Electroanalysis of Pyrocatechol in River Water Over Pt Electrode Modified with Polyaniline-Poly(3-methylthiophene)-Poly(3,3′-diaminobenzidine) Film

Polianilin-Poli(3-metiltiyofen)-Poli(3,3′-diaminobenzidin) Filmi ile Modifiye Edilmiş Pt Elektrot ile Nehir Suyunda Pirokatekolün Elektroanalizi

Research Article

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ABSTRACT

Determination of pyrocatechol was successfully achieved over polyaniline - poly(3-methylthiophene) - poly(3,3′-diaminobenzidine) (PANI - P_3MT - PDAB) coated Pt disc electrode using amperometric I-t method in $NaHSO_4/Na_2SO_4$ (SBS) (pH 2.0) solution. The potential range of 0.45 V-0.65 V were implemented and a potential of 0.50 V was found to be an optimum potential. Analytical parameters (LOD, LOQ and linear range) were 7.37×10^{-5}, 2.47×10^{-4} and 2.47×10^{-4}-25.0 mmol.L^{-1}, respectively. Furthermore, assay of pyrocatechol was performed in artificially contaminated river water samples over modified electrode at the pyrocatechol concentrations of 5.0 and 10.0 mmol.L^{-1} to check on the matrices interference and accuracy of the developed method. Recovery values were 101.1% and 101.2%, respectively. Without matrix effect, determination of pyrocatechol at lower peak potential (0.50 V) than oxidation peak potential (0.62 V) was carried out.

Key Words
Polyaniline, pyrocatechol, poly(3-methylthiophene), poly(3,3′-diaminobenzidine).

ÖZET

$NaHSO_4/Na_2SO_4$ (SBS) (pH 2.0) çözeltisi içerisinde amperometrik I-t yöntemi kullanılarak polianilin-poli(3-metiltiyofen)-poli(3,3′-diaminobenzidin) (PANI - P_3MT - PDAB) kaplı Pt disk elektrot üzerinden pirokatekol tayini başarılı bir şekilde gerçekleştirildi. 0,45 V–0,65 V aralığında potansiyel değerleri uygulandı ve 0.50 V optimum potansiyel olarak belirlendi. Analitik parametreler (gözlenebilme sınırı, alt tayin sınırı ve doğrusal çalışma aralığı) sırasıyla 7.37×10^{-5}, 2.47×10^{-4} ve 2.47×10^{-4}-25.0 mmol.L^{-1} olarak bulundu. Ayrıca, matriks girişimini ve geliştirilen yöntemin doğruluğunu test etmek için, pirokatekol derişimi 5.0 ve 10.0 mmol.L^{-1} olacak şekilde yapay olarak kirletilmiş nehir sularında pirokatakol tayini gerçekleştirildi. Geri kazanım değerleri sırasıyla % 101.1 ve % 101.2, olarak elde edildi. Pirokatekolün yükseltgenme potansiyelinden (0.62 V) daha düşük potansiyelde (0.50 V) matriks etkisi olmaksızın pirokatakol tayini gerçekleştirildi.

Anahtar Kelimeler
Polianilin, pirokatekol, poli(3-metiltiyofen), poli(3,3′-diaminobenzidin).

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INTRODUCTION

Pyrocatechol, also known as 1,2-dihydroxy benzene is an ortho isomer of dihydroxy benzenes. Pyrocatechol is a derivative of phenolic compounds used in the dye, pesticides, tanning, petrochemical and pharmaceutical industries [1, 2]. Because of this, it is given as industrial waste into the environment. Pyrocatechol is an important contaminant because of low degradability and high toxicity. Due to the major concern of growing environmental pollution, there is a lot of studies in the development of fast and reliable determination of pyrocatechol in samples environments, nutrients, medicines and industrial products [3].

Pyrocatechol and phenolic compounds can be determined by gas chromatography, liquid chromatography, capillary electrophoresis, spectrophotometry and electrochemical methods [4-7]. Among them, electrochemical methods are preferred because of low cost, rapidness, simplicity and not needed pre-treatment for examples [8]. As an electroactive substance, pyrocatechol can be analyzed electrochemically because of the presence of hydroxyl groups in the structure. Especially, modified electrodes were used for amperometric determination of pyrocatechol, which is based on measuring the resulting current following electrochemical oxidation reaction of catechol to quinone. Another advantage of amperometric determination is availability better analytical performances such as low detection limits, wide linear response range [9].

Modified electrode can be prepared directly polymerization of the molecule onto electrode. For this, conductive polymers are widely used for preparing modified electrode. Due to optical activity, low cost and environmental stability, polyaniline (PANI) and poly(3-methylthiophene) (P_3MT) modified electrodes were performed with electropolymerization of aniline and 3-methylthiophene monomers in different solution for determination of phenolic compounds. Kavanoz et al. reported synthesis of PANI composite film with Poly(vinilyferrocenium) perchlorate in dichloromethane solution to determine hydroquinone [10]. Tan et al. described a catechol biosensor based on the immobilization of polyphenol oxidase (PPO) into PANI deposited GCE [11]. Also, there are studies using P_3MT modified electrode for sensitive determination of phenolic compounds. Zhang et al. reported determination of catechol using dual-band P_3MT electrode by flow-injection amperometry [12]. In another study, P_3MT was deposited on Pt disc electrode in dichloromethane solution for determination of hydroquinone and it was stated that low detection limit and wide linear range were obtained [13].

Benzidine derivatives including two amine group, like 3,3′-diaminobenzidine (DAB), can be used for preparing modified electrode on different electrode surface. Several studies were reported polymerization of DAB in aqueous [14] and some organic solvents [15, 16]. Mulazımoğlu et al. developed a new GC electrode coated with Poly(3,3′-diaminobenzidine) (PDAB) in acetonitrile solution for phenol detection from tap water samples [15]. DAB polymerization was reported in acidic solution on different electrode surface (Pt, Au, GCE) [14]. Nateghi stated polymerization of DAB in ethanol for determination of Se (IV) [16]. Also, a composite film of DAB with electron transfer mediator polyvinylferrocene was reported in dichloromethane solution for determination of hydroquinone [17].

In a previous study, PANI - P_3MT - PDAB film was synthesized on Pt surface layer by layer in dichloromethane solution (CH_2Cl_2) and was characterized. Cyclic voltammetry, UV-vis, FT-IR, SEM and EDAX methods were used for characterization of this film [18]. Also, this synthesized surface was used for detection of epinephrine [19]. In this study, it was carried out amperometric detection of pyrocatechol using PANI - P_3MT - PDAB coated surface in Na_2SO_4-$NaHSO_4$ (SBS) (pH 2.0) solution. Also, repeatability of modified electrode and real sample assays in spiked river sample were performed. Recovery values were calculated from the results of these studies.

EXPERIMENTAL

Apparatus and Chemicals

All electrochemical studies were carried out using CHI Instruments system (1140B model). The working electrodes were a Pt disc (area = 7.85×10^{-3}

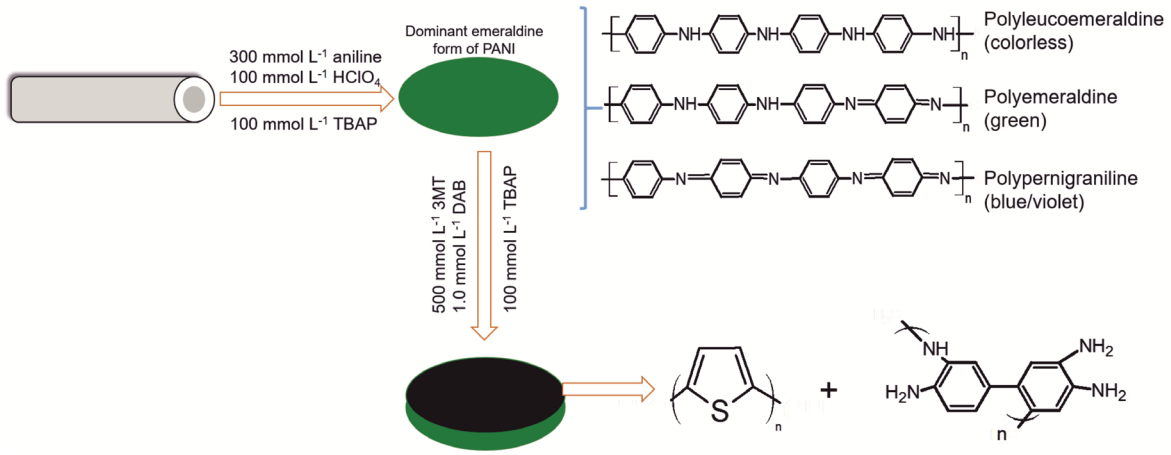


Figure 1. Schematic representation of the preparation of modified electrode.

cm^2) and Pt macroelectrode (area = 1.0 cm^2). The counter electrode a Pt wire electrode. Ag/AgCl and saturated calomel electrode (SCE) were used as reference electrode for non-aqueous medium and aqueous medium, respectively. Preparation of tetrabuthylammonium perchlorate (TBAP) as a supporting electrolyte and cleaning of electrodes were carried out as mentioned in the literature [10]. CH_2Cl_2 solvent was used for electropolymerization studies. For characterization of synthesized modified surface, FT-IR (Perkin Elmer Spectrum 100 spectrometer), UV-vis spectra (Perkin Elmer Lambda 35 spectrometer), Scanning electron microscopic (SEM) (FEG Quanta 450) and EDAX (Bruker EDS) were used [18]. Analytical grade chemicals were used without further purification. Pyrocatechol stock solutions in $NaHSO_4$/Na_2SO_4 (SBS) at pH 2.0 were prepared. All the electrochemical experiments were carried out nitrogen (Linde) atmosphere.

Preparation of Modified Electrode

PANI-P_3MT- PDAB film was coated on Pt disc surface in CH_2Cl_2 layer by layer as described in previous work [18]. For this, PANI film was deposited on Pt disc surface in CH_2Cl_2 containing 300 mmol.L^{-1} aniline monomer, 100 mmol.L^{-1} $HClO_4$ and 100 mmol.L^{-1} tetrabuthylammonium perchlorate (TBAP) as supporting electrolyte. Then, on this PANI film, P_3MT- PDAB was synthesized in CH_2Cl_2 containing monomers of 500 mmol.L^{-1} 3-methylthiophene and 1.0 mmol.L^{-1} 3,3′-diaminobenzidine and 100 mmol.L^{-1} TBAP as supporting electrolyte (Figure 1). In present study, this coated electrode was tested for amperometric detection of pyrocatechol in SBS (pH 2.0) at 0.50 V.

RESULT AND DISCUSSION

Electrochemical Behavior of Pyrocatechol over Prepared Electrode

In previous study, behavior of prepared modified electrode has been investigated in SBS solution at different pH (1.0-6.5) and the modified electrode showed the best electroactivity in pH 2.0 solution [18]. So, pH 2.0 solution was used to determine of pyrocatechol behavior in aqueous medium studies. Electrochemical oxidation of pyrocatechol was performed in pH 2.0 SBS solution at the potential ranging from 0.0 V - 0.9 V at the scan rate of 100 mV.s^{-1} over homopolymers (PANI, P_3MT, PDAB) and PANI-P_3MT-PDAB films synthesized on Pt disc surfaces (Figure 2A-D(a)). These voltammograms were compared with the taken pyrocatechol-free solution at the coated Pt disc electrodes in same figure (Figure 2A-D(b)). Also, Figure 2A-D (c) shows cyclic voltammogram of pyrocatechol at the uncoated Pt disc electrode. According to Figure 2A-D(c), pyrocatechol was oxidized at about 0.62 V and reduced at about 0.24 V at the uncoated Pt disc electrode. When PANI, P_3MT and PANI-P_3MT-PDAB films synthesized on Pt disc surfaces were used in pyrocatechol containing solution, the current was higher than the current observed when the experiment was conducted in solution without pyrocatechol (Figure 2A,B,D). Also, oxidation peak of pyrocatechol was shifted to a lower potential than 0.62 V and highest current

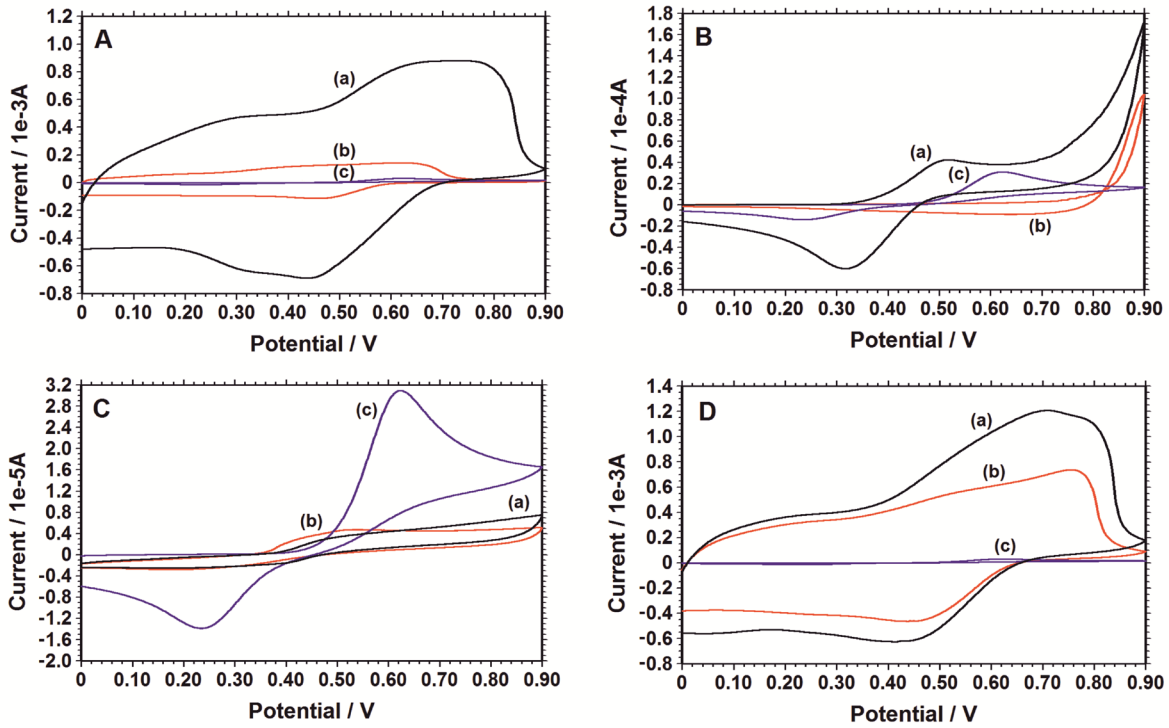


Figure 2. Electrochemical behavior of (A) PANI, (B) P_3MT, (C) PDAB, (D) PANI-P_3MT-PDAB modified surfaces in (a) SBS presence 5.0 mmol L-1 pyrocatechol, (b)SBS, and (c) 5.00 mmol L-1 pyrocatechol on uncoated Pt disc surface. V= 100 mV s-1, vs. SCE.

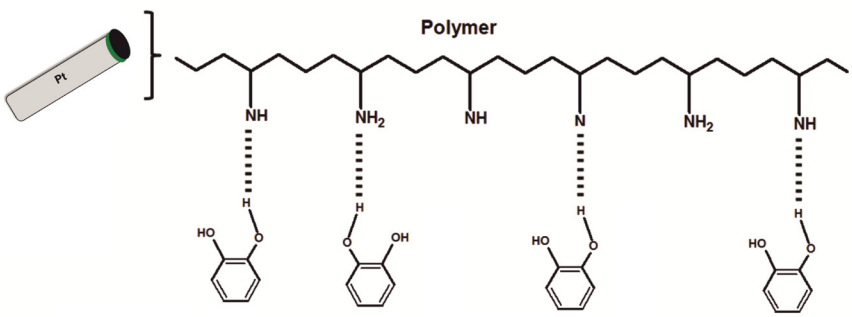


Figure 3. Alternatively holding of pyrocatechol to polymer matrix by hydrogen bond

value was obtained using PANI - P_3MT - PDAB film coated on Pt disc surface (Figure 2D (a)).

The reason for this can be explained that prepared electrode enriched in respect to functional groups (-N, -NH, -NH_2) supplied stronger retention of pyrocatechol with hydrogen bonding as shown in Figure 3 on this modified electrode. In addition, owing to the catalytic effects of each homopolymer, higher current peak was obtained.

Amperometric Determination of Pyrocatechol

The current response of PANI-P_3MT-PDAB coated Pt disc surface to pyrocatechol was investigated in at pH 2.0 solution vs SCE. Before the experiment, 0.45 V-0.65 V potential range were implemented to modified surface approximate 1200 s to obtain steady-state current values. After reaching this state, first addition of pyrocatechol as 9.77×10^{-4} mmol.L^{-1} was appended from stock solution containing pyrocatechol solved at pH 2.0 solution dissolved oxygen removed using nitrogen. Solution was stirred along 30 s at the same speed to supply

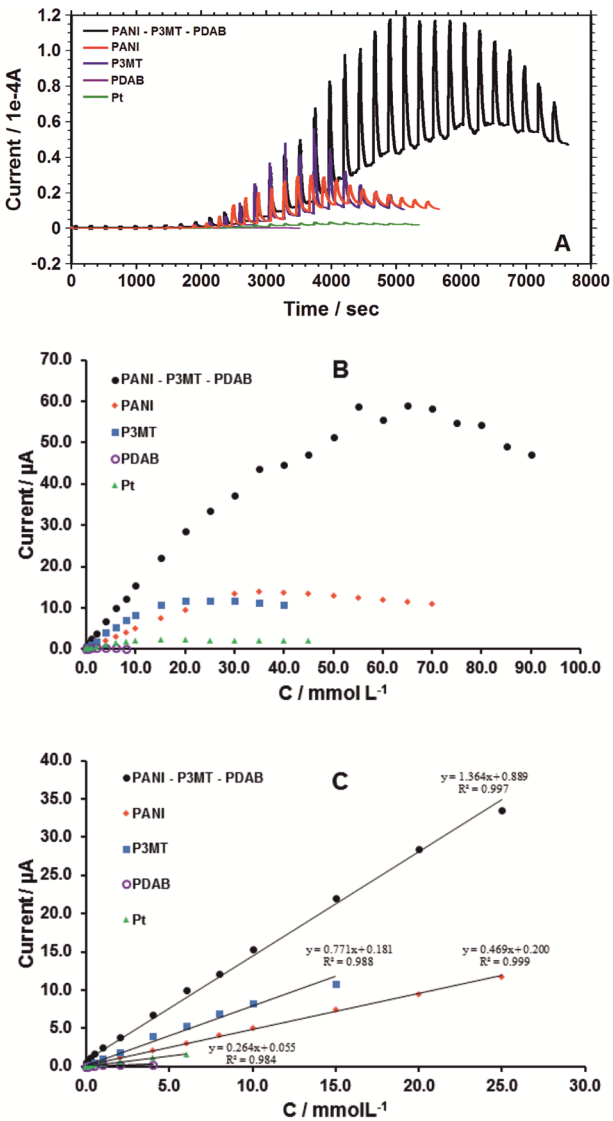


Figure 3. Determination of pyrocatechol (9.77×10-4 - 90.0 mmol L-1) using bare and PANI, P_3MT, PDAB, PANI-P_3MT-PDAB modified Pt surface at 0.50 V A: Current-time response recorded versus SCE B: Amperometric response versus successive addition of different concentrations of pyrocatechol C: Calibration curves of modified electrode for pyrocatechol concentration at the applied potential of 0.50 V.

homogeneity. Steady current values at the end of 200 s over synthesized modified surface were measured. Calibration graphs were plotted with current values vs. the increasing pyrocatechol concentrations. 0.50 V was optimum potential that the best result was obtained so obtained results over PANI-P_3MT-PDAB film were compared with its homopolymer films and bare Pt disc surface at this potential (Figure 4A). Amperometric response were plotted vs. successive addition of different concentrations of pyrocatechol (Figure 4B) and calibration curves were obtained for linearity range of pyrocatechol concentration over homopolymers, PANI-P_3MT-PDAB films and uncoated Pt disc electrode (Figure 4C). Among these modified electrodes, highest current values were found with PANI-P_3MT-PDAB coated Pt disc surface. Furthermore, pyrocatechol was detected at lower potential (0.50 V) using PANI-P_3MT-PDAB coated Pt disc surface than oxidation potential (0.62 V) of pyrocatechol over bare Pt electrode at pH 2.0 solution due to catalytical effect of film. This situation can be explained with both porous structure and more functional groups of this modified electrode. Analytical parameters (LOD, LOQ, linear dynamic range and correlation coefficient (R^2) values) were compared with the modified and the bare Pt surfaces in Table 1.

Table 1. Comparisons of analytical parameters results for the determination of pyrocatechol over bare and coated surface.

Applied Potential (V)	Electrode	LOD (a) (mmol.L^{-1})	LOQ (b) (mmol.L^{-1})	Linear Range (mmol.L^{-1})	Equation	R^2 (c)
0.50	PANI-P_3MT-PDAB	7.37×10^{-5}	2.47 ×10^{-4}	2.47 ×10^{-4}-25.0	y = 1.363x + 0.889	0.996
	PANI	1.74 ×10^{-4}	5.81 ×10^{-4}	5.81 ×10^{-4} – 25.0	y = 0.468x + 0.199	0.999
	P_3MT	2.69 ×10^{-4}	8.95 ×10^{-4}	8.95 ×10^{-4} – 10.0	y = 0.770x + 0.181	0.988
	Pt	2.75 ×10^{-4}	9.15 ×10^{-4}	9.15 ×10^{-4} – 6.0	y = 0.264x + 0.054	0.984

(a)Limit of detection (b)Limit of quantification (c)Regression coefficient

However, when PDAB coated electrode was used, LOD and LOQ values cannot be calculated because of the value 0.687of R^2.

Comparison of results for modified and bare Pt disc surface was shown in Table 1. LOD and LOQ values were calculated using 3s/m and 10s/m equations [20]. According to Table 1, it was observed that lower LOD value and greater linear range was obtained with PANI-P_3MT-PDAB coated surface than other electrodes. It might be due to mixed film has many functional groups (NH, N, and NH_2). As shown in Figure 3, hydroxyl in pyrocatechol are hold to these groups containing -N in polymer matrix by hydrogen bonding [10]. Therefore, continuous oxidation of the pyrocatechol group is provided with amperometric method. This modified electrode has different electrochemical behavior and the excellent analytical performance.

Repeatability Assay of Pyrocatechol With PANI-P_3MT-PDAB Coated Surface

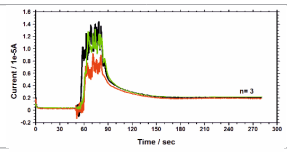
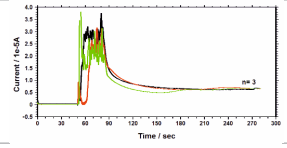
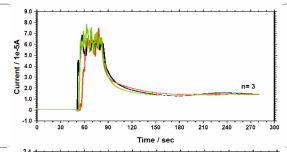
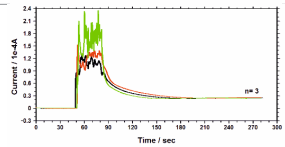
Repeatability of PANI-P_3MT-PDAB coated Pt surface responses to pyrocatechol was proved by utilizing three films for each amperometric measurement in SBS (pH 2.0) versus SCE. As mentioned above, the modified electrode was provided to reach a steady-state current by electrolysis about 1200 s at 0.50 V potential. At the end of 200 s, the current values were recorded for distinct pyrocatechol concentrations (1.0-20.0 mmol.L^{-1}) by utilizing sequential three measurement. Table 2 shows current-time curve, currents, standard deviations, percent relative standard deviation (RSD%) and confidence interval at confidence level 95 % for each measurement. At calculating the confidence interval to appraise the sensitive, combined standard deviation (scombined: 0.259 μA) was used.

Determination of Pyrocatechol in Real Samples

PANI-P_3MT-PDAB modified Pt disc surface was used for determination of pyrocatechol in river water in Turkey to identify matrix interference and accuracy of current method. Before the experiment, river water was adjusted to optimum working pH (2.0) with HCl solution and it was artificially contaminated by the addition of pyrocatechol. Under optimum conditions, modified electrode was electrolyzed approximately 1200 s (pH 2.0) to reach stability and then water samples containing pyrocatechol (5.0 and 10.0 mmol.L^{-1}) were added. To ensure homogeneity, solution was stirred for 30 seconds. After 200 seconds, the steady-state current values were recorded. This experiment was performed with at least three film and mean of currents was taken. These results were compared to standard pyrocatechol (5.0 and 10 mmol.L^{-1}) current values (Table 2), and then, the recovery values were determined. Table 3 shows results of recovery experiment. As can be seen, there is no matrix effects for the determination of pyrocatechol in real sample.

Finally, the comparison of results with other techniques for determination of pyrocatechol is listed in Table 4 and it can be said PANI-P_3MT-PDAB coated electrode displays the good analytical performance than the other modified electrodes.

Table 2. Results of repeatability experiment for different pyrocatechol concentrations with PANI-P_3MT-PDAB coated surface.

1.0		2.102		
		1.928	0.121	5.86
		2.161		
5.0		6.684		
		6.580	0.062	0.93
		6.691		
10.0		14.28		
		14.59	0.266	1.86
		14.06		
20.0		25.04		
		25.68	0.423	1.47
		24.88		

*95% confidence level was calculated.
Confidence intervals were calculated using standard deviations **group ***combined

Table 3. Recovery values for detection of pyrocatechol in real sample.

Samples	Added ($C_{pyrocatechol}$ / mmol L^{-1})	Found ($C_{pyrocatechol}$ / mmol L^{-1})	Recovery (%)
1	5.00	5.05	101.1
2	10.0	10.12	101.2

Table 4. Performance comparison of the fabricated electrode for pyrocatechol detection with other electrodes.

Electrochemical method	Used Modified Electrode	LOD (mmol.L^{-1})	Linear Range (mmol.L^{-1})	Reference
Differential Pulse Voltammetry	Poly(p-aminobenzoic acid) modified glassy carbon electrode	5.0×10^{-4}	2×10^{-3}–0.9	[21]
Cyclic voltammetry	Poly(malachite green) coated multiwalled carbon nanotube film	2.93×10^{-2}	0.36–4.05	[22]
Amperometry	An expanded graphite electrode (EGE) modified with intercalated montmorillonite (MMT)	1.13×10^{-3}	0.01-1.0	[23]
Cyclic voltammetry	Poly(phenylalanine) Modified Glassy Carbon Electrode	1.0×10^{-3}	0.010-0.14	[24]
Amperometry	Tyrosinase-3-mercaptopropionic acid (MPA) self-assembled monolayer (SAM) on a Au disk electrode	1.1×10^{-4}	2.0×10^{-4}–0.1	[25]
Amperometry	PANI/P_3MT-PDAB on Pt electrode	7.37×10^{-5}	2.47×10^{-4}-25.0	This work

CONCLUSION

Pt disc surface modified with three different conductive polymer was used for detection of pyrocatechol. Therefore, aniline, 3-methylthiophene, 3,3'-diaminobenzidine and tetrabuthylammonium perchlorate were used as monomers and supporting electrolyte, respectively. Synthesized modified electrode was used to determine pyrocatechol using Amperometric I-t method (0.50 V) in solution consisting of $NaHSO_4/Na_2SO_4$ (pH 2.0). For demonstration of method reproducibility and accuracy, validation parameters were calculated and LOD, LOQ and the linear range were determined as 7.37×10^{-5}, 2.47×10^{-4} and 2.47×10^{-4} -25.0 mmol.L^{-1}, respectively. Matrix interference for pyrocatechol detection in artificially contaminated Güneysu river water of Rize province in Turkey was investigated and recovery values were found as 101.10% and 101.20%, respectively. When found results were compared with literature studies (Table 4), present method was determined as utilizable, easy and fast.

ACKNOWLEDGMENTS

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References

1. J. Wang, J.-N. Park, X.-Y. Wei, C.W. Lee, Room-temperature heterogeneous hydroxylation of phenol with hydrogen peroxide over Fe^{2+}, Co^{2+} ion-exchanged Naβ zeolite, Chem. Commun., 9 (2003) 628.
2. N. Alizadeh, H. Zarabadipour, A. Mohammadi, Headspace solid-phase microextraction using an electrochemically deposited dodecylsulfate-doped polypyrrole film to determine of phenolic compounds in water, Anal. Chim. Acta, 605 (2007) 159.
3. Q. Ameer, S.B. Adeloju, Development of a potentiometric catechol biosensor by entrapment of tyrosinase within polypyrrole film, Sens. Actuators B: Chem., 140 (2009) 5.
4. M. Castillo, R. Domingues, M.F. Alpendurada D. Barceló, Persistence of selected pesticides and their phenolic transformation products in natural waters using off-line liquid solid extraction followed by liquid chromatographic techniques, Anal. Chim. Acta, 353 (1997) 133.
5. R. Gatti, M.G. Gioia, A.M. Di Pietra V. Cavrini, Analysis of phenols in pharmaceuticals by liquid chromatography after pre-column labelling and on-line post-column photochemical derivatization, Anal. Chim. Acta, 447 (2001) 89.
6. C.D. Chriswell, R.C. Chang J.S. Fritz, Chromatographic determination of phenols in water, Anal. Chem., 47 (1975) 1325.
7. M. Naczk and F. Shahidi, Extraction analysis of phenolics in food, J. Chromatogr. A, 1054 (2004) 95.
8. G. Wang, X. He, F. Zhou, Z. Li, B. Fang, X. Zhang L. Wang, Application of gold nanoparticles/TiO_2 modified electrode for the electrooxidative determination of catechol in tea samples, Food Chem., 135 (2012) 446.
9. K. He, X. Wang, X. Meng, H. Zheng S.-i. Suye, Amperometric determination of hydroquinone and catechol on gold electrode modified by direct electrodeposition of poly(3,4-ethylene dioxythiophene), Sens. Actuators B: Chem., 193 (2014) 212.
10. M. Kavanoz N.Ö. Pekmez, Poly(vinylferrocenium) perchlorate–polyaniline composite film-coated electrode for amperometric determination of hydroquinone, J. Solid State Electrochem., 16 (2012) 1175.
11. Y. Tan, X. Guo, J. Zhang J. Kan, Amperometric catechol biosensor based on polyaniline–polyphenol oxidase, Biosens. Bioelectron., 25 (2010) 1681.
12. H. Zhang, A. Galal, J.F. Rubinson, I. Marawi, T.H. Ridgway, S.K. Lunsford, H. Zimmer H.B. Mark Jr, Flow injection amperometric detection of catechol using dual-band poly(3-methylthiophene) electrodes, Electrochim. Acta, 43 (1998) 3511.
13. M. Kavanoz, U. Bük E. Ülker, Determination of hydroquinone using poly(3-methylthiophene) synthesized electrochemically on Pt electrode in methylene chloride, J. Appl. Polym. Sci., 131 (2014).
14. Q. Cai S.B. Khoo, Poly(3,3'-diaminobenzidine) film on a gold electrode for selective preconcentration and stripping analysis of selenium(IV), Anal. Chem., 6 (1994), 4543.
15. I.E. Mülazımoğlu, A.D. Mülazımoğlu E. Yılmaz, Determination of quantitative phenol in tap water samples as electrochemical using 3,3'-diaminobenzidine modified glassy carbon sensor electrode, Desalination, 268 (2011) 227.
16. M.R. Nateghi, M.H. Mosslemin H. Hadjimohammadi, Electrochemical preparation and characterization of poly(3,3-diaminobenzidine): A functionalized polymer, React. Funct. Polym., 64 (2005) 103.
17. E. Ulker M. Kavanoz, Synthesis of poly(vinylferrocene) perchlorate/poly(3,3'-Diaminobenzidine) modified electrode in dichloromethane for electroanalysis of hydroquinone, J. Braz. Chem. Soc., 26 (2015) 1947.
18. M. Kavanoz, E. Ülker U. Bük, A novel polyaniline–Poly(3-methylthiophene)-poly(3,3-diaminobenzidine) electrode for the determination of dopamine in human serum, Anal. Lett., 48 (2015) 75.
19. E. Ulker M. Kavanoz, Determination of epinephrine in human serum over polyaniline-poly(3-methylthiophene)-poly(3,3'-diaminobenzidine) modified Pt electrode, Can. J. Chem., 93 (2015) 1239.

20. G.L. Long J.D. Winefordner, Limit of detection a closer look at the IUPAC definition, Anal. Chem., 55 (1983) 712.
21. P. Yang, Q. Zhu, Y. Chen F. Wang, Simultaneous determination of hydroquinone and catechol using poly(p-aminobenzoic acid) modified glassy carbon electrode, J. Appl. Polym. Sci., 113 (2009) 2881.
22. Y. Umasankar, A.P. Periasamy S.-M. Chen, Electrocatalysis and simultaneous determination of catechol and quinol by poly(malachite green) coated multiwalled carbon nanotube film, Anal. Biochem., 411 (2011) 71.
23. Y. Kong, Y. Xu, H. Mao, C. Yao X. Ding, Expanded graphite modified with intercalated montmorillonite for the electrochemical determination of catechol, J. Electroanal. Chem., 669 (2012) 1.
24. L. Wang, P. Huang, J. Bai, H. Wang, L. Zhang Y. Zhao, Simultaneous electrochemical determination of phenol isomers in binary mixtures at a poly(phenylalanine) modified glassy carbon electrode, Int. J. Electrochem. Sci., 1 (2006) 403.
25. S. Campuzano, B. Serra, M. Pedrero, F.J.M.D. Villena J.M. Pingarrón, Amperometric flow-injection determination of phenolic compounds at self-assembled monolayer-based tyrosinase biosensors, Anal. Chim. Acta, 494 (2003) 187.