

Determination of Hydroquinone Using Poly(3-methylthiophene) Synthesized Electrochemically on Pt Electrode in Methylene Chloride

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ABSTRACT: Poly(3-methylthiophene) (P3MT) film was synthesized by potentiodynamic method on Pt electrode in methylene chloride solution containing 0.10M tetrabutylammonium perchlorate supporting electrolyte and used for the determination of hydroquinone (HQ) with amperometric $I-t$ method in solution consisting of $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ (SBS; pH 2.0). This modified electrode has a lower working potential and good operational stability due to reducing electrode fouling when compared with the direct oxidation of HQ at the bare Pt electrode. Limit of detection, limit of quantification, and the linear response range were found to be 1.32×10^{-5} mM, 4.41×10^{-5} mM, and between 4.41×10^{-5} – 50.0 mM ($R^2 = 0.997$), at 0.50 V versus saturated calomel electrode, respectively. HQ determination in complex matrix was checked using real samples to demonstrate the applicability of modified electrode. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40859.

KEYWORDS: amperometric determination; conductive polymer; hydroquinone; methylene chloride; poly(3-methylthiophene)

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INTRODUCTION

Some of phenolic compounds which are especially found in plants as antioxidants are useful; however, the rest are harmful for humans, animals, and environmental resources because of being released into the environment by a large number of industries such as coal mining industry, oil refining industry, paint industry, industry of photographic chemicals, pesticide industry, polymer industry, pharmaceuticals industry, tanning industry, industry of food antioxidants and production of polymerization inhibitors and organic-reducing agents, and cosmetic industries.^{1–3} Derivative of dihydroxybenzene can cause irritation and sensitization in the eyes, nose, and throat. In addition, it has been shown to be mutagenic in animals.⁴ Indeed, it has been included in the lists of priority pollutants to be monitored in the aquatic environment by international organization such as the European Union and the US Environmental Protection Agency.⁵ Thus, it is important for the determination of hydroquinone (HQ) by a sensitive and reliable method. Recently, some analytical techniques such as capillary electrochromatography, high-performance liquid chromatography, micellar chromatography, and kinetic spectrophotometry are being replaced by rapid, reliable, and inexpensive methods.⁶ Biosensors based on immobilized peroxidase such as polyphenol oxidase or tyrosinase,⁷ laccase,⁸ horseradish peroxidase,⁹ bienzyme electrode with horseradish peroxidase/glucose oxidase, and tyrosinase/laccase bienzyme¹⁰ have been used for the detection of phenolic com-

pounds. Electrodes containing modified chemical films are used in different fields of chemistry and material science in the application areas of electroanalysis and electrocatalysis. Electrochemical determination of HQ is made by the use of chemically modified electrode^{11,12} and chemically modified electrode containing immobilized bacteria.¹³ Of all these methods, electrochemical method is the most advantageous one because of its rapidness, simplicity, and sensitivity. In addition, electrochemical sensors can be fitted to extremely small dimensions, and thus, they become ideal for direct placement into biological samples with minimal damage to tissues. Nowadays, conductive polymers are used to modify electrode surface because of their electricity properties. They have an important role as electrochemical sensors for determination of analytes such as phenolic compounds.^{14,15} They respond better when compared with unmodified electrode. Poly(3-methylthiophene) (P3MT), which can be easily electrodeposited onto electrode surface by electrooxidation, is one of the most promising conductive polymers, which has high conductivity, good redox reversibility, and environmental stability.^{16,17}

Modified electrodes of P3MT are widely used for the determination of phenolic compounds because of their excellent electronic¹⁸ and optical properties, thermal stability,¹⁹ and electrocatalytic effect.²⁰ It is reported that P3MT and their derivatives were synthesized electrochemically in nonaqueous (acetonitrile and acetonitrile-containing ferrosulfonic acid,^{21–24} chloroform,²⁵ and

boron trifluoride diethyl ether^{26,27}) and aqueous (perchloric acid medium²⁸) solvents. P3MT-coated electrodes, which have conjugated double bond in molecular structure, have been shown suitable for the determination of some phenolic compounds,^{29–33} dopamine,²⁰ and 8-hydroxy-2'-deoxyguanosine (8-OH-dG),³⁴ based on excellent electrocatalytic effect that exert on the oxidation of these compounds.³⁵ The determination of inorganic anions based on their incorporation as counter ions into the positively held P3MT has been described.^{36,37} On the other hand, surface passivation of glassy carbon electrodes during the voltammetric analysis of phenolic compounds can be prevented by using P3MT coatings.²⁹ Besides, the particular characteristics of microelectrodes are being more and more advantageously applied in electroanalysis.^{38,39}

In this study, P3MT polymer film was synthesized electrochemically in methylene chloride solution containing 0.10M tetrabutylammonium perchlorate (TBAP), and amperometric $I-t$ method was used for the determination of HQ without using enzyme in solution consisting of $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ buffer solution (SBS; pH 2.0). This modified electrode was characterized electrochemically and also by the use of Ultraviolet visible spectrophotometry (UV-vis), Fourier Transform Infrared Spectrum (FT-IR), Raman Spectrum, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). It was used in the analysis of HQ in real sample.

EXPERIMENTAL

Apparatus

CH Instruments system, Model 1140B, was used for electrochemical studies. The electrochemical cell used has five inlets. Three of these inlets were used for the electrodes [Pt disc and Pt macroelectrode as working electrode; Pt spiral and platinum wire as counter electrode; Ag/AgCl (nonaqueous medium) and saturated calomel electrode (SCE; aqueous medium) as reference electrode], and the other two inlets were used for nitrogen gas inlet and nitrogen gas outlet. Pt disc [area = 7.85×10^{-3} cm² (for cyclic voltammetric studies)] and Pt foil [area = 1.0 cm² (for FTIR, SEM, and Raman measurements)] were used as working electrodes. Before each experiment, the working electrode was polished with a slurry of Cr₂O₃ with water, rinsed with triple distilled water, cleaned in the ultrasonic bath, washed with methylene chloride solution, and dried, respectively. For FTIR, SEM, and Raman spectroscopy measurements, Pt foil working electrode was cleaned by holding it in flame for a few minutes. The characterization of polymers obtained electrochemically was performed by FTIR (Perkin Elmer Spectrum 100 spectrometer) using KBr pellets. UV-vis spectrum (Perkin Elmer Lambda 35 spectrometer) was obtained by being dissolved in the polymer films in dimethyl sulfoxide. The images of SEM (FEG Quanta 450), EDS (Bruker EDS) and Raman Spectra (Deltan NU Raman Spectrometer) were performed using deposited polymer films on Pt foil electrode.

Chemicals

All chemicals were provided by chemical company with analytical grade and used without further purification. Methylene chloride (Sigma-Aldrich), which was used to prepare polymerization solutions, was kept under the nitrogen atmosphere

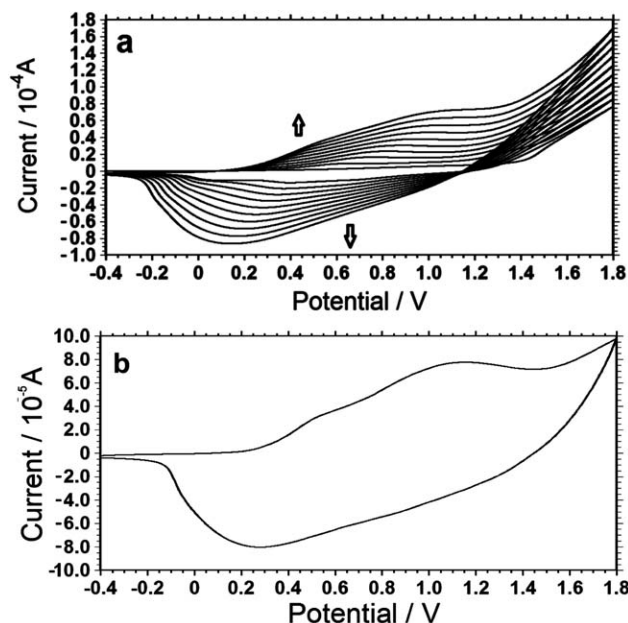


Figure 1. (A) Cyclic voltammograms recorded during potentiodynamically deposited P3MT film on Pt disc electrode in methylene chloride solution containing 0.100M TBAP/500 mM 3MT between -0.40 and 1.80 V, and (B) its cyclic voltammetric behavior in methylene chloride blank solution (vs. Ag/AgCl, $\nu = 100$ mV s⁻¹).

(Linde). TBAP used as supporting electrolyte in nonaqueous medium was obtained by the reaction of tetra-*n*-butyl ammonium hydroxide (40% aqueous solution; Sigma-Aldrich) with perchloric acid and recrystallized from the 1 : 9 mixture of water and ethyl alcohol by volume several times. It was then dried at 120°C under vacuum for 12 h and kept under nitrogen atmosphere. Double-distilled water was used to prepare the solutions. Buffer solutions (pH 2.0–6.5) were prepared using NaHSO₄ (Merck) and Na₂SO₄ (Merck). HQ solution was prepared in SBS at pH 2.0 of which medium was deoxygenated by bubbling pure nitrogen gas (Linde) prior to use in the electrochemical experiments.

RESULTS AND DISCUSSION

Preparation and Characterization of P3MT Film in Methylene Chloride Solution

Deposition of the P3MT film was achieved potentiodynamically on Pt disc electrode in a nonaqueous methylene chloride containing 20.0–500 mM 3MT monomer and 0.10M TBAP solution. Figure 1(A) shows the cyclic voltammetric scans (20 cycles) taken during the deposition on the Pt disc electrode between -0.40 and 1.80 V versus Ag/AgCl in solution containing 500 mM 3MT. As can be seen in Figure 1(A), all voltammetric peak currents increased linearly with each cycle. P3MT films deposited on Pt electrode were immersed in methylene chloride to remove adsorbed electrolyte, monomer, and the soluble oligomers formed during electropreparation of the P3MT films. Figure 1(B) shows the cyclic voltammogram of the P3MT films between -0.40 and 1.80 V in the methylene chloride solution containing 0.10M TBAP (blank solution). Anodic and cathodic peak currents and charge were compared with

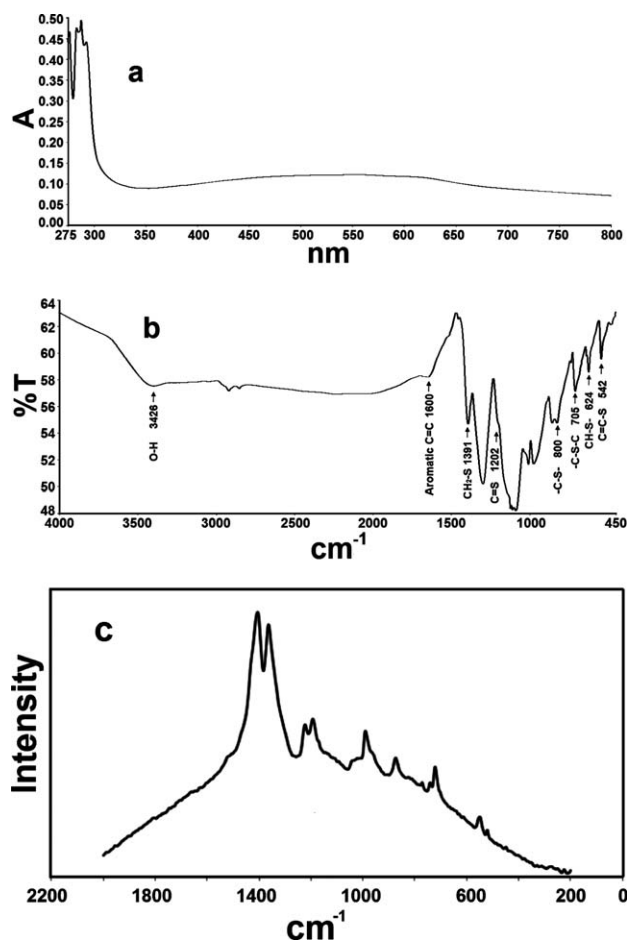


Figure 2. (A) UV-vis, (B) FTIR, and (C) Raman spectra of potentiodynamically deposited P3MT films between 1.80 and -0.40 V in methylene chloride solutions containing 500 mM 3MT and 0.10M TBAP on Pt macroelectrode (vs. Ag/AgCl, $v = 100$ mV s^{-1}).

blank solution voltammograms of P3MT films deposited with polymerization solutions containing 20, 100, 200, 400, and 500 mM 3MT. Anodic peak current values: 2.36×10^{-5} A, 6.04×10^{-5} A, 6.65×10^{-5} A, 7.31×10^{-5} A, 7.76×10^{-5} A; cathodic peak current values: 2.56×10^{-5} A, 5.88×10^{-5} A, 6.51×10^{-5} A, 7.19×10^{-5} A, 8.03×10^{-5} A; and charge values: 6.31×10^{-4} C, 6.95×10^{-4} C, 6.55×10^{-4} C, 9.88×10^{-4} C, 13.13×10^{-4} C were read. According to these results, the best electroactive P3MT film was obtained using 500 mM of 3MT monomer concentration in polymerization solution. After the determination of 3MT monomer concentration for the best electroactive P3MT film, working potential region was studied. P3MT films were obtained between 1.80 and -0.40 , -0.20 , 0.0, and 0.20 V versus Ag/AgCl potentiodynamically on Pt disc electrode in a nonaqueous methylene chloride containing 500 mM 3MT monomer and 0.10M TBAP solution. Cyclic voltammetric behavior of these electroactive films were compared in blank solution of which anodic peak current values of 7.76×10^{-5} A, 3.81×10^{-5} A, 4.06×10^{-5} A, 5.52×10^{-5} A; cathodic peak current values of 8.03×10^{-5} A, 3.82×10^{-5} A, 4.12×10^{-5} A, 5.81×10^{-5} A; and charge values of 13.13×10^{-4} C, 9.41×10^{-4} C, 9.73×10^{-4} C, 9.54×10^{-4} C were read. According

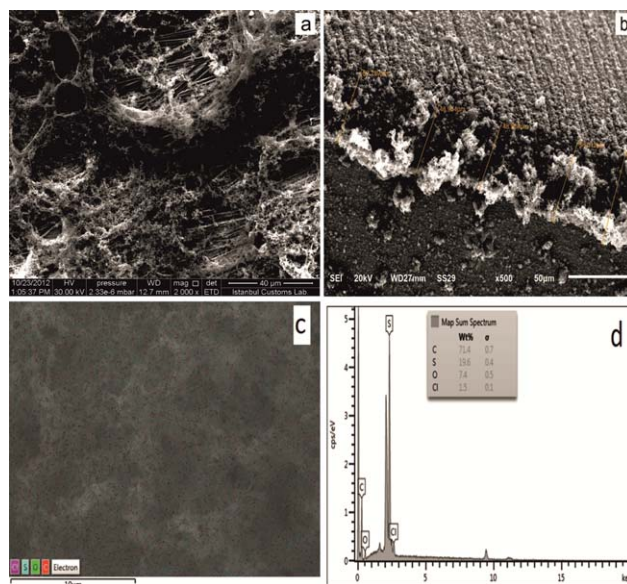


Figure 3. P3MT film deposited from -0.40 V to 1.80 V: (A) SEM images; (B) thickness; (C) EDS-layered mapping image; and (D) EDS spectrum. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to these results, the best working potential region was determined as film deposited between -0.40 and 1.80 V.

UV-vis, FTIR, and Raman spectra of film deposited in the optimum conditions are shown in Figure 2(A–C). UV-vis spectra show the formation of (bi)polaron bands in the polymer chains (i.e., the formation of a type of charge carriers)^{40,41} between 400 and 800 nm. There is an absorption band at about 400 nm [Figure 2(A)]. This absorption band in the P3MT is associated with the π - π^* interband transition as in other polythiophene homopolymers.^{25,42} The characteristic peaks of P3MT appearing in the FTIR spectrum are 3000 cm^{-1} asymmetric C–H, 1400 cm^{-1} CH_2S , 1300 cm^{-1} methyl, 1600 cm^{-1} C=C, 750 cm^{-1} C–S, and 680 cm^{-1} C–S–C peaks [Figure 2(B)]. These peaks show similarity to the literature reports.^{25,43} The FTIR and the Raman spectra [Figure 2(C)] of P3MT film were compared, and the absorption peaks of both FTIR spectra and Raman spectra were observed at 1600, 1400, 1300, 750, and 680 cm^{-1} .

The surfaces of films deposited on Pt macro electrode are different from each other. Figure 3(A) shows SEM image of P3MT film deposited in optimum conditions. This film is more porous than the other films. The film thickness was measured by SEM and was found as 52.16 μm [Figure 3(B)]. The chemical composition of P3MT film was investigated by using EDS mapping method. The peaks present in EDS spectra and related atoms are C at 0.28 keV, O at 0.52 keV, Cl at 2.82 keV, and S at 2.47 keV. The existence of Cl peak shows the existence of ClO_4^- in the structure of P3MT polymer as counter ion. Furthermore, the peak located at 2.47 keV is the evidence of S and, hence, existence of P3MT in the polymer film [Figure 3(C,D)].

Effect of pH in Aqueous Medium

The pH of the solution has a significant influence on the activity of the polymeric film. P3MT is electrochemically active in

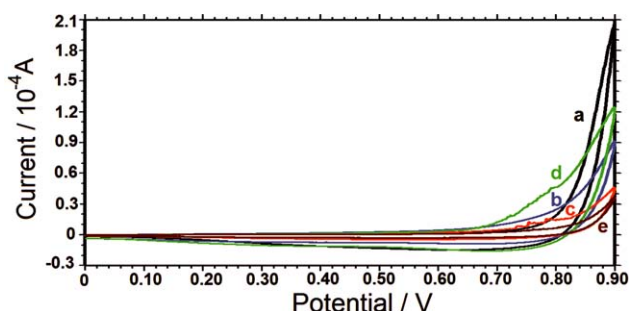


Figure 4. Effect of pH on electrochemical behavior of P3MT film deposited between -0.40 and 1.80 V to (a) 2.0, (b) 3.0, (c) 4.0, (d) 5.0, and (e) 6.5 in different SBS solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

both aqueous and nonaqueous media at anodic potentials. The effect of pH on electrochemical behavior of P3MT film, which was deposited under optimum conditions [Figure 1(A)], was investigated between 2.0 and 6.5 in SBS. It has the highest electroactivity at pH value of 2.0. At pH values greater than 2.0, its electroactivity decreases as can be seen in Figure 4 (curves a–e). For this reason, pH 2.0 was selected to be used for the amperometric I – t methods for the determination of HQ in this study.

Interaction of HQ with P3MT Film

Cyclic voltammograms of these uncoated and P3MT-coated Pt disc electrodes taken immediately after immersing into the same pH 2.0 medium (SBS or SBS containing 5.00 mM HQ) were given for comparison in Figure 5(A). Figure 5(A) shows the electrochemical behaviors over bare Pt electrode (a), P3MT-coated film (b), over bare Pt electrode (c), and P3MT-coated film (d) containing 5.0 mM HQ in SBS at pH 2.0. According to Figure 5(A), HQ causes change in electrochemical behavior of P3MT film. As can be seen in Figure 5(A–d), the oxidation of HQ shifts to lower potential in the presence of P3MT-coated film.

The interaction of HQ with P3MT film was investigated by UV–vis measurement. First, UV–vis spectra of 500 mM HQ solution under nitrogen atmosphere in SBS at pH 2.0 were taken. Second, P3MT film deposited on Pt macroelectrode was immersed in this solution for 60 min, and then, the UV–vis spectra of obtained solution were taken. Third, the UV–vis spectrum of HQ solution that was left to open atmosphere and oxidized by oxygen in the atmosphere to quinone (Q) was recorded and each spectra was compared in Figure 5(B). As can be seen in Figure 5(B–a), an absorption peak was not observed in freshly prepared clear HQ solution, and in Figure 5(B–b), a new peak was observed at about 410 nm as a result of the oxidation of HQ to Q by atmospheric oxygen. In Figure 5(B–c), the weak absorption peak was observed at 410 nm. This constitutes the evidence that HQ is oxidized chemically to Q by P3MT.

Surface images of P3MT film interacted with HQ dissolved in aqueous medium were investigated by SEM [Figure 5(C)]. Surface images of P3MT film [Figure 3(A)] and P3MT interacted with HQ [Figure 5(C)] were compared, and then, different images were obtained.

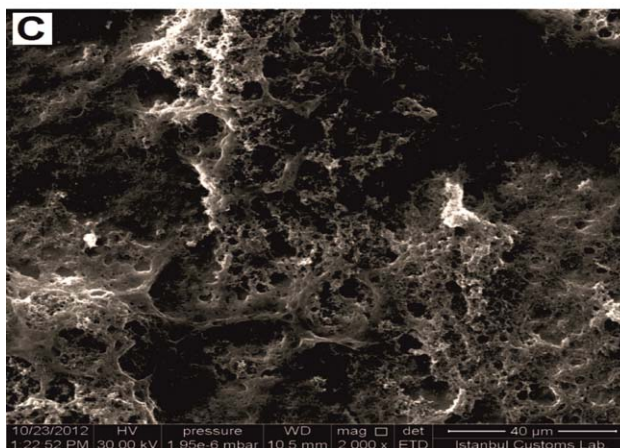
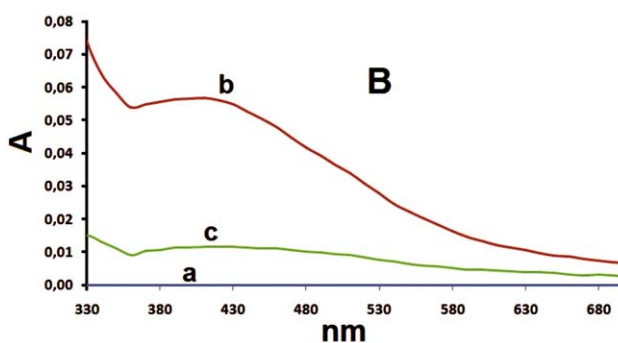
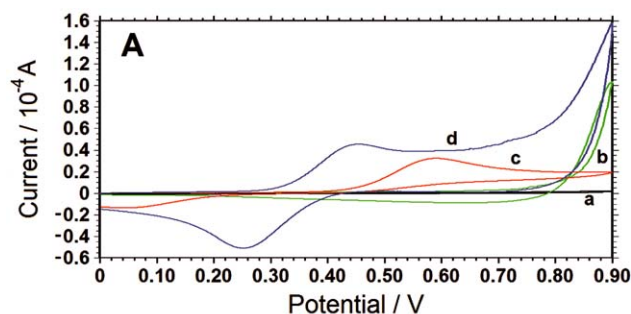


Figure 5. A: The electrochemical behaviors on (a) bare Pt electrode, (b) P3MT-coated film, (c) bare Pt electrode, (d) P3MT-coated film containing 5.0 mM HQ in SBS at pH 2.0. B: UV–vis spectra of HQ solution at pH 2.0: (a) freshly prepared in nitrogen atmosphere, (b) left to open atmosphere, and (c) after immersion of P3MT film for 60 min in nitrogen atmosphere $C_{\text{HQ}} = 500$ mM. C: Surface image of P3MT film (deposited between -0.40 and 1.80 V) interacted with HQ (vs. SCE, $\nu = 100$ mV s^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Determination of HQ

The response of the P3MT film deposited between potential from 1.80 to -0.40 V on Pt electrode for the determination of HQ was studied using amperometric I – t method (0.40 – 0.55 V) in SBS at pH 2.0 versus SCE and was compared with the responses of uncoated Pt electrodes [0.50 V; Figure 6(A)], a plot of the steady-state current values measured versus the HQ concentration [Figure 6(B)] and calibration curves for linearity range of HQ concentration over P3MT film and uncoated Pt electrode [Figure 6(C)]. These coverages were subjected to electrolysis during 1600 s at various constant potentials until

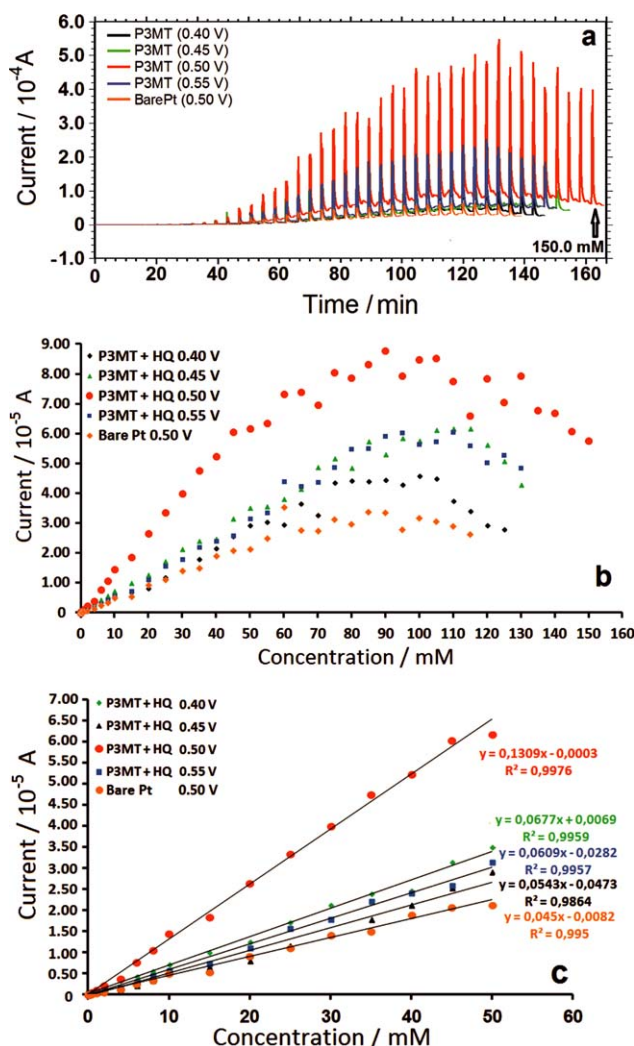


Figure 6. A: Amperometric $I-t$ curves recorded versus SCE on the successive additions of various HQ concentrations over uncoated Pt and P3MT film. B: A plot of the steady-state current values measured from amperometric $I-t$ curve over uncoated Pt and P3MT film versus the HQ concentration. C: Calibration curves for linearity range of HQ concentration over P3MT film and uncoated Pt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

they came to a steady state by using the conditions in which they show optimum electroactivity in $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ solution of pH 2.0. After each steady-state current values at the end of 200 s, applied potentials versus SCE were recorded on successive additions of various HQ concentrations. After reaching the stable current value, sufficient volume of stock solution was added to electrochemical cell that contained $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ solution of pH 2.0 to have HQ concentration of 9.77×10^{-4} mM, and current value was recorded when it approached the stable current value. Calibration curve was plotted in accordance with the increasing current and the increasing concentration of HQ. The results show that HQ was determined with lower potential (0.50 V) than its oxidation potential (0.60 V). The linear response range, limit of detection (LOD), and limit of quantification (LOQ) for P3MT film were found to be between 4.41×10^{-5} – 50.0 mM

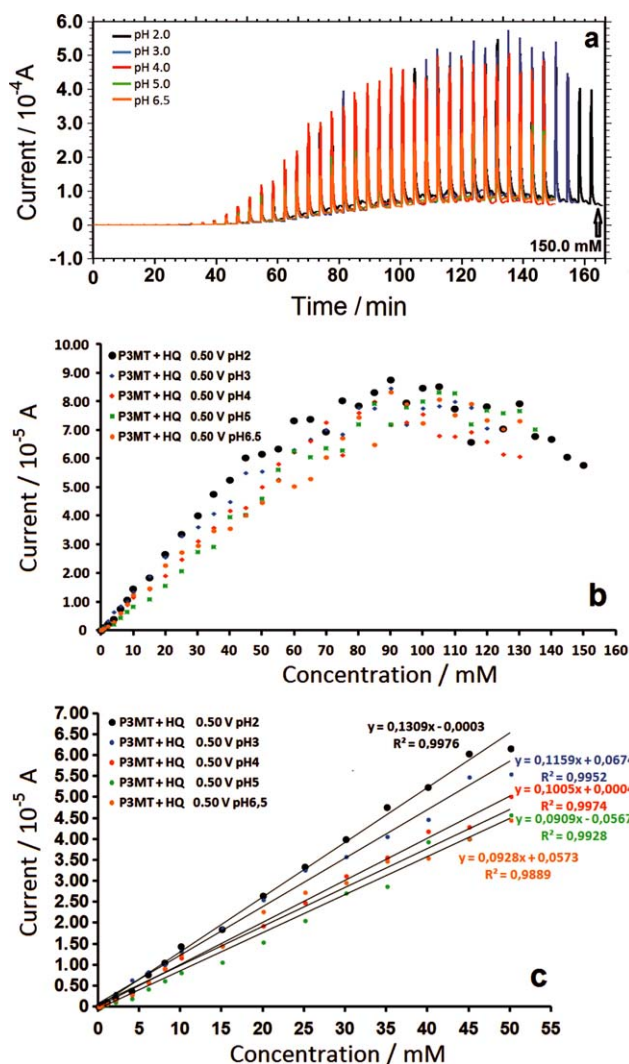


Figure 7. A: Amperometric $I-t$ curves recorded versus SCE on the successive additions of various HQ concentrations using P3MT film deposited on Pt electrode. B: A plot of the steady-state current values measured from amperometric $I-t$ curve versus the HQ concentration. C: Calibration curves for linearity range of HQ concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

($R^2 = 0.998$), 1.32×10^{-5} mM, and 4.41×10^{-5} mM at 0.50 V versus SCE, respectively.

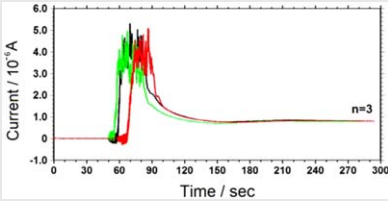
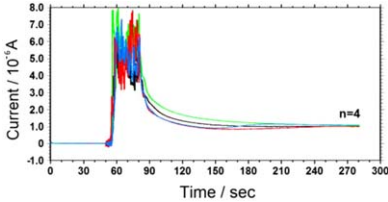
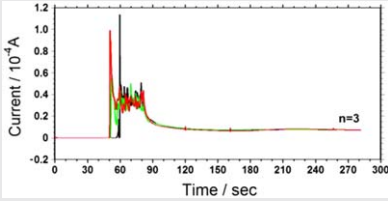
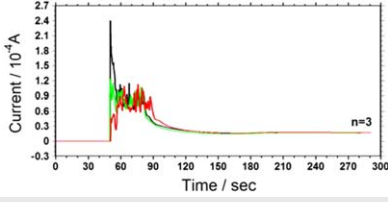
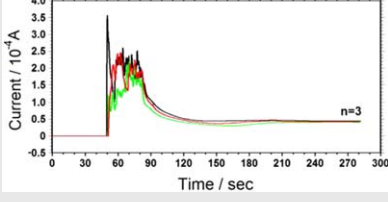
For the determination of HQ in different SBS mediums (2.0–6.5), amperometric $I-t$ (0.50 V) curves [Figure 7(A)], a plot of the steady-state current values measured from amperometric $I-t$ curve [Figure 7(B)], and calibration curves for linearity range [Figure 7(C)] versus the HQ concentration using P3MT film were obtained.

Applied potentials (between 0.40 V and 0.50 V), pH (2.0–6.5), electrodes (P3MT-modified and uncoated Pt), Limit of Detection (LOD), Limit of Quantification (LOQ), linear response range, linear equation, and regression coefficient (R^2) were given in Table I.

Table I. Analytical Parameters of Calibration Curves Obtained from Different SBS Buffer Solutions (2.0–6.5) and 0.40–0.55 V Potential Ranges by Using Bare, P3MT-Coated Pt Electrodes for Determination of HQ

Applied potentials (V)	pH	Electrodes	Sensitivity (mA/mM)	LOD (mM)	LOQ (mM)	Linear response range (mM)	Linear equation	Regression coefficient (R^2)	
0.40	2.0	P3MT	0.49	7.0×10^{-3}	2.34×10^{-2}	2.34×10^{-2} to 50.0	$y = 0.54x - 0.05$	0.9864	
0.45	2.0	P3MT	0.04	1.29×10^{-4}	4.31×10^{-4}	4.31×10^{-4} to 50.0	$y = 0.08x + 0.01$	0.9959	
		Pt	0.01	1.31×10^{-4}	4.40×10^{-4}	4.38×10^{-4} to 25.0	$y = 0.02x + 0.01$	0.9976	
0.50	2.0	P3MT	0.96	1.32×10^{-5}	4.41×10^{-5}	4.41×10^{-5} to 50.0	$y = 0.13x - 0.01$	0.9976	
		3.0	P3MT	0.18	7.76×10^{-5}	2.59×10^{-4}	2.59×10^{-4} to 50.0	$y = 0.12x + 0.08$	0.9952
		4.0	P3MT	0.06	1.08×10^{-4}	3.59×10^{-4}	3.59×10^{-4} to 50.0	$y = 0.10x + 0.01$	0.9974
		5.0	P3MT	0.16	8.30×10^{-5}	2.77×10^{-4}	2.77×10^{-4} to 50.0	$y = 0.09x - 0.06$	0.9928
		6.5	P3MT	0.31	1.94×10^{-4}	6.46×10^{-4}	6.46×10^{-4} to 50.0	$y = 0.09x + 0.06$	0.9889
0.55	2.0	Pt	0.05	1.19×10^{-4}	3.98×10^{-4}	3.98×10^{-4} to 50.0	$y = 0.06x - 0.01$	0.9950	
0.55	2.0	P3MT	0.08	2.56×10^{-4}	8.53×10^{-4}	8.53×10^{-4} to 50.0	$y = 0.06x - 0.03$	0.9957	

Table II. Assessment of Reliability of the Results Obtained from Reproducible Experiments for the Determination of Hydroquinone Using P3MT-modified Electrode

C_{HQ} (mM)	Amperometric $I-t$ curves	I (μA)	S (μA)	% RSD	$[\bar{x} \pm ts/\sqrt{N}]^{a,b}$ (μA)
0.50		0.804 0.796 0.802	0.0042	0.519	0.801 ± 1.10
1.0		1.022 1.054 1.011 1.059	0.0236	2.278	1.036 ± 0.704
5.0		7.003 7.336 7.244	0.1719	0.390	7.194 ± 1.10
10.0		16.33 16.01 16.77	0.3722	2.272	16.376 ± 1.10
20.0		43.85 40.71 42.70	1.5886	3.745	42.420 ± 1.10

^a 95% confidence level was calculated.

^b Confidence intervals were calculated using the value of the combined standard deviation.

Table III. Recovery Values for Determination of HQ in Real Sample

Samples	Added [C _{HQ} (mM)]	Found [C _{HQ} (mM)]	Recovery (%)
1	5.00	5.07	101.45
2	10.00	9.89	98.87

Performance parameters for this comparison are shown in Table I. LOD and LOQ were calculated from the equations $3s/m$ and $10s/m$ (s : standard deviation; m : slope), respectively.⁴⁴ The parameter “ s ” was calculated from the current responses of the lowest concentration that generate a measurable current in five replicated measurements. As it is clear from the table, P3MT-coated electrode has higher sensitivity than bare Pt electrode. It might be due to the immobilization of HQ molecules into P3MT polymer and also to the oxidation of HQ catalytically on P3MT polymer. A comparison between the P3MT-coated and uncoated electrode revealed that P3MT film-coated electrode has lower analysis potential (0.50 V). Using this coated electrode, higher sensitivity (0.96), lower LOD (1.32×10^{-5}), larger linearity range (4.41×10^{-5} –50.0), and better correlation coefficient (0.9976) were obtained in SBS at pH 2.0.

Repeatability Determination of HQ Using P3MT-Modified Electrode

Repeatability of read current value recorded from amperometric $I-t$ curves (0.50 V) for HQ determination over P3MT film, which was deposited under optimum conditions [Figure 1(A)], was tested by using different P3MT films for each measurement in SBS (pH 2.0) versus SCE. P3MT film was electrolyzed using amperometric $I-t$ methods (0.50 V, 1600 s) for steady-state current values. Afterward, steady-state current values at the end of 200 s were read between 0.50 and 20.0 mM of each HQ concentration using at least three different P3MT films. The ampero-

metric $I-t$ curves obtained for each concentration of HQ, current values for each concentration, standard deviations (s) of current values, percent relative standard deviation (% RSD), and confidence interval are shown in Table II. The combined standard deviation value ($S_{\text{combined}} = 0.4431 \mu\text{A}$) to evaluate the precision was calculated using current values of each sample obtained for the determination of HQ over P3MT film.

Determination of HQ in Real Samples

For an additional check on the accuracy of the developed method and the matrices interference, analytical recovery experiments were performed by adding known amounts of HQ in Güneysu river water sample of Rize Province in Turkey. This river water was taken and it was adjusted to optimum working pH (2.0) with HCl solution. It was artificially contaminated by the addition of HQ. For the determination of HQ, amperometric $I-t$ methods were used. P3MT film was electrolyzed for about 1600 s (pH 2.0) at 0.50 V to reach stability. After this, the prepared river water including HQ (5.0 and 10 mM) was added, and the steady-state current values were measured using at least three different films. The average of current values was compared with the standard HQ (5.0 and 10 mM) current values (Table II), and then, the percentage of the recovery values was calculated. The recoveries for the samples are shown in Table III. It can be clearly observed that there is no influence of the matrices for the determination of HQ in real sample on electrochemically synthesized P3MT film in methylene chloride medium.

Finally, Table IV shows the comparison chart for the selective determination of HQ based on literature reports. The current method is found to be simple, rapid, convenient, selective, and highly sensitive than any reported methods on HQ (Table IV), and the use of enzyme, catalyst, and oxidation agent is not necessary.

Table IV. Comparison of Electrochemical Methods for the Determination of HQ

Electrochemical methods	Using modified electrode	LOD (mM)	Linear response range (mM)	Regression coefficient (R^2)	Year	Reference
Amperometric	HRP afforded multilayer thin films on the surface of a thiol-modified gold electrode	2.0×10^{-3}	6.0×10^{-3} to 7.2×10^{-2}	0.999	2006	45
Cyclic voltammetry (CV)	Glassy carbon electrode modified with BSA	8.6×10^{-6}	2.5×10^{-5} to 1.3×10^{-3}	0.996	2008	46
Differential pulse voltammetry (DPV)	Poly- <i>p</i> -ABA/GCE	4.0×10^{-4}	1.2×10^{-3} to 0.60	0.998	2009	2
CV and DPV	Glassy carbon electrode	1.6×10^{-4}	5.0×10^{-4} to 0.20	0.980	2010	47
DPV	BMIMPF ₆	7.0×10^{-5}	1.3×10^{-4} to 0.10	0.995	2011	14
DPV	GCE/Pt-MnO ₂	3.9×10^{-4}	3.0×10^{-3} to 4.8×10^{-2}	0.989	2012	48
CV	CuHCF	2.2×10^{-3}	1.0×10^{-2} to 0.20		2013	49
Potentiostatic	CuHCF/Pt/ <i>n-n</i> -Si	6.2×10^{-6}	2.0×10^{-5} - 0.60	0.999	2013	50
Amperometric	Pt electrode modified with poly(3-methylthiophene)	1.32×10^{-5}	4.41×10^{-5} to 50.0	0.998	2014	This work

CONCLUSION AND RECOMMENDATION

P3MT film was successfully synthesized in methylene chloride solution for the determination of HQ. The statistical parameters and the recovery study data clearly indicate the reproducibility and accuracy of the method. The linear response range, LOD, and LOQ were found to be between 4.41×10^{-5} – 50.0 mM ($R^2 = 0.998$), 1.32×10^{-5} mM, and 4.41×10^{-5} mM at 0.50 V versus SCE, respectively. Good recovery values were obtained close to 100%, which indicate that the P3MT film can be applied very well in the analysis of this kind of real sample without significant influence of the matrix. Thus, this method can be adopted as a better alternative to the existing methods.

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