Int. J. Electrochem. Sci., 11 **(2016)** 6244 – 6255, doi: 10.20964/2016.07.74

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Sensitive Voltammetric Determination of Paracetamol on Poly(4-Aminobenzene Sulfonic Acid) Modified Glassy Carbon Electrode

Selehattin Yilmaz[1], *Zeynep Bas*[1], *Murat Sadikoglu*[2,*], *Sultan Yagmur*[1], *Gulsen Saglikoglu*[1]

[1] Canakkale Onsekiz Mart University, Faculty of Science and Arts, Department of Chemistry, 17020, Canakkale, Turkey
[2] Gaziosmanpasa University, Faculty of Education, Department of Science Education, 60240, Tokat, Turkey
[*]E-mail: murat.sadikoglu@yahoo.com

Received: 12 April 2016 / *Accepted:* 15 May 2016 / *Published:* 4 June 2016

A poly (4-aminobenzene sulfonic acid) (4-ABSA) modified glassy carbon electrode (GCE) was prepared for the quantitative determination of paracetamol (PCT). The 4-ABSA-modified GCE was prepared by electrochemical polymerization method in phosphate buffer solution (PBS) (pH 7.0). The polymer film-modified electrode has high catalytic ability for electrooxidation of PCT, which appeared at pH range of 5-8 by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The best results for the determination of PCT were obtained by DPV in PBS (pH 7.00). Calibration curve was obtained in the PCT concentration range of $6x10^{-7}$ to $9x10^{-6}$ mol L^{-1} by DPV. Limit of detection (LOD) and quantification (LOQ) were found as $9.33x10^{-8}$ mol L^{-1} and $3.10x10^{-7}$ mol L^{-1}, respectively. The results of experiments indicated that modified electrode have good stability, sensitivity and reproducibility for at least one month if stored dry in air.

Keywords: Poly(4-Aminobenzene Sulfonic Acid), modified-glassy carbon electrode, electropolymerization, electrocatalytic oxidation, paracetamol, determination, voltammetry.

1. INTRODUCTION

PCT is known as acetaminophen (Fig. 1) and used analgesic and antipyretic active material. It is generally used to reduce fever, relieve cough, cold, pain such as muscular aches, chronic pain, migraine headache, toothache, minor aches and pains [1]. PCT acts as painkiller by inhibiting prostaglandin's synthesis in the central nervous system and relieves fever by sedating the hypothalamic

heat regulating center [2]. Therefore, it is important to the assay of PCT from its pharmaceutical formulations by voltammetric tehniques.

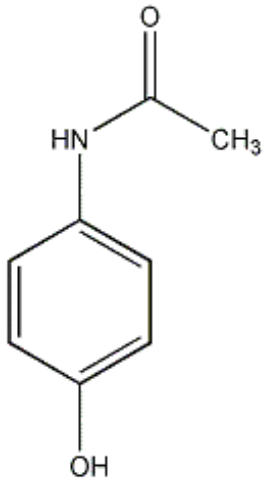


Figure 1. Chemical formule of PCT.

Several methods such as UV spectrophotometry and chemometric methods [3], flow-injection spectrophotometric [4], fluorescence spectroscopy [5], spectrofluorimetric [6], micellar electrokinetic capillary chromatography [7] have been reported for the determination of PCT. The electrochemical techniques, which are economical, sensitive and rapid methodologies, were commonly used to determination of PCT [8-18]. However, the electrooxidation of PCT at carbon electrodes is kinetically slow and require high overpotentials. Therefore, the use of modified carbon electrodes was preferred for PCT oxidation. Chemically modified electrodes were used to enhance the rate of electron transfer and minimize its overpotential. Glassy carbon modified by 4-vinylpyridine [19], nile blue [20], chromium Schiff base complex [21], chitosan [22] are of various modified electrodes used in electrocatalytic oxidation of PCT.

Poly(4-ABSA)-modified GCE was prepared for assay of mixture of phenylephrine and chlorprothixene [23], hydroquinone in the presence of catechol and resorcinol [24], uric acid [25], acyclovir [26] and phenazopyridine hydrocloride [27]. But, the assay of PCT at the 4-ABSA modified-GCE has not been reported so far. In present study, the electrochemical oxidation of PCT using the GCE modified with poly (*p*-ABSA) film was investigated. A simple, sensitive and fast analysis method has been developed at the 4-ABSA modified GCE for electrocatalytic assay of PCT.

2. EXPERIMENTAL

2.1. Apparatus

In this study, Metrohm 757 VA with Autolab PGSTAT 101 apparatus were employed for the electrochemical signals. GCE as working electrode [active surface area (ϕ) 7 mm; disc diameter (R) 2

mm], a platinum wire as auxiliary electrode and Ag/AgCl (KCl 3 mol $L^{-1,}$) as reference electrode were used. pH values were realized using Metrohm 744 pH meter apparatus. Measurements were realized at 15-20 °C. The surface of working electrode was clean with Wise Clean sonicator . The quality of 0.055 μS/cm ultra pure water (UPW) was used to prepare experimental solutions.

The electroactive surface area of the modified-GCE was calculated by the CV method in $1x0^{-3}$ mol L^{-1} $K_3Fe(CN)_6$ solution as a probe at various scan rates. Randles-Sevcik equation can be used for a reversible electrode reaction:

$$I_{pa}=0.4463\ (F^3/RT)n^{3/2}A_0D_0^{1/2}C_o\nu^{1/2}$$

Where I_{pa} refers to the peak current of oxidation. n is number of electrons transferred in the electrode process, A_0 is the area of working modified-GCE, D_0 is the diffusion coefficient, ν is the scan rate, and C_0 is the concentration values, respectively, of $1x0^{-3}$ mol L^{-1} $K_3Fe(CN)_6$ in 0.1 M KCl supporting electrolyte. T=298 K, R=8.314 JK^{-1} mol^{-1}, F=96500 C mol^{-1}(constant values) , n=1, and D_0= $1x10^{-5}$ cm^2 s^{-1}. From the slope of the plot of I_{pa} versus $\nu^{1/2}$ relation, the electroactive surface area was calculated as $2.04x10^5$ μA ($Vs^{-1/2}$) and the electroactive surface area of the 4-ABSA-modifed-GCE was calculated as 0.40 (±0.01) cm^2 which is exactly two times more than that was given as 0.20 (±0.01) cm^2 for the unmodified (bare)-GCE [26].

The specific parameters were used to voltammetric measurement: pulse amplitude was 50 mV; pulse time was 0.04 s, voltage step was 0.009 V, voltage step time was 0.04 and, potential step was 10 mV for DPV; and scan rates were between 50-200 mV s^{-1} used for CV.

2.2. Polishing and Cleaning Procedure of GCE

The working GCE was polished with 1 μm, 0.3 μm and 0.05 μm alumina slurries made from dry Buehler alumina and UPW on Buehler polishing microcloth. After polished GCE was sonicated in UPW, a mixture of 1:1 by volume (v/v) water/nitric acid (H_2O+HNO_3) (Fluka) and then, ethanol solution (Aldrich) about 10 min. The cleaned GCE electrode was rinsed with UPW and then, dried under a stream of pure argon gas.

2.3. Reagents and materials

PCT and its Parol tablet were provided by Atabay drug company (Istanbul, Turkey). A fresh stock solution of $1.0x10^{-2}$ mol L^{-1} of PCT was carefully prepared by dissolving a correct mass of the active drug in a convenient volume of methanol kept in the refrigerator before the measurements. The calibration solutions were prepared by dilution of the stock solution. Solutions were preserved from day-light and were used within 24 h to prevent decomposition. 0.5 mol L^{-1} H_2SO_4 (pH 0.51) solution, 0.067 mol L^{-1} phosphate (pH 4.40-7.28), 0.2 mol L^{-1} acetate (pH 3.51-5.62) and 0.04 mol L^{-1} Britton-Robinson (BR) buffers (pH 2.02-12.00) were used as supporting electrolyte. UPW (Sartorius Arium model UPW Systems) was used to prepare buffer solutions as supporting electrolytes.

2.4. Preparation of Poly(4-ABSA)-modified electrode

A bare GCE was steeped in 0.10 mol L^{-1} PBS buffer (pH 7.0) and 2.0×10^{-3} mol L^{-1} 4-ABSA solution mixture and qualified by CV technique from -1.5 to +2.5 V at 100 mV s^{-1} for 5 scans. The poly(4-ABSA)-modified electrode was activated in 0.10 mol L^{-1} PBS (pH 7.0) by CV technique from -1.0 to +1.0 V at 100 mV s^{-1} for 10 scans.

2.5. Calibration curve for quantitative assay of PCT

The fresh stock solution of PCT was diluted with methanol to get various PCT concentrations. At the decided experimental conditions (given in the experimental section) a calibration graph was obtained for PCT in the linear concentration range from $6x10^{-6}$ mol L^{-1} to $9x10^{-4}$ mol L^{-1} by DPV. For the validation of applied methods, parameters of the accuracy, precision and repeatability of measurement were checked.

2.6. Analysis procedure for PCT from its pharmaceutical preparation

Ten commercial parol tablets were weighed and crushed for a small dust. An appropriate amount of this dust (concentration as $1x10^{-2}$ mol L^{-1}) was weighed and put into a 10 mL flask and its volume was adjusted with methanol. The sample in the flask was centrifuged for 30 min. at 4000 rpm to terminate dissolution and then diluted to volume with the methanol solvent. Appropriate solutions were prepared by taking appropriate aliquots from the clear supernatant and diluting with supporting electrolyte. Solution was put into the electrochemical cell. The amount of PCT was calculated from regression equations obtained from calibration curve.

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymarization of 4-ABSA at the GCE

The typical CV voltammograms of $2.0x10^{-3}$ mol L^{-1} of 4-ABSA in 0.10 mol L^{-1} PBS (pH 7.0) on the bare GCE is given Fig. 2. As can be seen Figure 2, Initally, small oxidation and reduction peaks were obtained at E_{pa} = 0.99 V (between peaks 1 and 3) and E_{pc} = -0.70 V (peak 2), respectively. In the second cycle on two sharp oxidation peaks observed at potential +0.13 V (peak 3) and +1.45 V (peak1), respectively. The increasing peaks with continuous scanning, reflecting the continuous growth of the electrochemical polymerization film on the GCE surface. These results showed that 4-ABSA compound was deposited on the surface of GCE by electrochemical polymerization [23,25-30]. The poly(p-ABSA)-modified GCE was washed with UPW and stored in 0.1 mol L^{-1} PBS buffer (pH 7.0) until experiment.

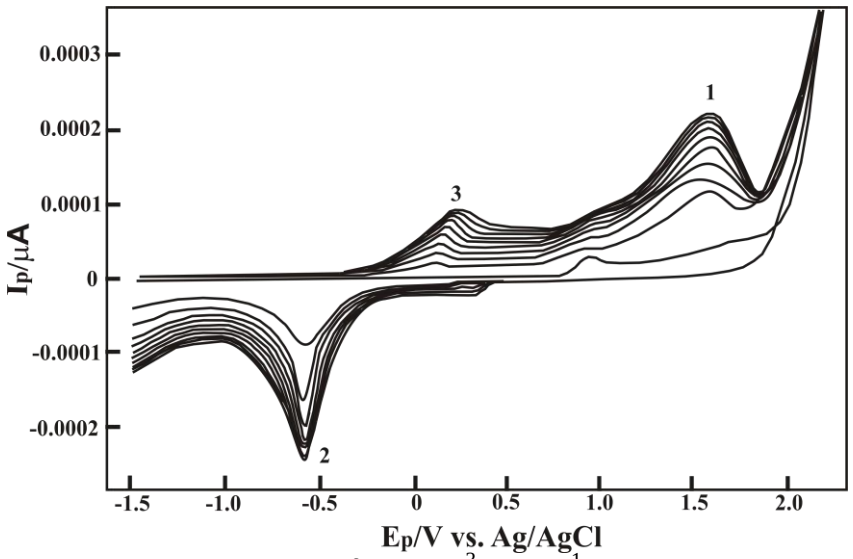
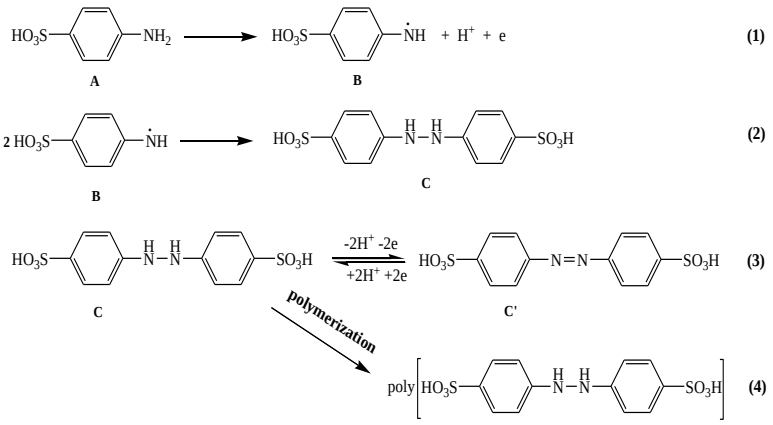


Figure 2. Repetitious CV voltammograms of $2.0x10^{-3}$ mol L^{-1} 4-ABSA in 0.10 mol L^{-1} PBS buffer (pH 7.0). Beginning potential value -1.5 V, final potential value +2.4 V and scan rate 100 mV s^{-1}.

The electrochemical polymerization properties of 4-ABSA on GCE was similar to reported [23,25-30]. The electrode reaction process is similar to that given in Scheme 1.



Scheme 1. Proposed mechanism of electrochemical polymerization for *p*-ABSA at surface of GCE .

p-ABSA (A) was oxidized to free radical (B, peak 1). The free radical (B) combined together to form hydrazobenzene sulfonic acid (C). Hydrazobenzene sulfonic acid (C) was oxidized to azobenzene sulfonic acid (C´, peak 3). Azobenzene sulfonic acid (C´) was reduced to hydrazobenzene sulfonic acid (C, peak 2). In the end of surface of bare GCE was covered by the formed polymer film (D).

3.2. The electrochemical oxidation of PCT on 4-ABSA modified- GCE

The oxidation of PCT on GCE and 4-ABSA modified- GCE have been realized by CV. The voltammograms of $5x10^{-5}$ mol L^{-1} PCT at a bare GCE (a) and poly(4-ABSA/GC) (b) at pH 7 in PBS at 100 mV s^{-1} , were given in Fig. 3.

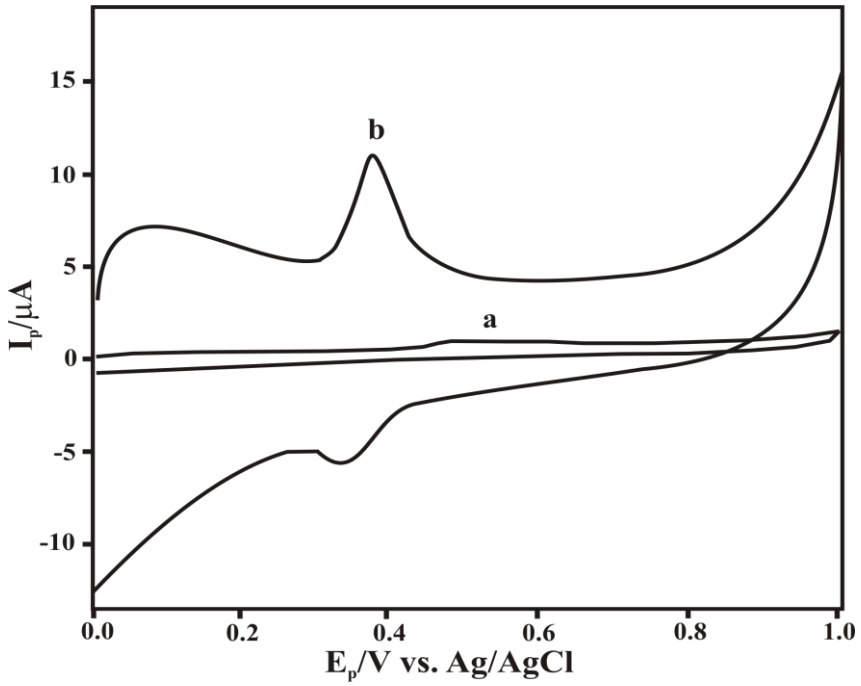


Figure 3. CV voltammograms of $5x10^{-5}$ mol L^{-1} PCT at bare GCE (a) and 4-ABSA modified - GCE (b) at pH 7 in PBS at scan rate 100 mVs^{-1}.

On the surface of bare GCE, PCT indicated a clearless voltammogram (Figure 3b). However, on the poly(4-ABSA/GC) electrode , it appears at 369 mV (Fig. 3a).

The dependence of peak current of PCT on pH using various buffer solutions ranging from pH 5.0 to 8.0 was determined (Fig. 4). For the oxidation of PCT, the oxidation potential shifts toward a less positive values with increasing pH up to 7.0. (Fig. 5). On the other hand, the peak current of PCT increases at pH 7.0. So, pH 7.0 was used for other studies.

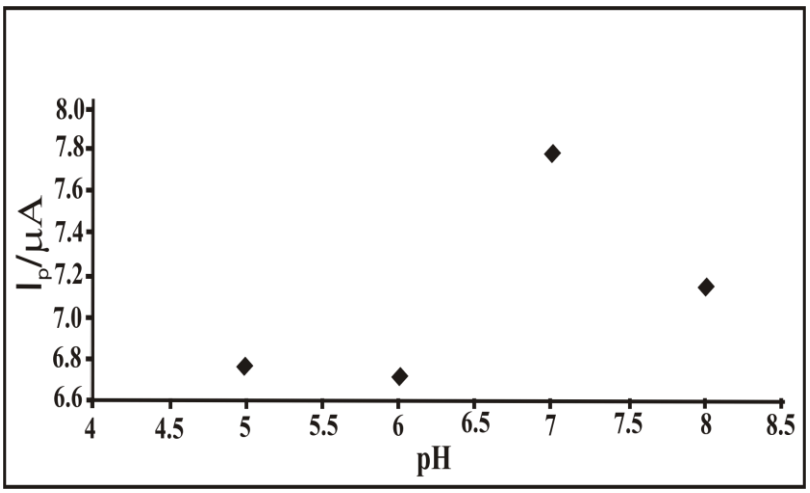


Figure 4. Changing of the oxidation peak current of $1x10^{-5}$ mol L^{-1} PCT on pH values in 0.1 mol L^{-1} PBS buffer solution, at a scan rate of 50 mV s^{-1}.

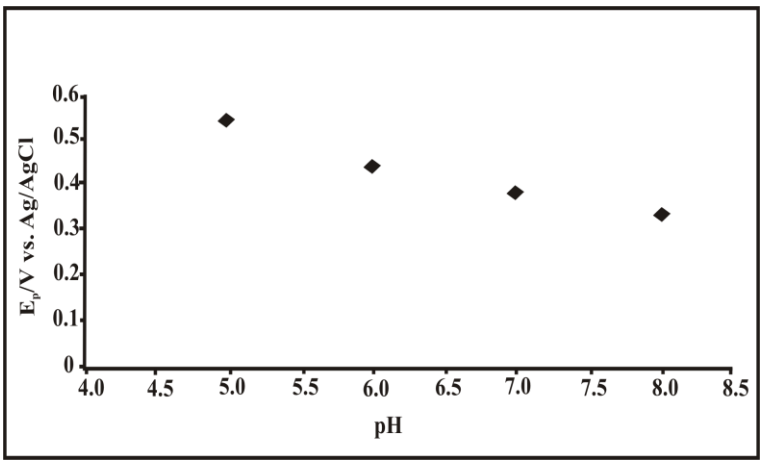
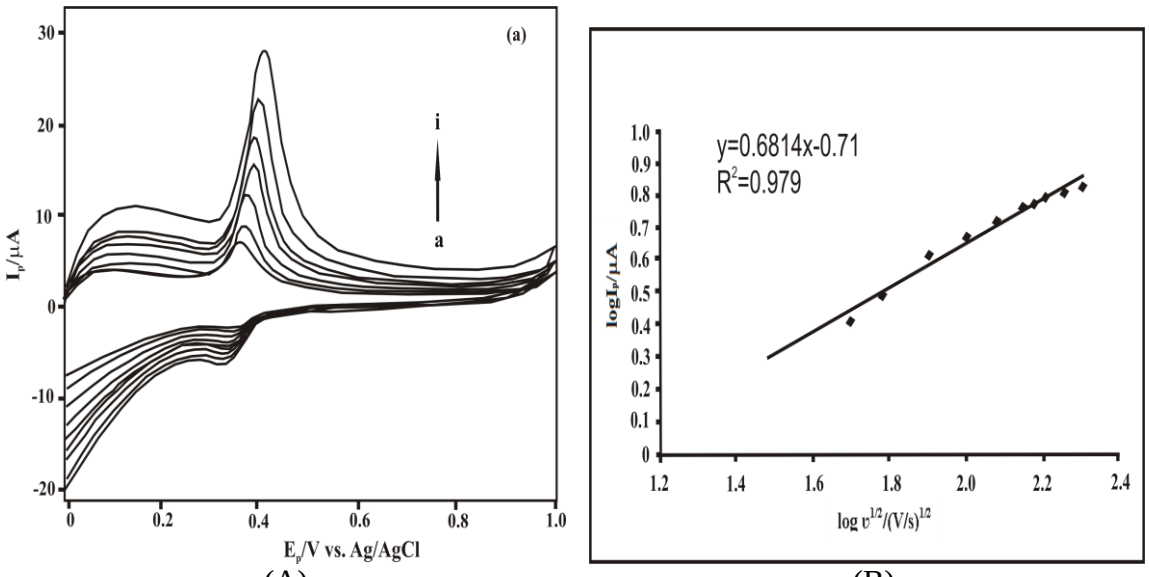


Figure 5. Changing of the oxidation peak potential of $1x10^{-5}$ mol L^{-1} PCT on pH values in 0.1 mol L^{-1} PBS buffer , at a scan rate of 50 mV s^{-1}.

The oxidation process was found as diffusion controlled in the PBS, as indicated from the plots of the peak current (Ip) versus square root of the scan rate ($v^{1/2}$) for PCT. Figure 6(A) shows the cyclic voltammograms of $1x10^{-5}$ mol L^{-1} PCT in 0.1 mol L^{-1} PBS (pH 7.0) on poly(4-ABSA/GC) electrode at scane rates: 50, 60, 80, 100, 120, 140, 150, 160, 200 mVs^{-1} . The current values plotted versus $v^{1/2}$ were given in Figure 6(B). The oxidation peak current increased with increasing scan rate. A high linearity between the square root of scan rate and peak current was found from the scan rates ranges of 50-200 mV s^{-1}. Regression equation was found as, Ip(μA)= $0.6002\upsilon^{1/2}$-1.4177 (r=0.9861). Coefficient of correlation was found close to theoric value (1.0) indicate that the current type is diffusion controlled [28,30].



(A) (B)

Figure 6. (A) CV voltammograms of the poly(4-ABSA/GC) electrode $1x10^{-5}$ mol L^{-1} PCT in 0.1 mol L^{-1} PBS (pH 7.0) at various scan rates: a) 50; b) 60; c) 80; d) 100; e) 120; f) 140; g) 150; h) 160; i) 200 mVs^{-1}. **(B)** Dependence of the peak current with square root of the scan rate in $1x10^{-5}$ mol L^{-1} PCT in 0.1 M PBS solution (pH 7.0).

The logarithm of peak current (log *I*) against the logarithm of scan rate (log *v*) was given in Figure 7.

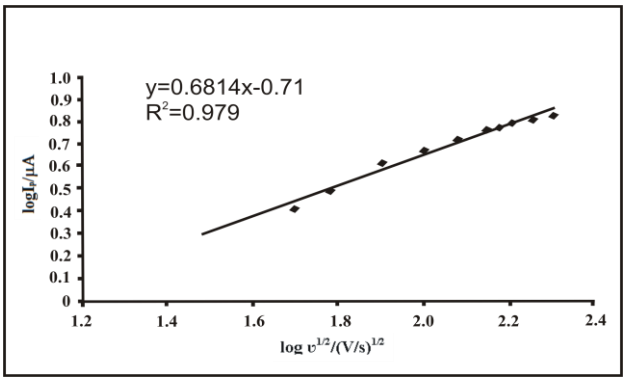


Figure 7. Dependence the log *I* against the log *v* at the poly(4-ABSA/GC) electrode $1x10^{-5}$ mol L^{-1} PCT in 0.1 M PBS buffer solution (pH 7.0). Scan rates: 50, 60, 80, 100, 120, 140, 150, 160, 200 mV s^{-1}.

The slope of the log *I* versus log *v* was found as 0.6814 which is close to the theoric value (0.5). The equation was obtained as log Ip(μA)=0.6814logυ-0.71 (R^2=0.9797) . Slope value is indicated that electrode process of PCT at the poly(4-ABSA/GC) electrode is diffusion controlled. Consequently, the analysis was determined based on diffusion controlled [26-30].

3.3. Quantitative Assay of PCT

The quantitative assay of PCT on poly(4-ABSA)-modified GCE was realized by voltammetry technique. The assay of PCT was realized at selected analytical conditions with calibration method (Fig. 8).

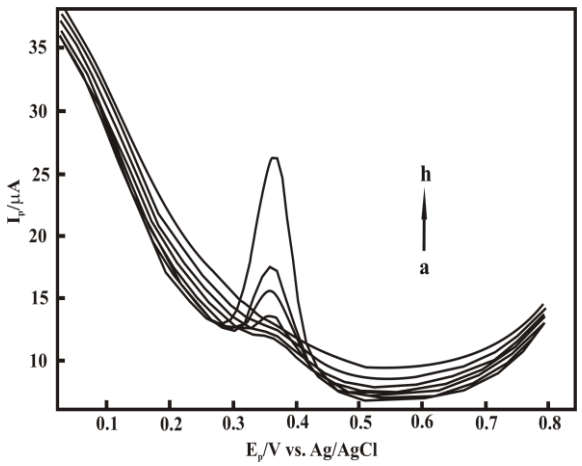


Figure 8. DPV voltammograms recorded at the poly(4-ABSA/GC) electrode for increasing concentrations of PCT a) 0.1 mol L^{-1} PBS (pH 7.0); b) $6x10^{-7}$- $1x10^{-4}$ mol L^{-1} PCT.

From current and concentration date of these voltammograms, calibration curve was constracted in the range from $6x10^{-7}$ to $9x10^{-6}$ mol L^{-1} of PCT in 0.1 mol L^{-1} PBS (pH 7.0) (Figure 9).

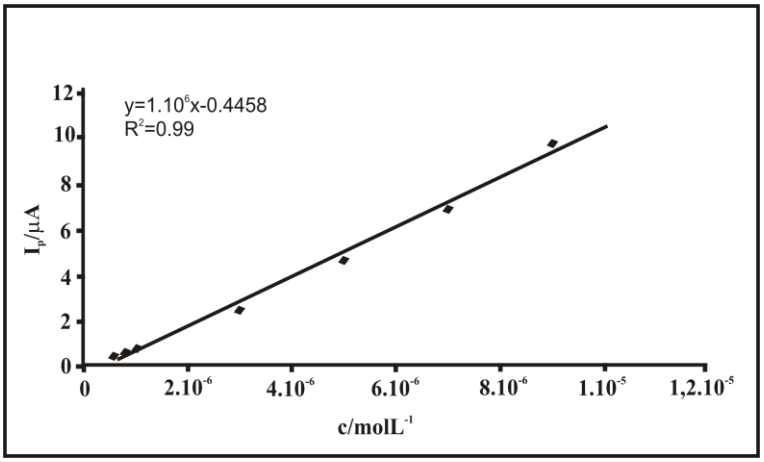


Figure 9. Plot of concentration versus current for PCT by DPV voltammograms.

The calibration curve was obtained linear in the concentration range of $6x10^{-7}$ to $9x10^{-6}$ mol L^{-1} PCT. From the regression analysis, the slope was found as $1x10^{6}$ µAM^{-1} and intercept was -0.4458 µA with the 0.9928 correlation coefficient.

Limit of detection (LOD) and quantification (LOQ) values was calculated from equations (LOD = 3 s/m, LOQ = 10 s/m) [28,30].

In here, s is the standard deviation of the peak currents (ten runs) and m is the slope of the calibration plot. LOD and LOQ were calculated as $9.33x10^{-8}$ and $3.10x10^{-7}$ mol L^{-1} respectively.

Table 1. The calibration date for determination of PCT by DPV. SD is standard deviation.

Parameters	**Results**
Measurement potential, V	0.369
Linear concentration range, M	$6x10^{-7}$ -$9x10^{-6}$ M
Slope, µA M^{-1}	$1x10^{6}$
SD of slope	24994
Intercept, nA	-0.4458
SD of intercept	0.041
Coefficient of correlation, r	0.9928
Number of measurement, n	10
LOD, mol L^{-1}	$9.33x10^{-8}$
LOQ, mol L^{-1}	$3.10x10^{-7}$

The LOD, LOQ and recovery studies was performed for the validation of the applied method for the assay of PCT by DPV methods (Table 1 and Table 2).

3.4. Analytical Applications

Calibration graph is formed using PCT standard method and used for quantitative determination. The content of PCT in commercial drug tablets was found from calibration curve (experimental section 2.5). The results are given in Table 2.

The recovery tests was applied by addition of a certain amount of active material to pre-analyzed formulations of PCT. Good recovery value was obtained (Table 2).

Table 2. Detection of PCT in parol tablet and mean value at poly(p-ABSA)- modified GCE by DPV method. RSD is relative standard deviation.

Parameters	**Results**
Labelled paracetamol, mg	500.00
found, mg	496.30
RSD / %	0.76
Bias, %	0.86
spiked PCT, mg	50.00
found, mg	49.35
Average recovery, %	98.70
RSD / %	0.57
Bias, %	1.30

% Recovery (98.70) value was showed that the applied methods could be successfully applied to PCT assay in tablets without any interference**.**

Linear range and limits of detection for PCT to the comparison of non-electrochemical method and electrochemical methods are given in Table 3.

Table 3. Linear range and limits of detection for PCT to the comparison of non-electrochemical method and electrochemical methods

Linear range	Limit of detection (LOD)	Limit of quantification (LOQ)	Method	Ref.
15–37 μg mL^{-1}	-	-	UV-vis	3
0-400 mg L^{-1}	-	-	FI-UV-vis	4
100–400 mg g^{-1}	13.0–16.7 mg g^{-1}	43.1–55.7 mg g^{-1}	fluorescence spectroscopy	5
0.1-100 μg mL^{-1}	0.1 μg mL^{-1}	-	Spectrofluorimetric	6
2–200 g mL^{-1}	0.6 μg mL^{-1}	-	electrokinetic capillary chromatography	7

$4x10^{-6}$ -$1x10^{-4}$ mol L^{-1}	1.06 μg mL^{-1}	-	Voltammetry	8
0.01- 2 mol L^{-1}	10 nM	-	AdsSV MWCNT-BPPGE	9
0.1–20 μM	3.2×10^{-8} μM	-	Square-wave voltammetry GCEs	10
$2.0x10^{-7}$–1.5x 10^{-3} mol L^{-1}	$1.8x10^{-7}$ mol L^{-1}	-	DPV(Nanogold modified-ITO)	11
4.0 $x10^{-8}$–1.0 $x10^{-4}$ mol L^{-1}	$6.8x10^{-10}$ mol L^{-1}	-	graphene oxide (ERGO)	12
0.02–100 μmol L^{-1}	0.034 μmol L^{-1}	-	DPV CFE	13
1-100 μmol L^{-1}	$2.1x10^{-7}$ μmol L^{-1}	-	Graphene-based electrochemical sensors	16
$2.0x10^{-10}$- $1.5x10^{-5}$ mol L^{-1}	$9.0x10^{-11}$ mol L^{-1}	-	Voltammetry GCE-MWCNTs	17
0.4-100 mol L^{-1}	0.21-0.32 mol L^{-1}	-	Voltammetry boron-doped diamond electrode	18
0.02–450 μmol L^{-1}	1.69 nmol L^{-1}	-	(P4VP) and (P4VP/MWCNT GCE)	19
$2.0x10^{-7}$- $1.62x10^{-5}$ mol L^{-1}	0.08 μmol L^{-1}	-	Voltammetry (PNBMGCE)	20
$6x10^{-7}$ -$9x10^{-6}$ mol L^{-1}	$9.33x10^{-8}$ mol L^{-1}	$3.1x10^{-7}$ mol L^{-1}	*p*-ABSA-GCE	Present work

4. CONCLUSION

GCE coated with poly (4-aminobenzene sulfonic acid) film was used for electrocatalytic assay of PCT. The applied modified-GCE indicated high electrocatalytic activity for PCT. The modified-GCE provides much sensitivity and selectivity in the assay of PCT. Besides, the modified electrode showed easy regeneration, good repeatability and stability. The modified-GCE can be used under selected conditions (in PBS, pH 7.0) for the determination of PCT.

It was shown that PCT can be analyzed by DPV technique based on its oxidation behaviour at poly(4-ABSA/GC electrode. These voltammetric techniques can be applied to the assay of PCT in pharmaceutical formulation.

ACKNOWLEDGEMENTS

This study was supported by Canakkale Onsekiz Mart University, Scientific Research Projects Commission (Project number FLY-2013-50). This study was derived from a master thesis *(Zeynep Bas)* supported by Graduate School of Natural and Applied Sciences, Canakkale Onsekiz Mart

University. Authors would like to thank Atabay (Istanbul, Turkey) for providing PCT and its commercial form (parol) to develop the applied voltammetric techniques.

References

1. R.T. Kachoosangi, G.G. Wildgoose, R.G. Compton, *Anal. Chim. Acta*, 618 (2008) 54.
2. R. N. Goyal, S. P. Singh, *Electrochim. Acta*, 51 (2006) 3008.
3. S. Glavanović, M. Glavanović , V. Tomišić, *Spectrochim. Acta Part A*, 157 (2016) 258.
4. M. Knochen, J. Giglio, B. F. Reis, J. *Pharm. and Biomed. Anal*., 33 (2003) 191.
5. A. B. Moreira, H. P.M. Oliveira, T. D.Z. Atvars, I. L.T. Dias, G. O. Neto, E. A.G. Zagatto, L. T. Kubota, *Analytica Chim. Acta*, 539 (2005) 257.
6. J. L. Vilchez, R. Blanc, R. Avidad, A. Navalon, *J. Pharm. and Biomed. Anal*., 13 (1995) 1119
7. D. Emre, N. Ozaltın , *J. Chromatogr. B*, 847 (2007) 126–132.
8. C. Engin, S. Yilmaz, G. Saglikoglu, S. Yagmur, M Sadikoglu, *Int. J. Electrochem. Sci*., 10 (2015) 1916.
9. M. Zidan, T. W. Tee, A. H. Abdullah, Z. Zainal, G. J. Kheng, *Int. J. Electrochem. Sci*., 6 (2011) 279.
10. X. Kang, J. Wang, H. Wu, J. Liu, I. A. Aksay, Y. Lin, *Talanta*, 81 (2010) 754.
11. R.N. Goyal, V. K. Gupta, M. Oyama, N. Bachhetti, *Electrochem. Communications*, 7 (2005) 803.
12. S. Kesavan, S. A. John, *J. Electroanal. Chem*., 760 (2016) 6.
13. A. R. Khaskheli, J. Fischer, J. Barek, V. Vyskocil, Sirajuddin, M. I. Bhanger, *Electrochim Acta*, 101 (2013) 238.
14. A. Asghari, M. Ameri, A. A. Ziarati, S. Radmannia, A. Amoozadeh, B. Barfi, L. Boutorabi, *Chinese Chemical Letters*, 26 (2015) 681.
15. P. R. Dalmasso, M. L. Pedano, G. A. Rivas, *Sensors and Actuators B*, 173 (2012) 732.
16. Y. Fan, J. -H. Liu, H.-T. Lu, Q. Zhang, *Colloids and Surfaces B*, 85 (2011) 289.
17. A. Kutluay, M. Aslanoglu, *Sensors and Actuators B*, 185 (2013) 398.
18. L. Švorc, J. Sochr, P. Tomčík, M. Rievaj, D. Bustin, *Electrochim. Acta*, 68 (2012) 227.
19. H. Ghadimi, R.M.A. Tehrani, A. S. M. Ali, N. Mohamed, S. A. Ghani, *Anal. Chim. Acta*, 765 (2013) 70.
20. S. Chitravathi, N. Munichandraiah, *J. Electroanal. Chem.*, 764 (2016) 93.
21. S.P. Kumar, K. Giribabu, R. Manigandan, S. Munusamy, S. Muthamizh, A. Padmanaban, T. Dhanasekaran, R. Suresh, V. Narayanan, *Electrochim. Acta*, 194 (2016) 116.
22. Y. E. Bouabi, A. Farahi, N. Labjar, S. E. Hajjaji, M. Bakasse, M.A. El Mhammedi, *Materials Science and Engineering C*, 58 (2016) 70.
23. F. Huang, G. Jin, Y. Liu, J. Kong, *Talanta, 74* (2008) 1435.
24. Z. Yang, G. Hu, Y. Liu, J. Zhao, G. Zhao, *Canadian J. Anal. Sci. and Spect.*, *52* (2006) 11.
25. M. Sadikoglu, G. Taskin, F. G. Demirtas, B. Selvi, M. Barut, *Int. J. Electrochem. Sci*., *7* (2012) 11550.
26. S. Can, S. Yilmaz, G. Saglikoglu, M. Sadikoglu, N. Menek, *Electroanalysis*, 27 (2015) 2431.
27. C. Demirtas, S. Yilmaz, G. Saglikoglu, M. Sadikoglu, *Int. J. Electrochem. Sci.*, 10 (2015) 1883.
28. S. Yilmaz, Electroanalytical chemistry with applied examples, *Gazi Kitabevi publishing (in Turkish)* March 2016, Ankara.
29. G. Saglikoglu, S. Yilmaz, Curr. Anal.Chem., 26 (2014) 831.
30. Z. Bas, Çanakkale Onsekiz Mart University, Graduate School of Science and Engineering Chair for Chemistry, Thesis of Master, 2014.