; (b) as (a) plus 1.5 mM sulfite; (c) and (d) as (a) and (b), respectively, using an UMCPE

This remarkable reduction in overpotential (about 700 mV) is larger than most other values reported by other research groups for catalytic oxidation of sulfite by other modifiers

[26,30,31,34-36], see (Table 1). This considerable electrocatalytic effect will make the determination of sulfite as more selective.

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

Electrode	Used catalyst	Catalytic effect (mV)	pH	References
CNTPE	FC	350	7.0	[26]
GCE	FC	400	8.0	[30]
CPE	2, 7-BFEF	420	8.0	[31]
GCE	CoPCNF	150	7.0	[34]
GCE	FeHCF	330	5.5	[35]
GCE	Poly[(Fe-NH ₂ -phen) ₃] ⁺²	220	2.0	[36]
CPE	TOB	700	2.0	This work

CNTPE: carbon nanotubes paste electrode, FC: ferrocenecarboxylic acid, 2,7-BFEF: 2,7-bis(ferrocenyl ethyl) fluoren-9-one, COPCNF: cobalt pentacyanonitrosylferrate, FeHCF: iron hexacyanoferrate.

The dependence of the catalytic peak current response to the potential scan rate was evaluated by varying the scan rate. Fig. 5A shows the cyclic voltammograms of the MCPE at the various scan rates (5-800 mV s⁻¹) in the presence of 0.75 mM sulfite. It was indicated that the response current varied linearly with the square root of the potential scan rate, which indicates that the electrocatalytic oxidation of sulfite at the TOBMCPE is a diffusion controlled process (Fig. 5B). It can also be noted from Fig. 5A that with an increasing scan rate, the peak potential for the catalytic oxidation of sulfite shifts to more positive potentials, suggesting a kinetic limitation in the reaction between the redox sites of MCPE and sulfite. As a result, the best sensitivity is obtained at a low potential scan rate, so we choose $v=10$ mV s⁻¹ for the following studies.

In order to obtain information on the rate-determining step, a Tafel slope, (b), was determined using the following equation for a totally irreversible diffusion controlled process [37,38]:

$$E_p = \left(\frac{b}{2}\right) \log v + constant \quad (2)$$

Based on Equation (2), the slope of E_p vs. $\log v$ plot is (b/2), where b indicates the Tafel slope. The slope of E_p vs. $\log v$ plot is $\Delta E_p/\Delta(\log v)$, which was found to be 78 mV in this work (Fig. 5C). Thus $=2 \times 78 = 156$ mV. This slope indicates a transfer coefficient of $\alpha=0.38$ for

one electron transfer process, which is the rate limiting step using CV. The value of αn_{α} (where α is the transfer coefficient and n_{α} is the number of electrons involved in the rate determining step) was calculated for the oxidation of sulfite at pH 2.0 at both MCPE and UMCPE, according to the following equation [38,39]:

$$\alpha n_{\alpha} = 0.048 / (E_p - E_{p/2}) \quad (3)$$

Where, $E_{p/2}$ is the potential corresponding to $I_{p/2}$. The values for αn_{α} were found to be 0.40 and 0.24 for the oxidation of sulfite at the surface of modified and unmodified electrodes, respectively. These values clearly show that not only overpotential for sulfite oxidation is reduced at the surface of TOBMCPE, but also the rate of electron transfer process is greatly enhanced. This phenomenon is thus confirmed by large I_{pa} values recorded during CV at TOBMCPE.

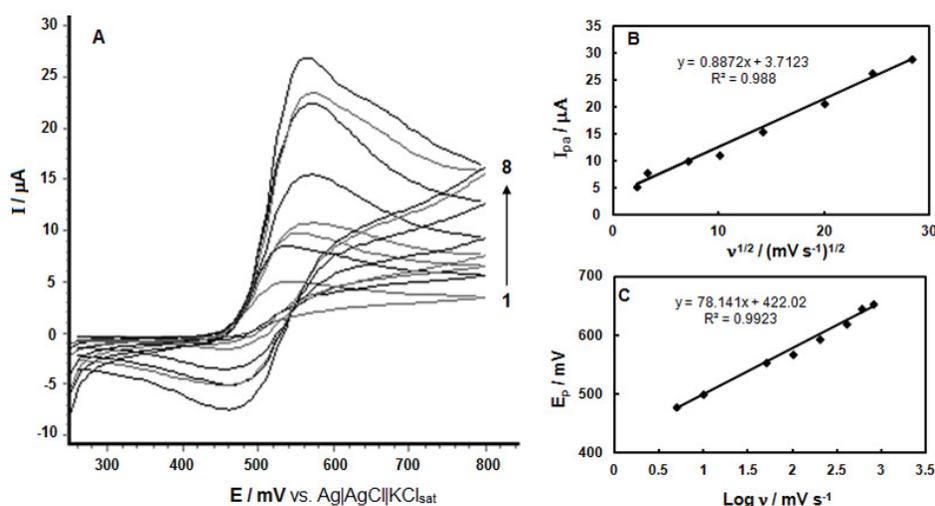


Fig. 5. (A) Cyclic voltammograms of the TOBMCPE in 0.1 M phosphate buffer solution (pH = 2.0) with 0.1 M KCl as supporting electrolyte, in the presence of 0.75 mM sulfite at various scan rates: 1) 5, 2) 10, 3) 50, 4) 100, 5) 200, 6) 400, 7) 600, 8) 800 mV s^{-1} . (B) The variation of the anodic peak currents vs. $v^{1/2}$. (C) Dependence of the peak potential, E_p , on $\text{log } v$ for the oxidation of sulfite at the surface of the TOBMCPE obtained from data of Fig. 5A.

3.5. Chronoamperometry

Fig. 6A shows the current-time curves (chronoamperograms) of the MCPE obtained by setting the working electrode potential at 0.9 V (step 1) and 0.0 V (step 2) for various concentrations of sulfite in a buffered aqueous solution (pH=2.0). As can be seen, there is not net cathodic current corresponding to the reduction of mediator in the presence of sulfite, while the forward and backward potential step chronoamperometry of the modified electrode

in the blank solution (absence of sulfite) showed very symmetrical chronoamperograms with an equal charge consumed for the oxidation and reduction of surface confined MCPE sites (Fig. 6B (a')). However, in the presence of sulfite, the charge value associated with the forward chronoamperometry is significantly greater than the observed for the backward chronoamperometry (Fig. 6B (d')). This behavior is typical of mediated oxidation. Fig. 6C shows the plots of currents measured at fixed time as a function of the sulfite concentration. Comparison of graphs in Fig. 6C suggests that in all cases, there is a similar connection between currents measured at the fixed time and sulfite concentration, but slope of the plot of current vs. of the sulfite concentration is slightly increased with decreasing elapsed time.

Chronoamperometry can be used for the evaluation of apparent diffusion coefficient (D_{app}). For an electroactive material, the current corresponding to the electrochemical reaction (under diffusion control) is described by Cottrell's law [38,40]:

$$I = nFAD_{app}^{0.5}C_0\pi^{-0.5}t^{-0.5} \quad (4)$$

Where D_{app} and C_0 are the apparent diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and the bulk concentration (mol cm^{-3}) of the substrate (sulfite in this case), respectively. A is the geometric area of this electrode (the diameter (d) of the TOBMCPE was measured and then the geometric area of the TOBMCPE was calculated according to $(\pi (d/2)^2)$.

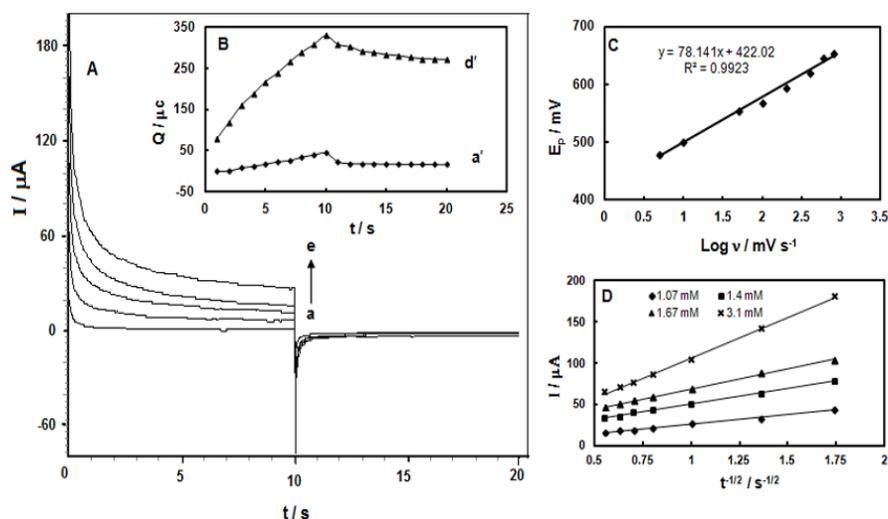


Fig. 6. (A) Chronoamperograms obtained with TOBMCPE in 0.1 M phosphate buffer (pH=2.0) with 0.1 M KCl: (a) in the absence of sulfite; (b-e) in the presence of sulfite: (b) 1.07, (c) 1.4, (d) 1.67, (e) 3.1 mM. First and second potential step were 0.9 and 0.0 V vs. Ag|AgCl|KCl_{sat} respectively. (B) Shows the charge-time curve: (a') for curve (a) and (d') for curve (d). (C) Dependence of the fixed-time current observed for 1, 2, 3 and 4 s after the first potential step on sulfite concentration, derived from the data of main panel. (D) The plots of I_{pa} vs. $t^{-1/2}$ in the presence of 1.07, 1.4, 1.67, 3.1 mM of sulfite.

The plot of I_{pa} vs. $t^{-1/2}$ will be linear, and from its slope, the value of D_{app} can be obtained. Chronoamperometry of the modified electrode in the presence of sulfite represents a typical I_{pa} - t curve, which indicated that the observed current must be controlled by sulfite diffusion in the solution. A plot of I_{pa} vs. $t^{-1/2}$ for a modified electrode in the presence of sulfite give a straight line (Fig. 6D), the slope of such lines can be used to estimate the diffusion coefficient of sulfite, the value of the D_{app} was found to be $8.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

3.6. Electrocatalytic Determination of Sulfite

The electrocatalytic peak current of sulfite oxidation at the surface of the MCPE was linearly dependent on the sulfite concentration, and the range of this linearity dependent on the amount of mediator in the electrode. Under the optimum condition, the plot of anodic peak current (I_p) vs. sulfite concentration for CV at the TOBMCPE is linear in the range of $1 \times 10^{-4} \text{ M}$ to $4.2 \times 10^{-3} \text{ M}$ with a correlation coefficient of 0.998. The detection limit (3σ) was $5.7 \times 10^{-5} \text{ M}$ (Fig. 7A, B)

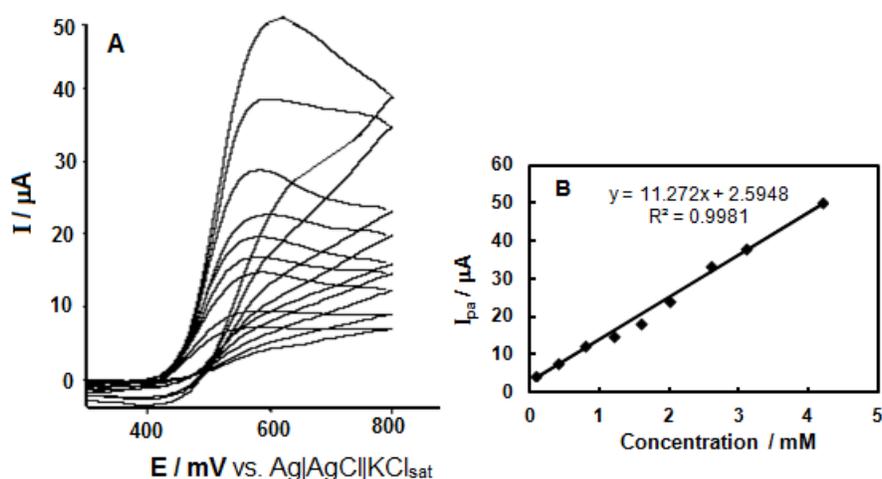


Fig. 7. (A) Cyclic voltammograms obtained with TOBMCPE in 0.1 M phosphate buffer (pH=2.0) with 0.1 M KCl: in the presence of sulfite: (1) 0.1, (2) 0.4, (3) 0.8, (4) 1.2, (5) 1.6, (6) 2, (7) 2.6, (8) 3.1, (9) 4.2 mM, scan rate is 10 mV s^{-1} . (B) Plot of electrocatalytic peak currents vs. the sulfite concentration from cyclic voltammograms (A)

3.7. Determination of Sulfite in a Real Sample

In order to examine the application of the proposed method, we have used the method for the determination of sulfite in weak liquor from the wood and paper factory of Mazandaran province in Iran. Weak liquor was analyzed by using two different procedures, including the proposed sulfite sensor and the standard iodometric method [41]. We have used this standard

procedure, based on titration with potassium iodide-iodate solution in acidic media, in order to validate our method and to show its usefulness. The direct determination of sulfite in weak liquor by the TOBMCPE is shown in Fig. 8A. Fig. 8B shows I_{pa} vs. sulfite concentration added to the liquor, and shows the linear response for determination of sulfite. By this method sulfite concentration in the weak liquor was about 91 μM . The related standard deviation obtained from the line equation ($R=0.99$) for the real sample was 2.7%. The results showed that there is a good agreement between the results obtained by both methods.

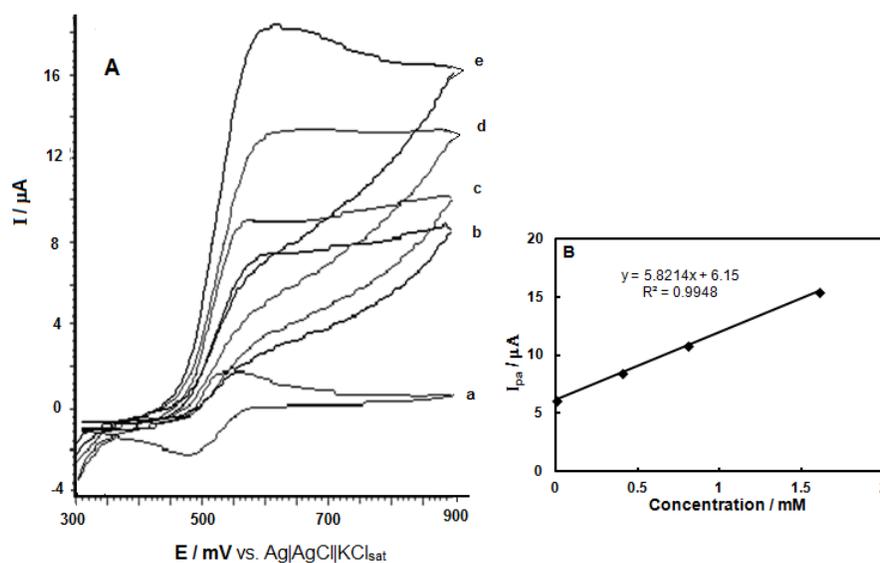


Fig. 8. (A) Cyclic voltammograms of (a) the TOBMCPE in 0.1 M phosphate buffer solution (pH=2.0) with 0.1 M KCl as supporting electrolyte; (b) as (a) plus 10 times diluted weak liquor solution; (c-e) as (b) after adding sulfite 0.4, 0.8 and 1.6 mM sulfite, respectively; $v=10 \text{ mV s}^{-1}$. (B) Plot of I_{pa} as a function of added sulfite concentration to the weak liquor.

4. CONCLUSION

This work shows the ability of tetrachloro-ortho-benzoquinone (TOB) as a modifier in carbon paste electrode for electrocatalysis of sulfite oxidation. The electrochemical behavior of the TOBMCPE has been studied by CV and chronoamperometry in both the absence and presence of sulfite. The results show that the oxidation of sulfite is catalyzed by TOBMCDE at pH=2.0 in aqueous solution. This electrocatalytic response, stable and reproducible, shows a linear dependence on the concentration of sulfite in solution, with a detection limit of about 57 μM . In addition, a diminution of about 700 mV in the potential of oxidation of this analyte with respect to the potential at bare carbon paste electrodes is obtained. The application of these chemically modified electrodes to sulfite determination in the real sample such as a weak liquor existing in the wood and paper industry was demonstrated. This method is a

good alternative to previously described methods because of its simplicity and no need of sample pretreatment.

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