

Scientific paper

# Electrode Prepared with Combination of Different Conductive Polymers for Hydroquinone Determination in River Water

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## Abstract

Modified electrode based on combination of different conductive polymers (polyaniline – poly(3-methylthiophene) – poly(3,3'-diaminobenzidine) (PANI – P3MT – PDAB)) was previously synthesized in dichloromethane containing  $\text{HClO}_4$  and tetrabutylammoniumperchlorate (TBAP) as supporting electrolyte. Herein, the determination of hydroquinone (HQ) with amperometric I-t method over this modified and its homopolymers coated electrode was successfully carried out in river water as a real sample and in solution consisting of  $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$  (pH 2.0). For this method, potentials between 0.45 V and 0.65 V were applied and the best analytical response was obtained at 0.55 V using this modified electrode when compared to its homopolymers. The limit of detection (LOD), limit of quantification (LOQ), the linear dynamic range and regression coefficient ( $R^2$ ) were found as  $1.31 \times 10^{-4}$  mM,  $4.37 \times 10^{-4}$  mM,  $4.37 \times 10^{-4}$ –95.0 mM and 0.998, respectively. These results were compared to homopolymers coated and uncoated Pt electrodes. For checking on the accuracy of the developed method and the matrices interference, determination of HQ was performed in artificially contaminated river water samples with HQ concentration of 5.0 mM and 10.0 mM using this modified electrode and recovery values were calculated as 100.6% and 100.1%, respectively.

**Keywords:** Hydroquinone, Polyaniline, Poly(3-methylthiophene), Poly(3,3'-diaminobenzidine), Amperometric determination

## 1. Introduction

Phenols are aromatic organic compounds having one or more hydroxyl groups. They are natural products resulting from the decomposition of some plant and animal organisms. Phenols also have a similar structure to some extensively used pesticides that are resistant to biodegradation. Phenols can be found in ecosystem due to the used chemicals, from oil and pharmaceutical industries and are spread to ecosystem as a result of domestic and industrial waste.<sup>1</sup> Hydroquinone (1,4-dihydroxybenzene) (HQ) is a phenol derivative containing two hydroxyl groups and is an important organic compound commonly used in the pharmaceuticals, antioxidants, dye, and cosmetics industry.<sup>2–4</sup> Products containing HQ are used to decolorize the skin. Overexposure to HQ causes irritation, skin sensitization and also discoloration of the nails.<sup>5</sup> However, HQ is classified as an environmental pollutant because of the low degradability and high toxicity similar to

other phenolic compounds by international organizations such as the European Union legislation and the US Environmental Protection Agency.<sup>6</sup> Because of all these factors, determination of HQ is important. HQ is electroactive due to the presence of hydroxyl groups and can be analyzed electrochemically. HQ is usually oxidized to quinone by electrochemical oxidation and it can be determined based on the measurement of the resulting current by amperometric method. Nowadays, several analytical techniques, including high performance liquid chromatography, capillary electrochromatography, micellar chromatography and kinetic spectrophotometry are being replaced by inexpensive, rapid and reliable techniques such as electrochemical methods<sup>5</sup> which are the most advantageous because of their simplicity, rapidness and sensitivity.

Conductive polymers are widely used to prepare modified electrodes. Among various conducting polymers, polyaniline (PANI) has attracted attention because

of its properties such as the presence of various oxidation forms, electrical and optical activity, low cost and environmental stability. These features of PANI film permit its use in a variety of areas such as rechargeable batteries, sensors, electrochemical capacitors and electrochromic devices. In addition, PANI film has the ability to catalyze redox reactions of some inorganic ions and organic compounds.<sup>7,8</sup> PANI film can be synthesized by chemical and electrochemical polymerization of aniline monomer. Kavanoz et al. reported composite film of PANI with poly(vinylferrocenium) perchlorate on Pt electrode in dichloromethane medium.<sup>9</sup> Another widely used conductive polymer is poly(3-methylthiophene) (P3MT) that can be directly synthesized on electrode surface by electrochemical polymerization of 3-methylthiophene. Synthesis of P3MT for modification of electrodes were reported in acetonitrile,<sup>6,10</sup> dichloromethane,<sup>4</sup> chloroform<sup>11</sup> and aqueous solution<sup>12</sup> and prepared P3MT modified electrodes have shown electrocatalytic effect on riboflavin,<sup>13</sup> some phenolics<sup>14,15</sup> and dopamine.<sup>16</sup>

Although polymers of aromatic amines have been extensively studied,<sup>17</sup> studies related to polybenzidine and its derivatives have not been observed in the literature. Electrochemical polymerization of benzidine derivative of 3,3'-diaminobenzidine (DAB) has been studied in ethanol<sup>18</sup> and acidic solution.<sup>19,20</sup> Mulazımođlu reported PDAB polymerization on glassy carbon electrode (GCE) for determination of phenol in tap water samples.<sup>21</sup> Also, composite film of PDAB with poly(vinylferrocenium) perchlorate for HQ determination<sup>22</sup> and copolymer film with PANI and P3MT for determination of epinephrine were reported.<sup>23</sup>

In this study, we prepared a modified electrode by combination of conductive polymers such as PANI, P3MT and PDAB on Pt disc and used this modified electrode for amperometric determination of HQ in river water samples. Good analytical results (LOD, LOQ, the linear dynamic range and regression coefficient etc.), good repeatability and good recovery values without matrix effects were obtained.

## 2. Experimental

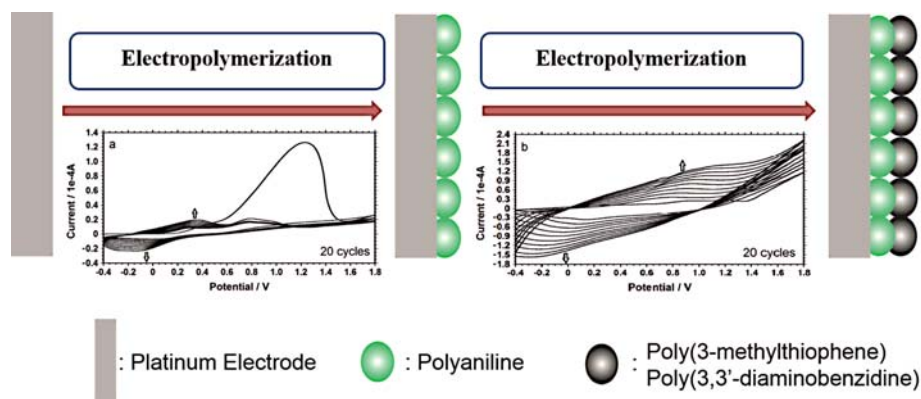
### 2. 1. Apparatus and Chemicals

Electrochemical studies were performed using an 1140B model CH Instruments system. The working cell has five inlets; three inlets were used for the electrodes: platinum disc as the working electrode; Pt spiral as the counter electrode; and Ag/AgCl (non-aqueous medium) and saturated calomel electrode (SCE) (aqueous medium) as the reference electrode. The other two inlets were used for nitrogen gas. Platinum discs (area =  $7.85 \times 10^{-3} \text{ cm}^2$ ) were used as working electrodes for cyclic voltammetry. These electrodes were cleaned with a slurry of  $\text{Cr}_2\text{O}_3$  in water, washed with distilled water, rinsed with dichloromethane and dried. All chemicals were of analytical grade and used without further purification. Electropolymerization in non-aqueous solution was performed in dichloromethane under nitrogen (Linde). TBAP used as a supporting electrolyte in non-aqueous media was obtained by the reaction of tetrabutylammoniumhydroxide (TBAOH) (40% aqueous solution, Sigma-Aldrich) with perchloric acid (BDH) and recrystallized in 1:9 (v:v) water and ethyl alcohol solution, dried at 120 °C under vacuum for 12 h and stored under nitrogen.<sup>24</sup> Buffer solutions (pH 1.0–6.5) were prepared by using  $\text{NaHSO}_4$  (Merck) and  $\text{Na}_2\text{SO}_4$  (Merck) for amperometric experiments in aqueous media. HQ solutions were prepared in the sulfate buffer solution (SBS, pH 2.0). Before electrochemical experiments, dissolved oxygen in HQ solution was removed using nitrogen (Linde).

## 3. Results and Discussion

### 3. 1. Preparation of PANI – P3MT- PDAB Film

As shown in Figure 1, in our previous work PANI – P3MT- PDAB film was synthesized on Pt disc electrode in dichloromethane solution layer by layer. Firstly, PANI



**Figure 1.** Voltammogram of the deposition and schematic representation of PANI – P3MT- PDAB film a) PANI film on Pt disc electrode b) P3MT – PDAB film deposited on PANI film.

films were potentiodynamically (between 1.80 V and  $-0.40$  V,  $-0.20$  V,  $0.0$  V and  $0.20$  V vs. Ag/AgCl (20 cycles)) deposited on Pt disc electrode in dichloromethane using polymerization solution containing 50.0 – 400 mM aniline monomer, 100 mM HClO<sub>4</sub> and 100 mM TBAP as supporting electrolyte. Then, on the PANI film, P3MT-PDAB films were potentiodynamically (between 1.80 V and  $-0.40$  V,  $-0.20$  V,  $0.0$  V and  $0.20$  V vs. Ag/AgCl (20 cycles)) synthesized in dichloromethane using polymerization solution containing both monomers (20.0 – 500 mM 3-methylthiophene and 1.0 mM 3,3'-diaminobenzidine) and 100 mM TBAP as supporting electrolyte. Cyclic voltammograms of these films deposited on the Pt disc electrode were obtained in methylene chloride containing only 0.10 M TBAP (blank solution) and peak currents and charge values of each film were compared. According to these results, the most electroactive PANI and P3MT films were obtained using 300 mM aniline and 500 mM 3-methylthiophene monomers, respectively (Figure 1a,b). Therefore, these monomer concentrations were determined as optimal in polymerization solutions. PANI and P3MT films have better electroactivity than PDAB film. The properties of PANI and P3MT films were enriched with regard to functional groups using PDAB film containing  $-NH_2$  groups without affecting the electroactivity or conductivity of the PANI and P3MT films. Consequently, low DAB monomer concentration (1.00 mM) was preferred for the preparation of modified electrode. Therefore, synthesized PANI – P3MT-PDAB film has better electroactivity and more active functional groups.<sup>25</sup>

### 3. 2. pH behavior of PANI – P3MT- PDAB Film

pH behavior of the PANI – P3MT – PDAB film was investigated in SBS (pH 1.0 – 6.5) in our previous study (Figure 2)<sup>25</sup> and the optimum pH value was determined as pH 2.0.

### 3. 3. Cyclic Voltammetric Behavior of Hydroquinone Over PANI – P3MT-PDAB Film

The pH 2.0 solution was used for the characterization of HQ behavior in aqueous medium over Pt disc electrode, coated with the PANI - P3MT - PDAB film. The cyclic voltammograms over uncoated Pt electrode (Figure 3A–D (c)), PANI, P3MT, PDAB homopolymer films and PANI - P3MT - PDAB film (Figure 3A–D(a)) in SBS (pH 2.0) containing 5.0 mM HQ were measured. Also, these voltammograms were compared with HQ-free solution over coated Pt electrodes (Figure 3A–D(b)). The oxidation and reduction peaks of HQ over uncoated Pt electrode at pH 2.0 were observed at about 0.58 V and 0.05 V, respectively (Figure 3A–D(c)). The oxidation peak of HQ over PDAB film decreased and shifted to lower potential (from about 0.58 V to about 0.45 V) (Figure 3C(a,c)). Furthermore, because of the limited electroactivity or conductivity of PDAB, the oxidation peak current of HQ recorded on an uncoated Pt electrode was higher than on PDAB coated electrode.<sup>25</sup> However, using PDAB in preparation of PANI – P3MT – PDAB modified electrode, the number of functional groups increased (the PDAB film contains many  $-NH$  and  $-NH_2$  functional groups) and this enrichment provided greater hold of HQ by hydrogen bonding on this electrode surface. Thus, the current values obtained using PANI, P3MT and PDAB coated Pt electrodes containing HQ (Figure 3A–C(a)) were higher than on coated electrode surfaces without HQ (Figure 3A,C(b)). When we compared the interactions of HQ with uncoated and coated Pt electrodes, the current values obtained over PANI - P3MT - PDAB coated Pt electrode at pH 2.0 solution containing 5.0 mM HQ were higher than in all other cases (PANI, P3MT and PDAB coated Pt electrodes at pH 2.0 both containing HQ and without HQ) (Figure 3D(a)). As a result, because modified film structure contains many  $-NH$ ,  $-N$  and  $-NH_2$  sites, HQ molecules can form hydrogen bonds at these sites that originate from PANI and PDAB.<sup>24,26</sup> In ad-

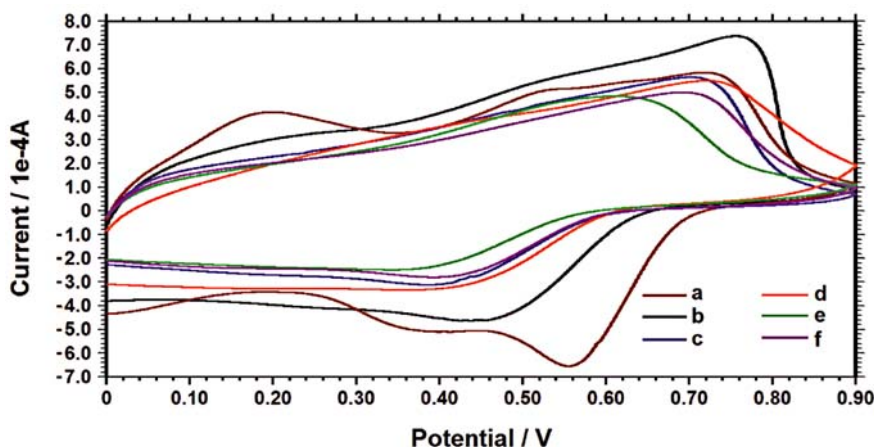
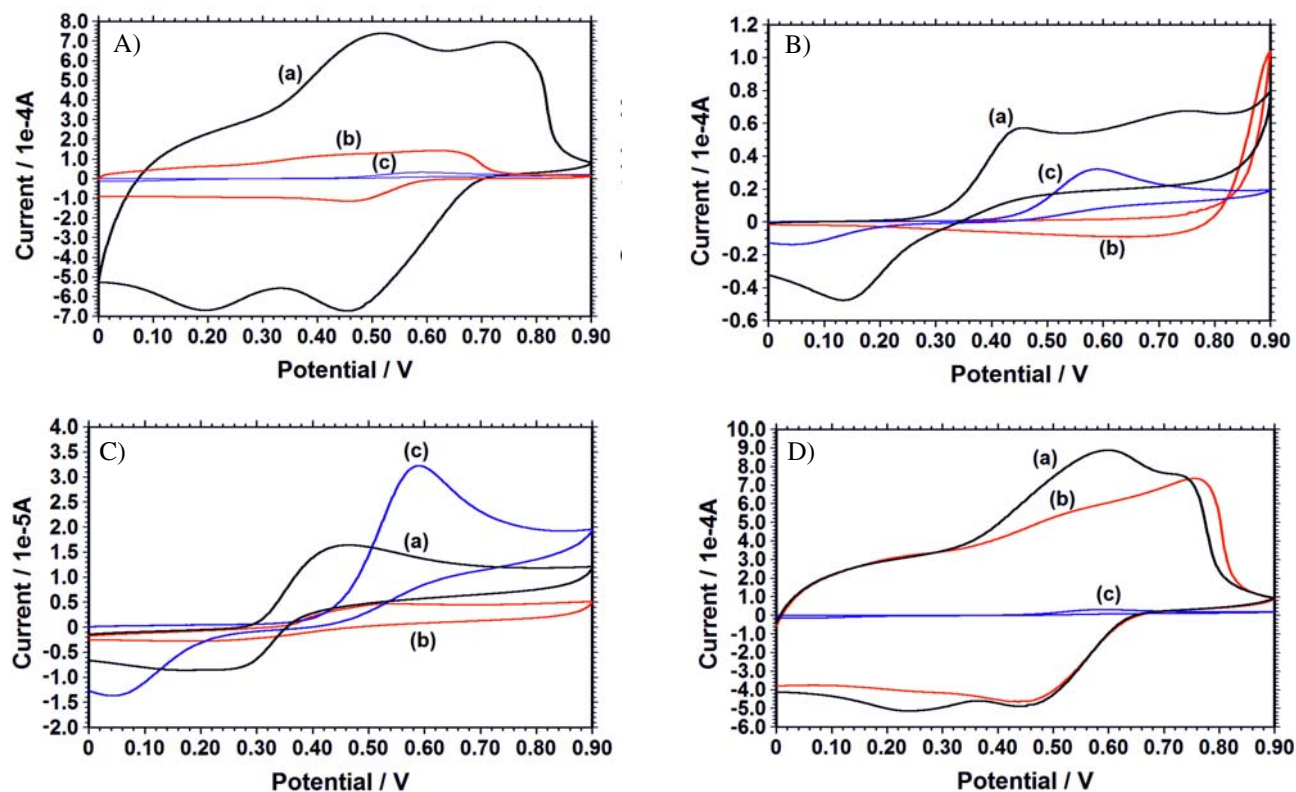


Figure 2. Electrochemical behavior of the PANI – P3MT – PDAB film in SBS at pH values of (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0, (e) 5.0, and (f) 6.5



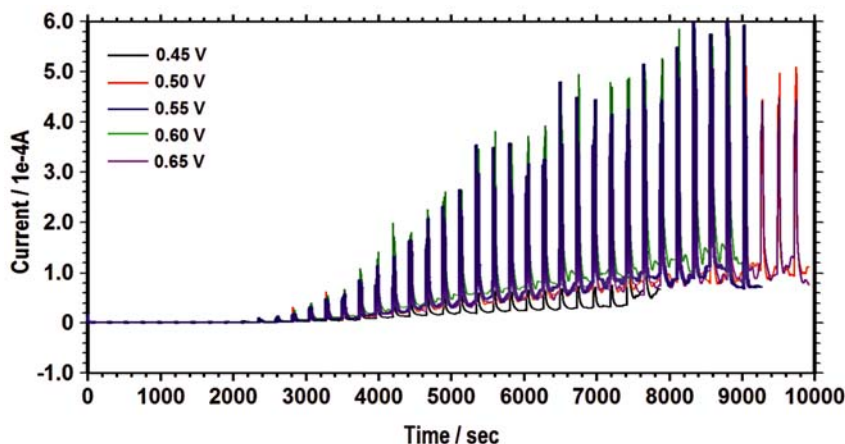
**Figure 3.** Cyclic voltammograms of (A) PANI, (B) P3MT, (C) PDAB, and (D) PANI-P3MT-PDAB coated electrodes of (a) sulfate buffer containing 5.0 mM HQ of the films, (b) sulfate buffer of the films, and (c) 5.00 mM HQ over uncoated Pt electrode ( $v = 100 \text{ mV s}^{-1}$ , vs. SCE)

dition, HQ molecules not only form hydrogen bonds but also cause reduction of PANI film<sup>24</sup> and provide continuous oxidation of HQ over synthesized film.

### 3. 4. Amperometric Determination of Hydroquinone

The PANI-P3MT-PDAB film deposited on Pt disc electrode that was enriched in terms of functional groups

was used for the determination of HQ in SBS (pH 2.0) and artificially contaminated river water samples with HQ by amperometric I-t method. The film was electrolyzed between 0.45 V and 0.65 V until steady-state current (about 1000 s) was reached in pH 2.0 solution vs SCE. After reaching the steady state of the film, first addition of HQ as  $9.77 \times 10^{-4} \text{ mM}$  was added from stock solution containing HQ dissolved in pH 2.0 solution. It was stirred for 30 s to ensure homogeneity and then the current values were recorded



**Figure 4.** Amperometric I-t curves recorded for determination of HQ over PANI – P3MT – PDAB coated Pt electrode at different potentials (0.45 V – 0.65 V, vs. SCE)

at the end of the 200 s period. Currents versus increasing concentrations of HQ were measured in a similar manner and amperometric I-t curve was recorded (Figure 4).

When compared to calibration graphs, the best analytical parameters were obtained at 0.55 V (Table 1). Therefore, the amperometric I-t response of the PANI-P3MT-PDAB film was compared with its homopolymer coated and uncoated Pt electrodes at 0.55 V (Figure 5a). The steady-state currents measured on these amperometric I-t curves were plotted against HQ concentration (Figure 5b) and calibration graphs were constructed using these values (Figure 5c). According to the Figure 5c, we obtained the highest currents when we used the PANI-P3MT-PDAB film. LOD, LOQ, linear dynamic range and  $R^2$  values were compared for PANI-P3MT-PDAB coated (between 0.45 and 0.65 V potentials), its homopolymer coated (0.55 V) and the uncoated platinum electrodes (0.55 V) in Table 1.

Table 1 shows the comparisons of analytical parameters for coated and uncoated Pt electrodes. 3s/m and 10s/m (s: standard deviation, m: slope) equations were used to calculate the LOD and LOQ values.<sup>4,25,27</sup> The parameter of “s” was calculated from the current values of the lowest concentration that generate a measurable current in three replicate measurements. As it is clear from the table, lower LOD value and wider linear range were obtained when the PANI-P3MT-PDAB coated electrode was used. It might be due to enrichment of PANI and P3MT film using PDAB film containing  $-NH_2$  groups. Advantage of  $-N$ ,  $-NH$  and  $-NH_2$  group containing modified electrode is the ability to form hydrogen bonds with  $-OH$  groups in HQ structure.

### 3. 5. Repeatability of the PANI-P3MT-PDAB Modified Electrode for Determination of Hydroquinone

Repeatability of current recorded from amperometric I-t curves (0.55 V) for HQ determination over PANI-P3MT-PDAB film deposited at optimum conditions on

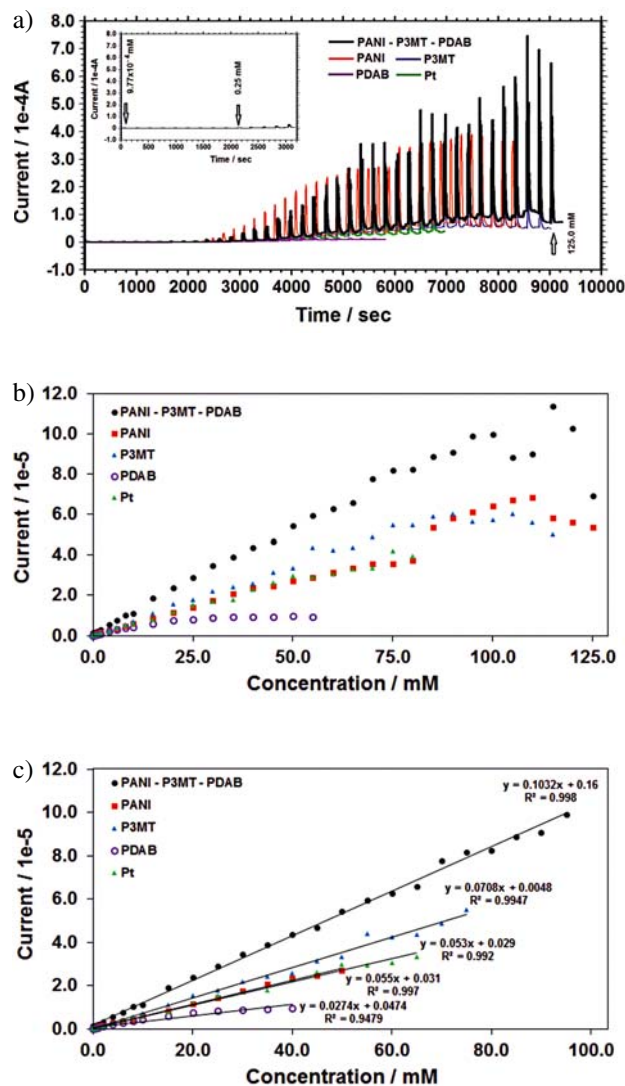


Figure 5. Determination of HQ ( $9.77 \times 10^{-4}$  – 125.0 mM) over uncoated and PANI, P3MT, PDAB, PANI-P3MT-PDAB coated Pt electrodes at 0.55 V a) Amperometric I-t curves recorded vs. SCE b) A plot of the steady-state currents measured from amperometric I-t curve vs. increasing HQ concentrations c) Calibration curves for linearity range of HQ concentrations.

Table 1. Comparison of analytical parameters over uncoated and coated Pt electrodes for the determination of HQ.

Applied Potential (V)	Electrode	LOD* (mM)	LOQ** (mM)	Linear Range (mM)	Equation	$R^{2***}$
0.45	PANI-P3MT-PDAB	$9.07 \times 10^{-4}$	$3.02 \times 10^{-3}$	$3.02 \times 10^{-3}$ – 50.0	$y = 0.038x - 0.021$	0.994
0.50	PANI-P3MT-PDAB	$1.62 \times 10^{-3}$	$5.41 \times 10^{-3}$	$5.41 \times 10^{-3}$ – 100.0	$y = 0.084x + 0.110$	0.998
0.55	PANI-P3MT-PDAB	$1.31 \times 10^{-4}$	$4.37 \times 10^{-4}$	$4.37 \times 10^{-4}$ – 95.0	$y = 0.103x + 0.159$	0.998
	P3MT	$1.27 \times 10^{-4}$	$4.24 \times 10^{-4}$	$4.24 \times 10^{-4}$ – 75.0	$y = 0.070x + 0.004$	0.994
	PANI	$6.57 \times 10^{-4}$	$2.19 \times 10^{-4}$	$2.19 \times 10^{-3}$ – 50.0	$y = 0.055x + 0.031$	0.997
	PDAB	$2.76 \times 10^{-4}$	$9.19 \times 10^{-4}$	$9.19 \times 10^{-4}$ – 40.0	$y = 0.027x + 0.047$	0.947
	Pt	$1.56 \times 10^{-4}$	$5.20 \times 10^{-4}$	$5.20 \times 10^{-4}$ – 65.0	$y = 0.053x + 0.029$	0.992
0.60	PANI-P3MT-PDAB	$2.76 \times 10^{-3}$	$9.23 \times 10^{-3}$	$9.23 \times 10^{-3}$ – 50.0	$y = 0.132x + 0.115$	0.997
0.65	PANI-P3MT-PDAB	$1.99 \times 10^{-3}$	$6.62 \times 10^{-3}$	$6.62 \times 10^{-3}$ – 70.0	$y = 0.083x + 0.085$	0.993

\* Limit of detection \*\*Limit of quantification \*\*\* Regression coefficient

Pt disc electrode<sup>25</sup> was tested by using at least three films for each measurement in SBS (pH 2.0) vs. SCE. For each concentration of HQ (1.0, 5.0, 10.0 and 20.0 mM), the obtained amperometric I-t curves, currents, standard deviations (s) of currents, percent relative standard deviation (% RSD) and confidence interval are shown in Table 2. Confidence interval was calculated to evaluate the precision using combined standard deviation ( $s_{\text{combined}}$ : 0.349  $\mu\text{A}$ ).

### 3. 6. Determination of HQ in Artificially Contaminated River Water Samples

To check for the accuracy of the improved modified electrode and to demonstrate the matrix interference, electrochemical response of HQ was investigated in artificially contaminated river water from Turkey. Before the experiments, the pH of river water was adjusted to optimum working pH (2.0) with HCl solution and it was artificially contaminated by the addition of HQ. As previ-

**Table 2.** Assessment of reliability of the results obtained from repeatability experiments for the determination of HQ over PANI-P3MT-PDAB modified electrode

$C_{\text{HQ}}$ (mM)	Amperometric I-t Curves	I/ $\mu\text{A}$	S/ $\mu\text{A}$	% RSD	$[\bar{x} \pm \frac{ts}{\sqrt{N}}]^*$ / $\mu\text{A}$
1.00		1.903 1.854 1.845	0.031	1.671	$1.867 \pm 0.077^{**}$ $1.867 \pm 0.866^{***}$
5.00		8.351 7.907 8.361	0.259	3.15	$8.206 \pm 0.643^{**}$ $8.206 \pm 0.866^{***}$
10.0		14.90 14.30 13.81	0.545	3.80	$14.33 \pm 1.353^{**}$ $14.33 \pm 0.866^{***}$
20.0		26.16 26.69 26.82	0.349	1.316	$26.55 \pm 0.866^{**}$ $26.55 \pm 0.866^{***}$

\* 95% confidence level was calculated.

Confidence intervals were calculated using standard deviations \*\* group \*\*\* combined.

ously described, amperometric I-t method was used for the determination of HQ in this solution. At optimum conditions (0.55 V), the PANI-P3MT-PDAB film was electrolyzed for about 1000 s (pH 2.0) to reach stability and then river water samples containing HQ (5.0 and 10.0 mM) were added and currents were measured. These results were compared to the standard HQ (5.0 and 10 mM) currents (Table 2), and then, the percentage of the recovery values was calculated. As seen in Table 3, there is no influence of the matrices for the determination of HQ in river water samples.

**Table 3.** Recoveries for determination of HQ in artificially contaminated river water from Turkey.

Samples	Added ( $C_{\text{HQ}}/\text{mM}$ )	Found ( $C_{\text{HQ}}/\text{mM}$ )	Recovery (%)
1	5.00	5.03	100.6
2	10.0	10.1	100.1

**Table 4.** Comparison of the improved method with the other modified electrodes for determination of HQ

Electrochemical method	Used Modified Electrode	LOD (mM)	Linearity Range (mM)	Reference
Differential Pulse Voltammetry	poly(p-aminobenzoic acid) modified glassy carbon electrode	$4.0 \times 10^{-4}$	$1.2 \times 10^{-3} - 0.6$	28
Differential Pulse Voltammetry	PEDOT/CNT/CPE	$3.0 \times 10^{-4}$	$1.10 \times 10^{-3} - 0.125$	29
Cyclic voltammetry	Poly(phenylalanine) Modified Glassy Carbon Electrode	$7.0 \times 10^{-4}$	0.010 – 0.14	30
Differential Pulse Voltammetry	Poly(glutamic acid) Modified Glassy Carbon Electrode	$1.0 \times 10^{-3}$	$5.0 \times 10^{-3} - 0.08$	31
Square wave voltammetry	Immobilization of gilo ( <i>Solanum gilo</i> ) crude extract in the chitosan biopolymer	$2.0 \times 10^{-3}$	0.250 – 5.50	32
Amperometry	PANI – P3MT – PDAB on Pt electrode	$1.31 \times 10^{-4}$	$4.37 \times 10^{-4} - 95.0$	This work

The obtained results were compared with other electrochemical methods<sup>28–32</sup> in Table 4. The PANI-P3MT-PDAB modified electrode displays better parameters such as lower LOD value and longer linear range in terms of analytical performance than the other modified electrodes. These might be due to enrichment of properties of the PANI-P3MT-PDAB film by combining the catalytic effects of each homopolymer and functional groups (-N, -NH, -NH<sub>2</sub>) of PDAB and PANI. Advantage of this modified electrode is the ability to form hydrogen bonds with -OH groups in HQ structure.

## 4. Conclusion and Recommendation

The PANI-P3MT-PDAB modified electrode deposited with combination of different conductive polymers using aniline, 3-methylthiophene, 3,3'-diaminobenzidine monomers on Pt disc electrode was successfully used for the

determination of HQ using amperometric I-t method and results of its homopolymers coated and uncoated Pt electrodes were compared. The validation parameters (LOD, LOQ and the linear dynamic range) of the PANI-P3MT-PDAB modified electrode were found as  $1.31 \times 10^{-4}$  mM,  $4.37 \times 10^{-4}$  mM and  $4.37 \times 10^{-4} - 95.0$  mM, respectively. Assessment of reliability of the results obtained from repeatability experiments has shown satisfactory statistical results: standard deviations between 0.031 and 0.545; RSD between 1.316 and 3.80%. Matrix interference on the HQ determination was investigated in artificially contaminated river water from Turkey. Recovery values were found as 100.6% and 100.1%, respectively. Consequently, the developed method is found to be usable, simple and rapid.

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## Povzetek

V diklorometanu, ki je vseboval HClO<sub>4</sub> in tetrabutylamonijev perklorat (TBAP) kot podporni elektrolit, smo sintetizirali modificirano elektrodo, osnovano na kombinaciji različnih prevodnih polimerov (polianilin – poli(3-metiltofien) – poli(3,3'-diaminobenzidin) (PANI – P3MT – PDAB)). Zatem smo uspešno izvedli določitev hidrokinona (HQ) z amperometrično I-t metodo na tej modificirani elektrodi in na elektrodah, prevlečenih s homopolimeri. Določitev smo izvedli v rečni vodi kot realnem vzorcu in v raztopini NaHSO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> (pH 2,0). Uporabili smo potenciale med 0,45 V in 0,65 V ter z modificirano elektrodo v primerjavi z njenimi homopolimeri dobili najboljši analizni odgovor pri 0,55 V. Meja zaznave (LOD) je bila 1,31 × 10<sup>-4</sup> mM, meja določitve (LOQ) 4,37 × 10<sup>-4</sup> mM, linearno dinamično območje 4,37 × 10<sup>-4</sup>–95,0 mM in regresijski koeficient (R<sup>2</sup>) 0,998. Te rezultate smo primerjali z rezultati za elektrode, prevlečene s homopolimeri, in za neprevlečene Pt elektrode. Za preverjanje točnosti razvite in interferenc matrice smo izvedli določitev HQ z modificirano elektrodo v umetno onesnaženih vzorcih rečne vode s koncentracijo HQ 5,0 mM in 10,0 mM. Izkoristki so bili 100,6% in 100,1%.