

Non-Enzymatic Phenol Determination in River Water Over Modified Electrode with Poly(3-methylthiophene)

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ABSTRACT

This paper describes non-enzymatic phenol determination using poly(3-methylthiophene) coated Pt electrode. Modified electrode was prepared on Pt disc surface in dichloromethane medium containing 500 mM 3-methylthiophene (3MT) and 100 mM tetrabutylammonium perchlorate (TBAP). This electrode was used for amperometric determination of phenol in $\text{NaHSO}_4 / \text{Na}_2\text{SO}_4$ (SBS) solution at pH 2.0. For this purpose, 0.70, 0.80 and 0.90 V potentials were applied and results were compared. Limit of detection and linear range were found as 4.22×10^{-5} and $1.41 \times 10^{-4} - 4.00$ mM (with $R^2=0.9932$) at 0.90 V working potential, respectively. Repeatability of method was tested by using at least three modified electrode for 0.5, 1.0 and 2.0 mM phenol concentrations and relative standard deviation (RSD) were found as 2.49%, 1.92% and 2.75%, respectively. To test the accuracy of method and matrix effect, phenol determination was carried out for 1.0 and 2.0 mM phenol concentrations in artificially contaminated river water samples at optimum condition and recovery values were found as 96.44% and 99.60%, respectively. Proposed method was found as simple, rapid and economic for phenol determination.

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Phenol, Poly(3-methylthiophene), amperometric determination, non-enzymatic.

INTRODUCTION

Phenol is the simplest compound of benzene, and the main structure of phenolic compounds like hydroquinone and catechol. Phenol and its chemical derivatives are widely used in industrial area such as pharmaceutical drugs, cosmetic, pesticides, textile, dyes and petroleum refineries [1,2]. Phenol is released to the environment during its production, its use in phenolic resins, and organic synthesis [3]. Phenol is found in petroleum products, and it can be released by combustion of wood and auto exhaust [3]. Phenol is also released by the natural corruption of organic wastes including benzene. Phenol is a major metabolite of benzene [4], which is found widely in the environment, therefore, phenol may be occurred in the environment as a result of the natural corruption of benzene. Phenol and its vapors are toxic, and may give rise to harmful effects on the central nervous system and heart. Because of its toxicity and resistance to common microorganisms, detection of phenol is important in the environment [5]. A number of chromatographic [6,7] and spectrophotometric

[8] studies were reported for detection of phenol. However, these methods require sample preparation, expensive equipment and long analysis time. To overcome these problems, and for low-cost, simple and rapid determination of phenol, electrochemical methods attract attention. Especially, amperometric analysis based on modified electrode coated with conductive polymers [9], composite films [10,11], nanoparticles [12,13] and biosensors [14,15] is widely used for detection of phenol and its derivatives. .

Conductive polymer-based modified electrodes can easily be prepared on direct electrode surface by electrochemical methods. Poly (3-methylthiophene) (P3MT) is widely used conductive polymer for preparation of modified electrode. It was reported that P3MT was electrochemically synthesized on solid substrate material (Pt, Au, Glassy carbon) [16]. It was stated that P3MT films had electrocatalytic effect on phenolic compounds [17] and detection of phenolic compounds which using P3MT coated

electrodes give better responses compared to with bare electrodes [18]. P3MT-based modified electrode is used for detection of phenolic compounds due to its electronic [19] and optical properties, thermal stability [20], and electrocatalytic effect [17]. P3MT and its derivatives were electrochemically synthesized in dichloromethane [21], acetonitrile and acetonitrile-containing ferro sulfonic acid [22,23], chloroform [24] and perchloric acid solution [25]. Some studies were reported that P3MT-coated modified electrodes were used for determination of some phenolic compounds [26,27], riboflavin [28] and dopamine [17]. Also, polyaniline - poly(3-methylthiophene)-poly(3,3'-diaminobenzidine) (PANI - P3MT - PDAB) film for detection of dopamine [29], epinephrine [30] and PDAB - P3MT film for detection of catechol [31] were reported.

In a previous study, P3MT was synthesized in polymerization solution containing 500 mM 3MT and 100 mM TBAP [22] on Pt disc electrode in dichloromethane. In present study, this electrode was used for non-enzymatic phenol detection in SBS solution at pH 2.0 using amperometric I-t method. Also, real sample experiments in artificially contaminated river water samples were performed. Recovery values were calculated from the results of these studies.

MATERIAL AND METHODS

Reagent

3-methylthiophene monomer and phenol were purchased from Aldrich and Merck companies, respectively, and used without further purification. Electro-polymerization studies were carried out in dichloromethane medium containing TBAP as supporting electrolyte. TBAP was synthesized as mentioned in the literature [10]. Aqueous media studies were performed in sodium hydrogen sulfate (NaHSO_4) (Merck) and sodium sulfate (Na_2SO_4) (Merck) solution (SBS) of pH 2.0. Phenol solution was prepared in this solution at pH 2.0. All experiments were carried out in nitrogen atmosphere (Linde). Spiked sample assay was done for artificially contaminated river water samples with phenol. Before the experiment river water was adjusted to pH 2.0 by adding HCl.

Apparatus

All electrochemical experiments were performed with CH Instruments system, Model 1140B electrochemical analyzer. Conventional three-electrode electrochemical cell with Pt disc (area = $7.85 \times 10^{-3} \text{ cm}^2$) as working electrode, Pt wire as counter electrode and Ag/AgCl (for non-aqueous assay), and saturated calomel electrode (SCE) (for aqueous assay) as reference electrode were used. Before the experiments, Pt disc electrode was

cleaned with slurry of Cr_2O_3 with water, rinsed with triple distilled water, cleaned in the ultrasonic bath, washed with dichloromethane solution, and dried, respectively. All experiments were carried out in room temperature.

RESULTS AND DISCUSSION

Electrode preparation

In a previous study, P3MT was coated on Pt disc working electrode (P3MT/Pt) in dichloromethane medium containing 500 mM 3MT and 100 mM TBAP between -0.4V and 1.8V potential range vs. Ag/AgCl reference electrode (20 cycles) and washed with dichloromethane to remove the non-polymeric species [21]. In the present study, as prepared modified electrode was used for amperometric detection of phenol in SBS solution of pH 2.0 and river water artificially contaminated with phenol was used as analyte.

Electrochemical behavior of phenol over P3MT/Pt electrode

pH effect on modified electrode was investigated in SBS solution (pH 2.0 - 6.5) between 0.0 V and 0.9 V potential range vs. SCE. pH value in which the film has the most electroactivity was determined as 2.0. Therefore, electrochemical behavior of phenol was performed at pH 2.0 solution containing 5.0 mM phenol and results were compared with those of bare Pt electrode. Despite the oxidation potential of phenol was observed at about 0.87 V over bare Pt electrode (curve a), onset oxidation potential was measured at about 0.60 V over P3MT/Pt electrode (curve c) (Figure 1). Shifting the potential to smaller value is evidence of catalytic effect of P3MT film on Pt surface for the oxidation of phenol. Also, current value obtained over P3MT/Pt electrode in at pH 2.0 solution containing phenol is greater than obtained over bare Pt electrode. This can be explained with the fact that the interaction of P3MT film with phenol is greater than bare Pt electrode because of porous structure of the P3MT film [32].

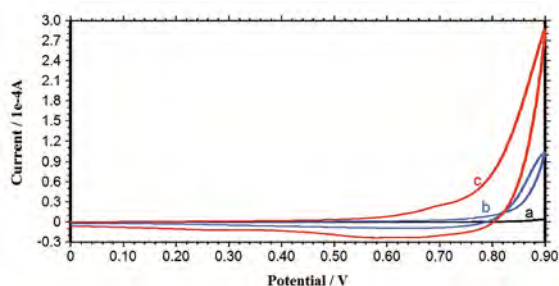


Figure 1. The cyclic voltammograms of (a) bare Pt electrode containing 5.0 mM phenol, (b) P3MT/Pt electrode and phenol free solution, (c) P3MT/Pt electrode containing 5.0 mM phenol in SBS solution at pH 2.0 (vs. SCE, $v = 100 \text{ mV s}^{-1}$)

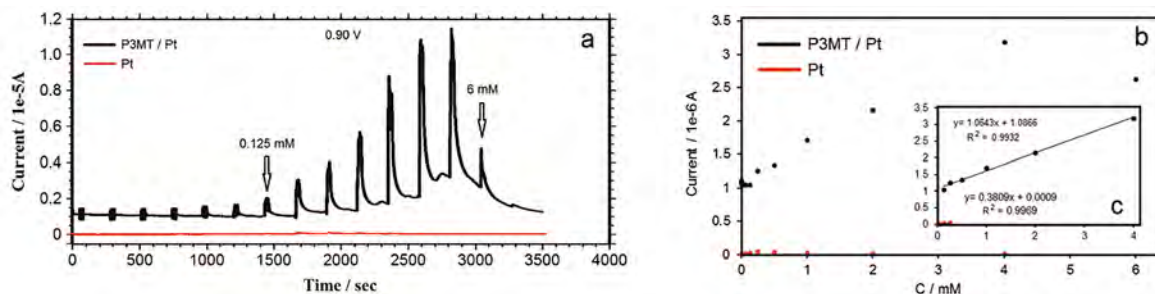


Figure 2. a) The current versus time curve for coated P3MT and uncoated Pt electrodes at 9.77×10^{-4} - 6.0 mM phenol concentration range b) current values versus phenol concentration and c) calibration graph (applied potential 0.90 V vs. SCE).

Amperometric phenol determination

For determination of phenol with amperometric I-t method in SBS of pH 2.0, P3MT film coated on Pt disc electrode between -0.4 V and 1.8 V potential was used. Initially, 0.70, 0.80 and 0.90 V potentials were separately applied on P3MT/Pt electrode about 1000 s to obtain steady-state current value. Afterwards, sufficient volume of stock phenol solution was added to attain the phenol concentration of 9.77×10^{-4} mM and the solution was stirred to obtain homogeneity. A typical current-time response was recorded with the successive addition stock phenol solution to the SBS solution for each potential and 0.90 V was determined as an optimum potential in which the maximum currents obtained. Figure 2 shows the amperometric I-t curves for an applied potential of 0.90 V (Figure 2a), current versus phenol concentration (Figure 2b) and calibration curves in linear scale (Figure 2c). In addition, same experiments were performed over uncoated Pt electrode and results were compared in Figure 2 (red). As seen in Figure 2a, current values increased as linearly until 4.0 mM phenol concentration. Over this concentration, the current values started to decrease. Limit of detection (LOD), limit of quantification (LOQ) and linear range values for P3MT/Pt electrode were calculated as 4.22×10^{-5} , 1.41×10^{-4} and 1.41×10^{-4} - 4.0 mM, respectively. 3 s/m and 10s/m equations were utilized for calculating of LOD and LOQ values [33] where s symbolizes the standard deviation calculated from the current values at the lowest concentration that generates a measurable current for three replicated measurements. Analytic parameters of different potentials over P3MT/Pt

and bare Pt electrode were summarized in Table 1.

Also, amperometric determination of phenol over P3MT/Pt electrode at optimum potential, and different pH solutions (2.0-6.5) was carried out. Typical current-time response was shown in Figure 3 (a) and it can be seen that results of pH 2.0 and pH 3.0 is competitive with each other. Therefore, response curve vs. phenol concentration obtained from amperometric I-t curve of pH 2.0 and pH 3.0 media and calibration graphs were compared in Figure 3 (b,c). According to Figure 3 (c), linear range obtained at pH 2.0 was longer than that of pH 3.0.

Repeatability studies

Repeatability of current values P3MT modified Pt electrode was investigated at pH 2.0 solution. Steady-state current values at the end of 200 s were recorded for each 0.50, 1.0 and 2.0 mM phenol concentrations after the electrolysis of P3MT/Pt electrode about 1600 s at 0.90 V. The results of repeatability experiment (amperometric I-t curves, current values, standard deviations, relative standard deviations and confidence intervals in 95% confidence level) for each phenol concentrations were shown in Table 2. To assess the accuracy, combined standard deviation was calculated as 0.1618 μ A using current values and it was used for calculating confidence interval. Standard deviations within the group were low and percent relative standard deviations were lower than 5% (Table 2). In addition, current values were close to each other in the group and they increased in proportion

Table 1. Analytic parameters for determination of phenol at different potentials over P3MT/Pt and bare Pt electrode

Applied Potential (V)	Electrode	LOD, (mM)	LOQ (mM)	Linear range (mM)	Equation	R ²
0.70	P3MT	2.69×10^{-4}	8.96×10^{-4}	8.96×10^{-4} - 20.0	$y = 0.0368x + 0.2601$	0.9847
	Pt	1.99×10^{-3}	6.64×10^{-3}	6.64×10^{-3} - 35.0	$y = 0.0005x + 0.0008$	0.9965
0.80	P3MT	1.44×10^{-5}	4.81×10^{-5}	4.81×10^{-5} - 1.0	$y = 0.7407x + 0.5136$	0.9781
	Pt	3.15×10^{-4}	1.05×10^{-3}	1.05×10^{-3} - 4.0	$y = 0.0122x + 0.0269$	0.9530
0.90	P3MT	4.22×10^{-5}	1.41×10^{-4}	1.41×10^{-4} - 4.0	$y = 1.0643x + 1.0866$	0.9932
	Pt	1.18×10^{-5}	3.94×10^{-5}	3.94×10^{-5} - 0.25	$y = 0.3809x + 0.0009$	0.9965

Table 2. Evaluation of the reliability of the results found from the repeatability experiment for detection of phenol over P3MT/Pt electrode.

C_{Phenol} (mM)	Amperometric I-t Curve	I μA	S μA	RSD %	$[\bar{X} \pm \frac{ts}{\sqrt{N}}]^{*,**}$ μA
0.50		1.650 1.681 1.600	0.0409	2.486	1.644±0.401
1.00		2.101 2.180 2.161	0.0412	1.920	2.147±0.401
2.00		2.782 2.641 2.756	0.0750	2.752	2.726±0.401

*95% confidence level was calculated.

**Confidence intervals were calculated using combined standard deviations.

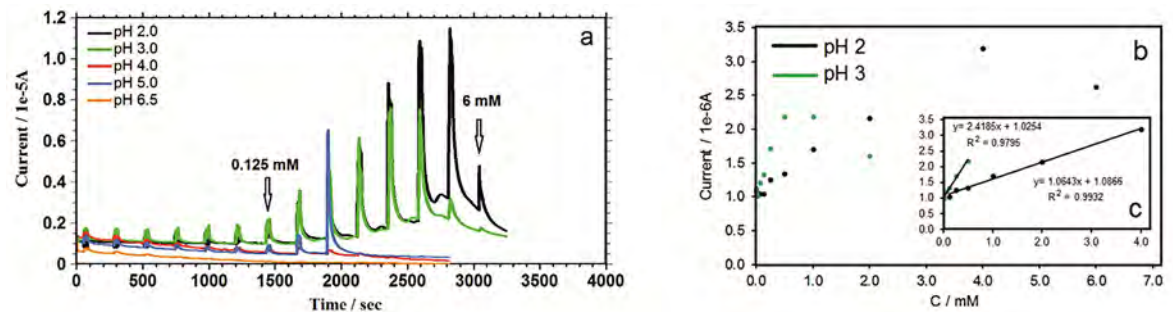


Figure 3. Calibration studies of phenol over P3MT/Pt electrode (a) Current-time responses for different pH values (b) current vs. phenol concentration for pH values of 2.0 and 3.0 (c) calibration graphs for pH 2.0 and pH 3.0 (applied potential 0.90 V vs. SCE).

to the concentration. These results supported the repeatability of the P3MT/Pt electrode.

Determination of phenol over P3MT/Pt electrode in artificially contaminated river water

In order to test applicability and matrix effect, detection of phenol over P3MT/Pt electrode was carried out in artificially contaminated river water in Rize, Turkey. Three samples were measured using three independently deposited electrodes. P3MT/Pt electrode prepared at optimum conditions was tested in spiked samples as described above for 1.0 and 2.0 mM phenol concentrations

and results were compared with standard 1.0 and 2.0 mM phenol concentrations (Table 2) and recovery values were calculated as 96.44% and 99.60%, respectively. Recovery values which are close to 100 % showed that the values obtained by the proposed P3MT/Pt electrode were in good agreement with the standard solutions. It is understood that the present electrode had great potential for practical application for the analysis in spiked samples.

Finally, obtained results were compared with previous studies. It was seen in Table 4, presented surface had better parameters compared to other modified electrode. Proposed

Table 3. Recovery results in artificially contaminated river water for phenol detection.

Samples	Added (C_{phenol}/mM)	Found (C_{phenol}/mM)	Recovery (%)
1	1.00	0.96	96.44
2	2.00	1.99	99.60

method was found simple, rapid and highly sensitive for phenol. Also, another advantage of the electrode was that it did not contain enzyme. This allows a lower-cost phenol determination.

CONCLUSION

Present study reported deposition of P3MT on Pt disc surface in dichloromethane solution for determination of phenol. Non-enzymatic phenol detection was successfully carried out in NaHSO₄ / Na₂SO₄ solution (at pH 2.0) applying 0.70, 0.80 and 0.90 V potentials. LOD, LOQ and linear range were found as 4.22×10^{-5} , 1.41×10^{-4} and 1.41×10^{-4} - 4.0 mM, respectively over the P3MT/Pt electrode. Also, to test availability for practical application, this electrode was used in artificially contaminated river water from Rize, Turkey and recovery values for 1.0 and 2.0 mM phenol concentrations were found as 96.44% and 99.60%, respectively. Proposed method was found simple, rapid, sensitive and low-cost for determination of phenol.

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Table 4. Comparison of the analytical performance for the detection of phenol

Method	Electrode	LOD (mM ²)	Linear Range (mM)	R ²	Reference
Amperometry	Copper phtalocyanine and histidine on CPE	2.9×10^{-2}	0.040–0.350	-	[35]
Amperometry	HRP immobilised on silica gel modified with titanium oxide.	1×10^{-3}	1.0×10^{-2} – 5.0×10^{-2}	0.999	[36]
Amperometry	Tyrosinase immobilization on PAPCP/ITO	9×10^{-4}	1.8×10^{-3} –0.17	-	[37]
Amperometry	tyrosinase entrapped in polyacrylamide microgels	1.4×10^{-3}	5×10^{-3} – 2.2×10^{-2}	0.999	[38]
Amperometry	Con A and HRP thin films on a thiol–modified gold electrode	2×10^{-4}	7.6×10^{-3} – 6.84×10^{-2}	0.999	[39]
Amperometry	P3MT/Pt	4.22×10^{-5}	1.41×10^{-4} –4.0	0.993	This work

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