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Investigation of the electrochemical behavior of catechol and 4-methylcatechol in the presence of methyl mercapto thiadiazol as a nucleophile: application to electrochemical synthesis

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Abstract The present study concerns the electrochemical behavior of catechol and 4-methylcatechol in the presence of 2-mercapto-5-methyl-1,3,4-thiadiazole (MMT) in aqueous medium on the surface of the glassy carbon electrode by means of cyclic voltammetry and controlled-potential coulometry. The oxidation mechanism was deduced from voltammetric and spectrophotometric data. The electro-generation of quinoid intermediates and their subsequent Michael-type reaction with MMT has been investigated as a clean and convenient strategy for the synthesis of corresponding reaction products. In addition, electro-synthesis of Michael addition products has been successfully accomplished by controlled-potential coulometry in a divided H-type cell in mild conditions that can be considered as a green procedure. The reaction products were characterized by spectrophotometric, ^{1}H and ^{13}C NMR, and mass spectrometric methods.

1 Introduction

Among the most interesting and innovative chemical technologies, the electro-chemical method provides a very

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interesting and powerful means for the small-scale and high purity production of high added value compounds. It seems that the electrochemical procedures will emerge in organo-synthesis, where the special advantages of the electrochemistry such as energy specificity, absence of toxic reagents and solvents, chemical selectivity and specific activation of small molecules can be applied. 1,3,4-Thiadiazoles are among the class of heterocycles which have attracted significant interests in medicinal chemistry. These compounds have a wide range of pharmaceutical and biological activities including antimicrobial, anti-fungal, anti-inflammatory, and antihypertensive [1–6]. 1,3,4-Thiadiazole nucleus itself exhibits anticonvulsant, sedative-hypnotic, and CNS neurotoxicity activities possibly by virtue of N–C=S toxophoric moiety. During last two decades, different compounds of substituted 1,3,4-thiadiazoles, which have special structures and properties, have been widely reported in the fields of synthesis, spectroscopic analysis, and traditional medical applications [7]. The applications of mercapto-functionalized thiadiazole derivatives were introduced about 50 years ago [8].

Mercapto-functionalized thiadiazoles and derivatives are used as bioactive compounds, metal chelating agents, lubricant additives like corrosion inhibitors and anti-wear agents, cross-linkers for polymers, and as components in cathode material battery systems [9–11]. 2-Mercapto-5-methyl-1,3,4-thiadiazole (MMT) is used as an intermediate of Cephalosporin side chains. (Cefazolin, Cefamandole). On the other hand, catechols are important species in chemistry and biology, because of their facility to undergo electron transfer [12]. For instance, they are involved in the primary photoelectron donor–acceptor center in bacterial photosynthesis [13]. Because electrochemical oxidation very often parallels the oxidation of catechols in the mammalian central nervous system and

this process occurs in the human body, it was promoted many workers to study the anodic oxidation of catechols in the presence of various nucleophiles [14–17]. When catechol species are electrochemically oxidized to the corresponding quinines, they can undergo a nucleophilic attack by the nucleophilic species through a 1,4 Michael addition [18–20]. Depending on some parameters such as, nature of nucleophile (electron withdrawing or donating), electrolysis medium (solvent, acidity or pH), and catechol type, the mechanism of addition may be different. Therefore, potential biological activities of catechols and 1,3,4-thiadiazoles derivatives made them good leads for the synthesis of new compounds.

In the present study, electro-oxidation of catechol and 4-methyl catechol in the presence of 2-mercapto-5-methyl-1,3,4-thiadiazole as a nucleophile in aqueous buffered solutions was studied by cyclic voltammetry and controlled-potential coulometry. In the following, the electro-synthesis process was conducted for the bulk addition of MMT to the electrochemically generated *o*-quinone under the controlled-potential coulometric method. In conclusion, we have described a general, convenient, environmentally friendly, and reagent-less protocol for the synthesis of a series of new 1,3,4-thiadiazole derivatives via ECE and EC electrochemical mechanism pathways in a high selectivity and an excellent purity.

2 Experimental

2.1 Instruments

Cyclic voltammetric experiments were performed using a Metrohm Computrace Voltammetric Analyzer Model 757 VA. A conventional three-electrode system was used with a glassy carbon disc electrode (GC, 2 mm diameter), a saturated Ag/AgCl reference electrode, and a platinum wire as the counter electrode. Controlled-potential coulometric experiments were performed by using a PC-controlled potentiostat/galvanostat EG&G Model 273A (Princeton Applied Research Corp., Princeton, NJ). The working electrode used in the controlled-potential coulometry was a graphite rod with a diameter of 15 mm and the length of 10 cm (EK20, Germany) and an assemble of four platinum rods (each with a 3 mm in diameter and 10 cm in length) was used as counter electrode. The working electrode potential was monitored versus Ag/AgCl reference electrode (from Azar electrode, Iran). NMR spectra were recorded on a Bruker DRX-500 Avance Instruments. MS spectra were obtained using a Shimadzu GC–MS QP1100EX/UP1100 (EI at 70 eV). Thin layer chromatography (TLC) was carried out on alumina sheets pre-coated with silica-gel 60F254 (Merck), and spots were visualized with UV light ($\lambda_{max} = 254$ nm). Melting point of the product was monitored on a BU-CHI Melting Point Model B-540. A digital pH/mV/Ion meter (Cyberscan model 2500) was used for preparing of the buffer solutions, which were used as the supporting electrolyte in voltammetric and coulometric experiments. A photodiode array UV–Vis spectrophotometer (Sinco S-3500 series) was used for obtaining the absorption spectra.

2.2 Chemicals and reagents

Catechol and 4-methylcatechol were purchased from Merck and MMT was prepared from Acros. All reagents of analytical reagent grade were also prepared from Merck. Aqueous solutions for cyclic voltammetric and coulometric studies were prepared with de-ionized double distilled water from dilute and alkaline solutions of potassium permanganate.

2.3 Electro-synthesis of 4-[(5-methyl-1,3,4-thiadiazole-2-yl) sulfanyl]-1,2-benzendiol (TSBD)

The synthesis was performed with 100 mL phosphate buffer solution (0.1 M, pH = 7.0) containing 0.005 M catechol and 0.005 M MMT in an H-type divided coulometric cell. The controlled-potential coulometry was performed at the chosen working potential from the cyclic voltammetric data (760 mV vs. Ag/AgCl). The electrolysis was terminated when the current is decayed to 97.5% of the initiated current. During the electrolysis, cyclic voltammograms and UV–Vis spectra were recorded in various times of the process. At the end of electrolysis, evaporation of the solvent under the reduced pressure afforded a product which was purified by column chromatography over silica gel (eluent was a mixture of ethanol/chloroform). After re-crystallization of the separated product, ^{1}H-NMR, ^{13}C-NMR, MS, and UV/Vis spectrophotometric analysis were used for the characterization of the product.

2.4 Electro-synthesis of 4-methyl-5-[(5-methyl-1,3,4-thiadiazole-2-yl) sulfanyl]-1,2-benzendiol (MTSBD)

The synthesis was performed with 100 mL phosphate buffer solution (0.1 M, pH = 7.0) containing 0.005 M 4-methylcatechol and 0.005 M MMT in an H-type divided coulometric cell. At the end of electrolysis, a few drops of phosphoric acid were added to the solution and cell was placed in refrigerator overnight. The precipitated solid was collected by filtration and re-crystallized from a mixture of methanol/acetone. After re-crystallization process, IR, ^{1}H-NMR, ^{13}C-NMR, MS, and UV/Vis spectroscopic

analysis were used for the characterization of the product. The final product was obtained purely and no extra purification was needed.

2.5 Characteristics of the product TSBD

IR (KBr): 3440 (–O–H), 3326 (–O–H), 3050 (C–H aromatic stretching absorption), 690–900 (C–H aromatic),1460, 1389 (C=C aromatic), ^{1}H NMR, δ (500 MHz MeOD-d4): 5.352 (d, $^3J_{HH}$ = 8.15 Hz, 6-H); 5.537 (dd, ^4J = 1.92 Hz, $^3J_{HH}$ = 8.12 Hz, 5-H); 5.569 (d, $^4J_{HH}$ = 1.8 Hz, 3-H); 1.107 (s, 9-H, Methyl group); 3.345 (H-coupling between protons of phenol and MeOH solvent); ^{13}CNMR, δ(500 MHz MeOD-d4): 171.991,165.515(8-C, 7-C), 147.261, 145.417 (1-C, 2-C), 125.849, 120.101, 115.173 (3-C, 5-C, 6-C), 121.825(4-C), 12.761 (9-C). MS, m/e (relative intensity): 240 (M$^+$, 70), 172 (12), 141 (40), 123 (90), 99 (25), and 59 (23). m.p.: 219–225 °C.

2.6 Characteristics of the product MTSBD

^{1}H NMR, δ (500 MHz MeOD-d4): 5.352 (d, $^3J_{HH}$ = 8.15 Hz, 6-H); 7.02 (s, 3-H); 6.795 (s, 6-H); 2.576 (s, 9-H, Methyl groups); 2.253 (s, 10-H); 3.653 (H-coupling between protons of phenol and MeOH solvent); ^{13}CNMR, δ (500 MHz MeOD-d4): 171.216, 166.242 (8-C, 7-C), 149.769, 145.557 (1-C, 2-C), 119.179, 123.369, 133.816 (3-C, 4-C, 5-C, 6-C), 20.321, 16.044 (9-C, 10-C). MS, m/e (relative intensity): 254 (M$^+$, 8.15), 237 (11.25), 221 (6.25), 180 (2.5), 132 (85), 78 (30) and 56 (85). m.p.: 250–255 °C.

3 Results and discussion

3.1 Electro-oxidation of catechol in the presence of MMT

Initial electrochemical studies for obtaining information about the mechanism of the oxidation of catechol in the presence of MMT on the surface of GC electrode in 0.1 M phosphate buffer of pH 7 was carried out using cyclic voltammetry and the recorded responses are shown in Fig. 1A. Oxidation of catechol was observed as a well-defined peak at 0.212 V with corresponding reduction process found at 0.139 V. Repetitive cycling of catechol incurred no losses in the height of the redox peaks with the super-impossibility of subsequent scans (not shown). This suggests the stability of the electrode oxidation product and no occurrence of side chemical reactions under applied experimental conditions. As can be seen in Fig. 1A, in the presence of MMT as nucleophilic species, the cathodic counterpart of the anodic peak 1a is disappeared. The

positive shift of the 1a peak in the presence of MMT that was enhanced during repetitive of potential cycling is probably due to the formation of a thin film of product at the surface of electrode, inhibiting (to a certain extent) the performance of electrode process. On the other hand, a new reversible coupled peak appeared with $E_{p,a}$ and $E_{p,c}$ values of 0.116 and 0.0203, respectively, in the second scan.

The multi-cyclic voltammetric investigations of catechol in the presence of MMT show a graduate decrease in anodic peak current of catechol. The new anodic and cathodic peak current of nucleophilic addition product increases and becomes constant after the second scan (Fig. 1B). The decrease in anodic peak current in consecutive scans can be attributed to the consumption of catechol in nucleophilic addition reaction with MMT that cause to scavenge the oxidized form of catechol such that on the reverse sweep there is little available for the electro-reduction, so there is little catechol in the diffusion layer and at the electrode surface in the followed scans, leads to reduction in anodic current in the next scans. We can say that the rate of cathodic reaction in the reversed scan becomes slower due to the reduction of o-quinone, so there is little catechol in the diffusion layer leads to decrease in anodic current in the next scans.

The influence of pH on the electrochemical behavior of catechol in the presence of MMT was studied through examining the electrode response at various pHs. It was found that the positions of two redox couples for catechol and its nucleophilic reaction product were depending upon pH. The cyclic voltammetric investigations of catechol in the presence of MMT in a pH range of 3–7 showed that by increasing the pH of solution, a negative shift in the peak potentials is resulted. This means that the deprotonation step is prior to the electron transfer process (Fig. 2). The cathodic peak for reduction of o-quinone to catechol can been seen clearly in solutions with pHs 3 and 4. However, this cathodic peak is disappeared as pH increases and a new redox couple appears in less positive potential in pHs 6 and 7. The result indicates that the nucleophilic strength of MMT is completely pH-dependent. According to previous literatures [21–23] and these results obtained, due to the decrease in the rate of the polymerization reaction of catechol at pH 7 and increase in the rate of the nucleophilic reaction between catechol and MMT, a solution containing phosphate buffer (0.1 M, pH 7) has been selected as suitable condition for the electrochemical studies and electro-synthesis procedure. Proportionally to the augmentation of the potential sweep rate (Fig. 3), anodic peak current for both two peaks increase linearly with square root of the scan rate and it was highlighted a diffusion-controlled process in the electrochemical behavior of catechol and the addition product. On the other hand, the current function ($I_{p,a1}/v^{1/2}$) for catechol oxidation decreases slightly with

Fig. 1 A Cyclic voltammograms of 1 mM catechol (*solid line*), 1 mM MMT (*dashed line*), and 1 mM catechol in the presence of 1 mM MMT (*dotted line*) at the surface of glassy carbon electrode. **B** Multi-cyclic voltammograms of 1 mM catechol in the presence of 1 mM MMT. Supporting electrolyte was 0.10 M phosphate buffer (pH 7.0). Potential sweep rate was 100 mV s^{-1}
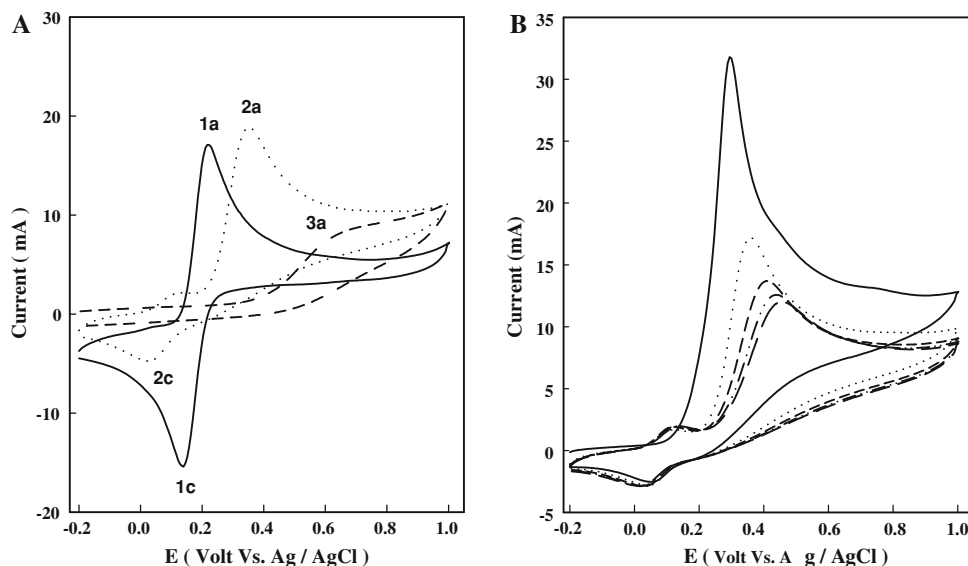
increasing the potential sweep rate. This voltammetric data reveals that MMT participates in nucleophilic addition reaction with the oxidized *o*-quinone species via an ECE electrochemical pathway leading to a product that shows a new and nearly reversible two electron transfer process. Removal of the electro-generated quinone through reaction with the thiol functionality of the MMT means that on the reverse sweep, there is a less quinone present to the electro-reduction and hence the elimination of the cathodic (reduction) peak [24].

For coulometric studies, the potential of the carbon electrode, which is placed in a phosphate buffer solution (pH 7) containing 0.5 mmol of catechol and 0.5 mmol of MMT, was fixed at 0.76 V vs. Ag/AgCl, at a potential
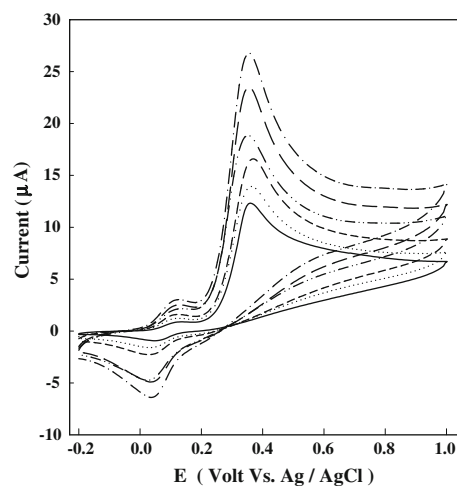

Fig. 3 Typical cyclic voltammograms of 1 mM catechol in the presence of 1 mM MMT at the surface of glassy carbon electrode in various potential sweep rates (from up to down) 200, 150, 100, 75, 50, and 25 mV s^{-1}
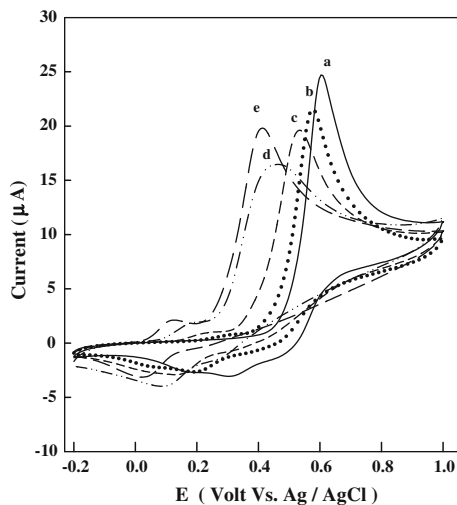
immediately following the peak 1a. In these studies, a coulometric value of 4 was found for the number of electrons (*n*) involved in the oxidation of one molecule of catechol in the presence of MMT. The monitoring of the electrolysis progress was accomplished using cyclic voltammetry and UV–Vis spectrophotometry. It is shown in Fig. 4 that by progression the electrolysis process, the anodic peak current for catechol decreases and peaks current for newly appeared anodic and cathodic waves in less positive potentials increase. The electrolysis progress is continued until the anodic wave for catechol completely disappeared and the ratio $I_{p,a}/I_{p,c}$ for the final product becomes 1, which shows a nearly reversible electrochemical behavior in the pH and potential sweep rate studied. The progress of the electrolysis was simultaneously

Fig. 2 Cyclic voltammograms of 1 mM catechol and 1 mM MMT at the surface of glassy carbon electrode in buffered solution with pH (*a*) 3.0, (*b*) 4.0, (*c*) 5.0, (*d*) 6.0 and (*e*) 7.0. Potential sweep rate was 100 mV s^{-1}

followed by monitoring the ultraviolet and visible (UV–Vis) absorption spectrum (Fig. 5A): after applying the potential 0.7 V, a decrease in the UV–Vis absorption band due to the MMT (276 nm) and an increase in intensity of 207 nm peak corresponding to catechol with partially red shift were observed. Moreover, a new broad band at λ_{max} of nearly 304 nm appeared and its height increased with progress of coulometry. This absorption peak belongs to the addition product of thiol species to *o*-quinone (Fig. 5A). The spectrum of catechol and MMT as initial materials respect to the final separated product in aqueous solutions with pH 7.0 is compared in Fig. 5B. These spectra show absorption bands with λ_{max} of 207 and 294 nm for catechol, 276 nm for MMT, and 340 nm for synthetic product. The result obtained from voltammetric,

coulometric, and spectrophotometric data indicates an ECE mechanism in electrochemical behavior of catechol in the presence of the MMT as a nucleophile. On the basis of these results, a mechanistic pathway is depicted in Scheme 1. It could be anticipated from the reaction pathway that in the first step, catechol is anodically converted to *o*-quinone in aqueous solutions. Then the molecule of thiol could attack the quinoid intermediate via 1 + 4 Michael addition before it is electrochemically reduced back due to producing the quinone–thiol adducts. The cyclic voltammograms of final separated coulometric product in comparison with the initial catechol is shown in Fig. 6. The presence of thiol backbone with its electron-donating property in the structure of intermediate d caused that the oxidation of this compound is performed more easily than catechol. The reaction product can also be oxidized at a lower potential than the starting compound.

3.2 Electro-oxidation of 4-methylcatechol in the presence of MMT

The effect of a group located at the reactive site of *o*-quinines (C-4 or β-position to carbonyl group) on their reactivity toward MMT was investigated in some details. The electrochemical oxidation of 4-methylcatechol bearing methyl at the C-4 position was studied in the presence of MMT in aqueous solution. Figure 7 shows the cyclic voltammograms obtained for 1 mM of 4-methylcatechol in the absence and presence of MMT. However, in this case, the presence of methyl group as an electron-donor on the aromatic ring, causes a decrease in the activity of 4-methylcatechol as a Michael acceptor towards the 1,4-addition (Michael) reaction. As mentioned in Fig. 7, the new cathodic and anodic peaks are not observed in the presence of nucleophile, mainly due to the low concentration of intermediate at the surface of the electrode. These findings indicate that the addition reaction is very slow and
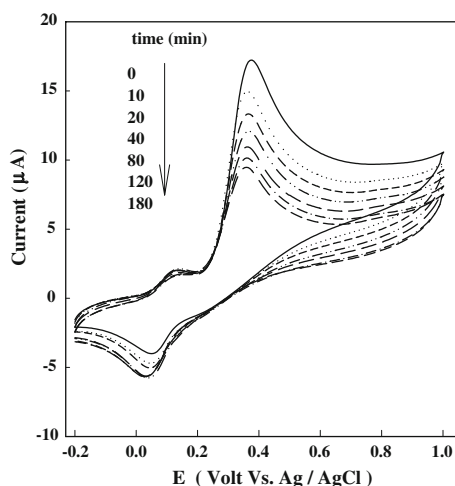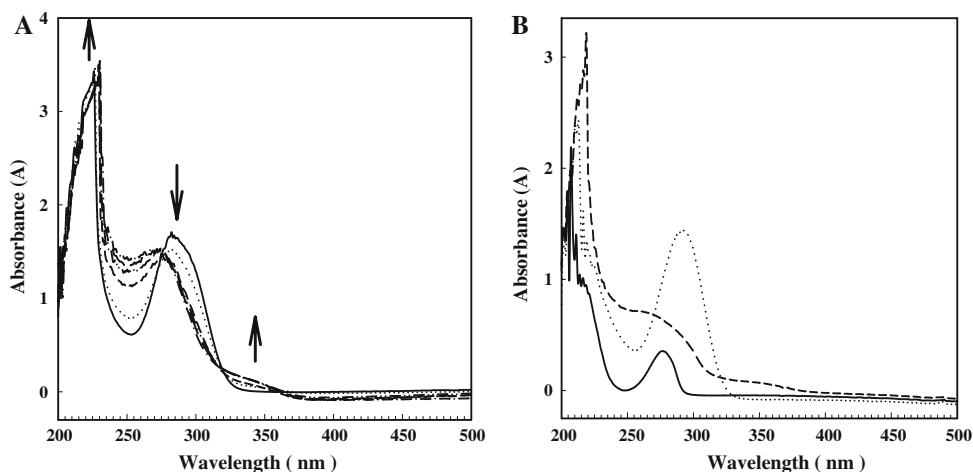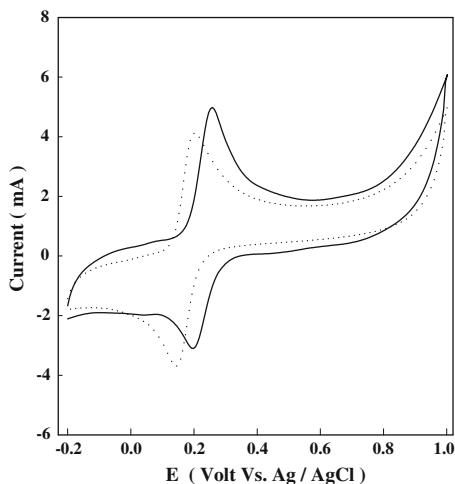

Fig. 4 Cyclic voltammograms of 1 mM catechol in the presence of MMT at the surface of glassy carbon electrode during controlled-potential coulometry at +0.76 V vs. Ag/AgCl. CV curves, up to down, corresponding to the solution after 0, 10, 20, 40, 80, 120, and 180 min of the electrolysis progress. Potential sweep rate was 100 mV s^{-1}

Fig. 5 A UV–Vis spectra of the solutions containing 0.1 mM catechol and 0.1 mM MMT during controlled-potential coulometry (the electrolysis solution is diluted by 100-fold). The spectra, up to down, are corresponding to times 0, 10, 20, 40, 80, and 120 min of electrolysis, respectively. **B** Comparison spectra of 0.1 mM catechol (*solid line*), 0.1 mM MMT (*dotted line*), and separated final product (*dashed line*) in 0.1 M phosphate buffer solution with pH 7.0

Fig. 6 Cyclic voltammograms of 0.1 mM catechol (*solid line*) and separated coulometric product (*dotted line*) at the surface of glassy carbon electrode. Supporting electrolyte was phosphate buffer (0.10 M, pH 7.0) and scan rate was 100 mV s^{-1}
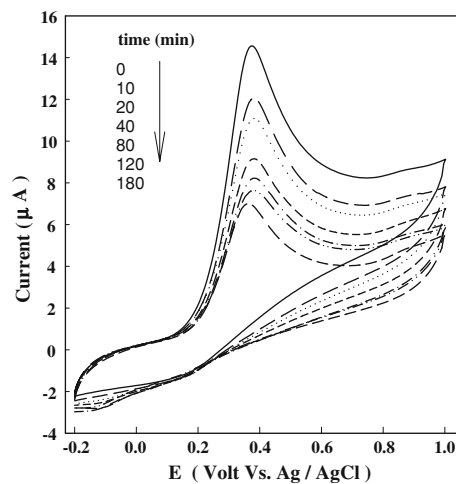

Fig. 8 Cyclic voltammograms of 1 mM 4-methylcatechol in the presence of MMT at the surface of glassy carbon electrode during controlled-potential coulometry at +0.70 V vs. Ag/AgCl after 0, 10, 20, 40, 80, 120, and 180 min of the electrolysis progress. Potential sweep rate was 100 mV s^{-1}
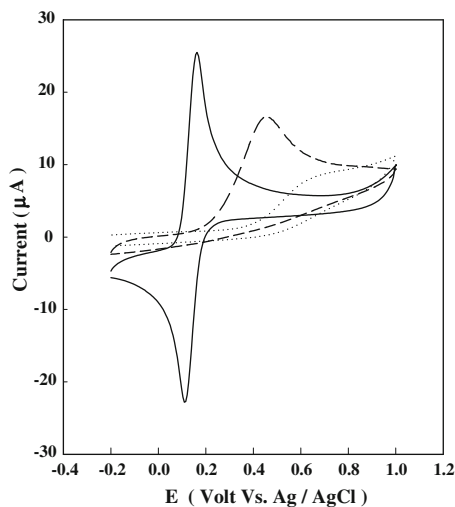

Fig. 7 Cyclic voltammograms of 1 mM 4-methylcatechol (*solid line*), 1 mM MMT (*dotted line*) and 1 mM 4-methylcatechol in the presence of 1 mM MMT (*dashed line*) at the surface of glassy carbon electrode. Supporting electrolyte was 0.10 M phosphate buffer (pH 7.0). Potential sweep rate was 100 mV s^{-1}

cannot proceed in the limited time scale of cyclic voltammetry. However, on the longer time scale of electrolysis, the conditions become favorable for the completion of the chemical reaction and the quinone–thiol addition product can be obtained.

By comparison of the results of cyclic voltammetry performed at different times for both systems, it was found that the rate of the reduction of the current of methylcatechol's oxidation is less than catechol's oxidation current and the cathodic and anodic peaks due to new products are not observed in the presence of nucleophile in the similar

time interval. We can say the presence of methyl group as an electron-donor on the molecular ring, causes a diminution in the activity of 4-methylcatechol as a Michael acceptor towards the 1,4-addition (Michael) reaction. So, concentration of intermediate at the surface of the electrode is less than can be attacked by nucleophile. These findings indicate that the addition chemical reaction is so much slower that it cannot proceed in the limited time scale of cyclic voltammetry. However, on the longer time scale of electrolysis, the conditions are favorable for the completion of the chemical reaction and the quinone–thiol adduct product is obtained (as mentioned this, we can see a little cathodic current due to new synthetic product in consecutive scans of CV voltammograms during coulometry).

The variation of current function ($I_{p,a1}/v^{1/2}$) with the scan rate, confirms a chemical reaction between electrolytically produced 4-methylbenzoquinone and MMT. In order to achieve the optimum conditions for the synthesis of products, the pH was optimized. The best yield and purity were obtained in a phosphate buffer solution (0.1 M, pH 7), due to the decrease in polymerization of catechol and increase in coupling of *o*-quinone and thiol in this solution. Therefore, controlled-potential coulometry was performed in aqueous solution containing 5 mM of 4-methylcatechol and 5 mM of MMT at 0.70 V vs. Ag/AgCl. Parallel to the advancement of coulometry, the monitoring of electrolysis progress by cyclic voltammetry showed that the anodic peak corresponding to oxidation of 4-methylcatechol decreases and disappears when the charge consumption becomes about 2 e$^-$ per molecule of this compound (Fig. 8). Based on these observations and considering the results obtained from the analysis of
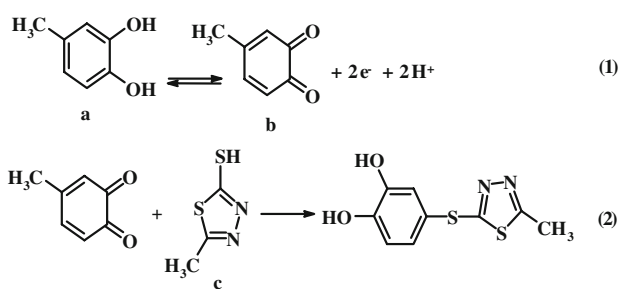
Scheme 1
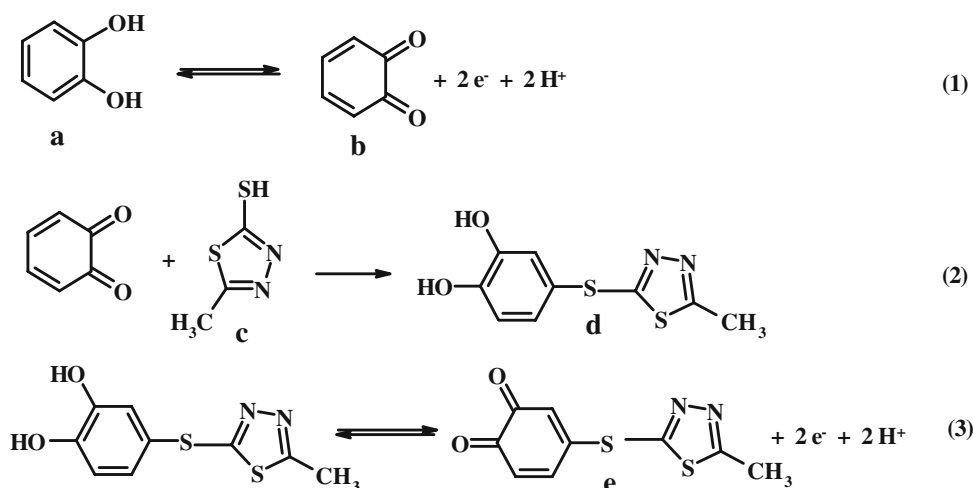
spectroscopic data, a mechanism can be proposed for the electrochemical oxidation of 4-methylcatechol in the presence of MMT as shown in Scheme 2. According to the results, it seems that upon anodic oxidation of 4-methyl-catechol to *o*-benzoquinone (Scheme 2(1)), an intermolecular Michael-type addition of MMT with *o*-benzoquinone occurs in sequential fashion and this reaction is faster than other side reactions, leading to the formation of thiadiazole derivative (Scheme 2(2)). The over oxidation of quinone–thiol adduct was circumvented during the preparative reaction because of the insolubility of the product in phosphate buffer solution. According to the results obtained from the thin layer chromatography (TLC), ^{1}HNMR, ^{13}CNMR, and mass spectrometry (MS), it is concluded that *o*-quinone is attached mostly in the C5 position to the MMT from thiol moiety leading to the formation of only one final product.

Scheme 2

and aqueous media which has great potential in green chemistry.

4 Conclusions

The anodic oxidation of catechol and 4-methylcatechol in aqueous solution in the presence of MMT as a nucleophilic agent is discussed in the present work. The overall reaction mechanisms for anodic oxidation of catechols in the presence of MMT are presented in Schemes 1 and 2. The voltammetric and spectrometric investigations revealed that MMT attached to the *o*-quinones via its thiol moiety in a 1 + 4 Michael addition and new derivatives of thiadiazol can be resulted, which have many important drug applications. In addition, our results suggest that the electronic and steric nature of the substituents attached to benzoquinone rings have important effects on their reactivity toward nucleophile. This electrolysis procedure is an alternative route for the synthesis of pharmaceutical compounds with good selectivity, yield, and purity from the simple molecules such as catechols and MMT in ambient conditions

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