

Full Paper

Electrochemical Investigation of 4-Aminophenol at CTAB Modified Carbon Paste Electrode: A Cyclic Voltammetric Technique

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Abstract- 4-aminophenol is the main impurity present in preparations of paracetamol. Using the cyclic voltammetry, the electrode behaviour of 4-aminophenol has been studied in 0.1 M phosphate buffer solutions at carbon paste electrode and surfactant modified carbon paste electrode. The optimal potential window of wide range from -0.4 V to 0.7 V was selected. The electron transfer kinetics of the CTAB/CPE in the detection of analyte was determined by the scan rate effect and concentration variation studies. The scan rate effect showed the electrode process is adsorption controlled. The oxidation peak currents represented a linear dependence on 4-aminophenol concentration from 1 mM to 4 mM with correlation coefficient $r^2=0.9942$. The effect of cationic surfactant shows good high sensitivity and stability for the redox process of the 4-amino phenol. The detection limit was found to be 1×10^{-7} M.

Keywords- 4-aminophenol, CTAB Modified Carbon Paste Electrode, PBS, Cyclic Voltammetry

1. INTRODUCTION

4-aminophenol has highly toxic and mutagenic effects and induces DNA cleavage in mouse and human lymphoma cells [1,2]. Aminophenols are interesting electrochemical materials [3,4-6]. This is because, unlike aniline [7] and other substituted anilines [8], they have two oxidizable groups (NH₂ and OH) providing more reactive sites. Therefore, in principle, they could show electrochemical behavior resembling anilines [9] and phenols [10]. This compound is an intermediate in the degradation of azo dyes [11]. However, little is known about the metabolism of 4-aminophenol by bacteria [12]. 3-Nitrophenol-grown cells of *Ralstonia eutropha* JMP 134 convert nitrobenzene to hydroxylaminobenzene, 2-aminophenol and 4-aminophenol [13]. Hydroxylamino benzene is transformed by 3-nitrophenol-grown cells of *Pseudomonas putida* 2NP8 to 1,4-benzenediol via 4-aminophenol [14]. A number of reports indicated that 4-aminophenol might be a key intermediate in the biodegradation of nitrobenzenes and amines [11, 14]. 4-aminophenol is a well-known compound that has been used as a redox agent in photography [6]. In neutral media, it is oxidized to a complex oligomeric dye that can be used in enzymatic assays [15]. Voltammetric studies [16] showed that the first step of the oxidation of 4-aminophenol in organic and aqueous media on gold electrodes probably results in the uptake of one electron, producing an intermediate oxidation product (semiquinoneimine) in agreement with the literature [17,18]. Heras et al. [18] studied the electrochemical oxidation of 4-aminophenol on a mercury electrode in aqueous medium. They indicated that the electrooxidation of 4-aminophenol occurs by the loss of one proton and one electron. The next step is the loss of another electron and of a second proton to yield *p*-quinoneimine that is hydrolyzed to *p*-benzoquinone. Investigations of the modification of platinum [19-21], graphite [4] and gold [22] by polymers derived from 4-aminophenol have been carried out. Graphite electrodes coated with poly (4-aminophenol) are efficient for the immobilization of purine bases [4]. In the present work, it describes the electrochemical investigation of 4-aminophenol on CTAB modified carbon paste electrodes. Many of the analytes have been detected by cyclic voltammetric technique by our research group [23,24]. The aim of the work reported here was to investigate the electrochemical properties of 4-aminophenol on carbon paste and CTAB/CPE as well as the electrochemical characterization of electrodes by cyclic voltammetric technique. It can be applied to routine investigations of pharmaceutical preparations in the form of tablets by using the cyclic voltammetric technique.

2. EXPERIMENTAL SECTION

2.1. Reagents

4-aminophenol obtained from Sigma-Aldrich, dissolved in ethanol to prepare 10 mM standard stock solutions and stored at dark place. CTAB was dissolved in double distilled

water to form 5 mM solutions. All solutions were prepared with double distilled water, were of analytical grade and used without further purification. Phosphate buffer solution (PBS) was prepared by standard method. All experiments were performed at room temperature.

2.2 Apparatus and Procedure

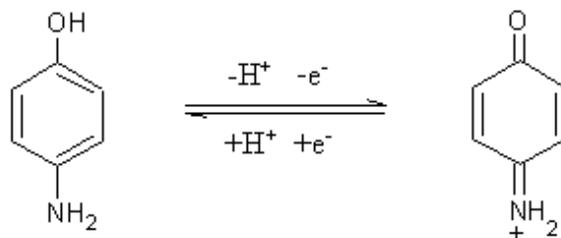
The electrochemical experiments were carried out using a Model CHI-660c electrochemical work station. All experiments were carried out in a conventional three-electrode system. The electrode system contained a working carbon paste electrode, homemade cavity of 3 mm diameter, a platinum wire as counter electrode and saturated calomel electrode as reference electrode. Bare carbon paste electrode was prepared by grinding 70% graphite powder and 30% silicon oil in an agate mortar by hand mixing for about 30 min to get homogenous mixture. The paste was packed into the cavity of CPE and smoothed on weighing paper.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Investigation of 4-amino phenol.

4-amino phenol was studied at CTAB/CPE by cyclic voltammetric study. Fig. 1 shows the cyclic voltammograms of 4-amino phenol which exhibited two good anodic peaks and a cathodic peak current at 0.1886 V, 0.3983 V and 0.1217 V respectively. At bare carbon paste electrode the reduction peak is good compared over the oxidation peak current. But at the CTAB/CPE both the oxidation peak current and reduction peak current were increased. At bare carbon paste electrode the anodic peak current could have not been properly observed. CTAB immobilized on the carbon paste electrode has formed a uniform layer which possessed a positive charged group on the electrode; the 4-amino phenol undergoes oxidation and forms a positive charge. Due to the electrostatic interaction between the positive charged 4-amino phenol and the CTAB/CPE increases the peak current which results in the good sensitivity. Scheme.1 shows the 4-aminophenol undergone oxidation with the loss of one electron and hydrogen transfer and it undergoes reduction with addition of one electron to the oxidised product of 4-aminophenol. The current sensitivity may be due to the electrostatic repulsion between the quinone moiety of the 4-aminophenol and the positively charged CTAB modified carbon paste electrode. Electron-withdrawing groups accelerate reduction whereas electron donating groups lowers reduction. Since 4-aminophenol undergoes reversible reaction the hydroxyl group of the phenol was deprotonated which gave well defined oxidation peak and followed by reduction peak.

The probable electrochemical reactions of 4-aminophenol has shown in the Scheme.1



Scheme. 1. Mechanism of electrochemical redox reaction of 4-aminophenol at CTAB/CPE

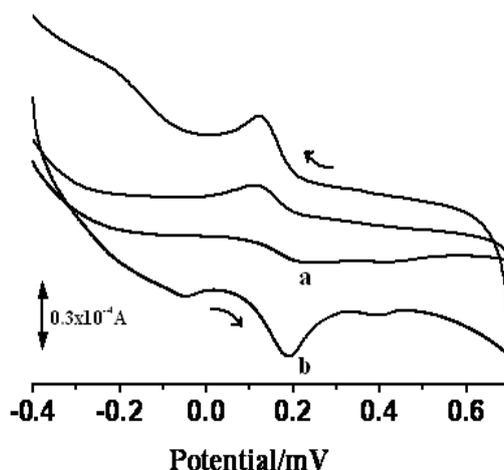


Fig. 1. Cyclic voltammogram of 1 mM *p*-aminophenol at (a) Bare Carbon paste electrode (b) CTAB/CPE in 0.1 M PBS of 7.5 pH ; Sweep rate- 100 mVs⁻¹

3.2. Effect of scan rate

The effect of scan rate on the redox of 4-aminophenol was examined in 0.1 M phosphate buffer solution of pH-7.5 as a supporting electrode. Fig. 2(a) shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 50 to 500 mVs⁻¹, suggesting that the electron transfers for 4-aminophenol at the CTAB modified CPE is adsorption controlled reaction. Fig. 2(b) shows the linear relationship between the scan rate vs. anodic peak currents of 4-amino phenol at CTAB/CPE. The cathodic peak shifted towards positive potential with increased in scan rate.

3.3. Effect of concentration of 4-amino phenol

Fig.3(a) shows the CV curves of different concentration of 4-aminophenol at CTAB/CPE was increased from 1 mM to 5 mM in 0.1 M phosphate buffer solution at pH-7.5 at a sweep rate of 100 mVs⁻¹. Both the anodic and cathodic peak current increases linearly with the

concentration of 4-aminophenol and the plot of current versus concentration obeys Randles-Sevcik equation, which implies that the electrode process is adsorption controlled reaction.

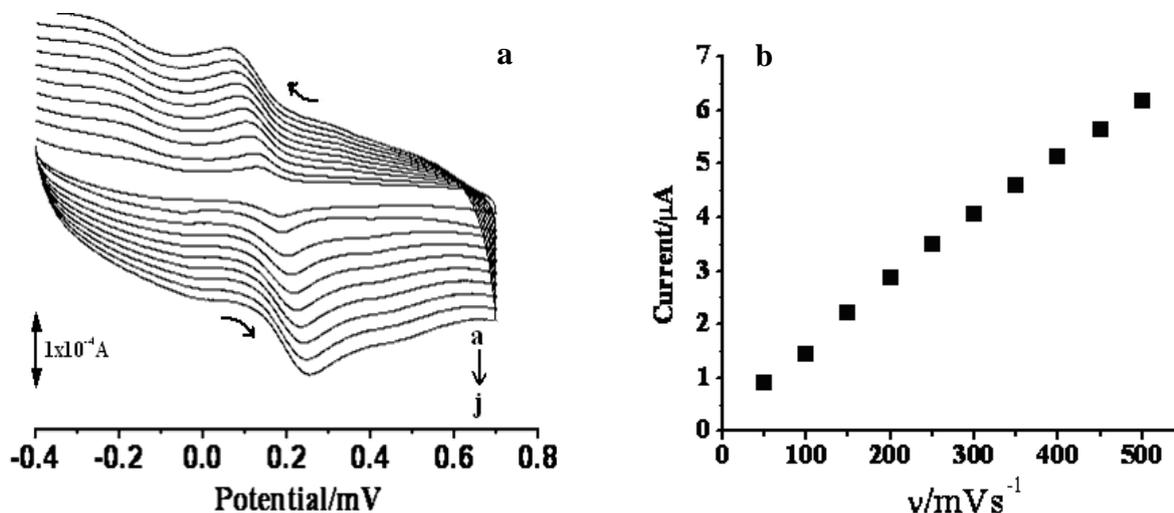


Fig. 2(a). Cyclic voltammograms of 1 mM para amino phenol in 0.1 M phosphate buffer solution at pH 7.5 using a CTAB/CPE at scan rates of (curve a) 50 mVs^{-1} , (curve b) 100 mVs^{-1} , (curve c) 150 mVs^{-1} , (curve d) 200 mVs^{-1} , (curve e) 250 mVs^{-1} , (curve f) 300 mVs^{-1} , (curve g) 350 mVs^{-1} , (curve h) 400 mVs^{-1} , (curve i) 450 mVs^{-1} , (curve j) 500 mVs^{-1} , **(b).** Plot of anodic peak current vs. scan rate

As the concentration increases the first anodic peak potential is followed by the another anodic peak with the peak potential difference of 230 mV is due to the adsorption of first oxidised product and allowed the following scan at stepwise oxidation process. It was also observed that the cathodic peak potential shift towards negative values and anodic peak potential shift towards positive side. This kind of shift in E_p in the cathodic and anodic direction with increasing concentration of the 4-aminophenol indicates that the product of 4-aminophenol molecules are adsorbed over the electrode surface. The plot of current versus the concentration gives correlation coefficient value of $r^2=0.9942$ (Fig. 3b) which revealed the electrode process is adsorption controlled process. The detection limit of 4-aminophenol at CTAB/CPE was 10^{-7} M.

3.4. Effect of pH variation of buffer solution

In most cases, the solution pH is important to the electrochemical reaction. The pH was varied in the range from 5.0 to 9.0 with the 0.5 interval difference using 0.1 M phosphate buffer as the supporting electrolyte. Fig. 4(a) shows the cyclic voltammograms of the 4-aminophenol at different pH. The anodic peak potential shifted towards positive side and

cathodic peak potential E_{pc} shifted towards more negative potential. The anodic and cathodic peak current of 4-aminophenol increased at pH- 7.5. Fig. 4(b) shows the graph of different pH versus peak current, it could be confirmed that at pH 7.5 the electrode acts as a good sensor.

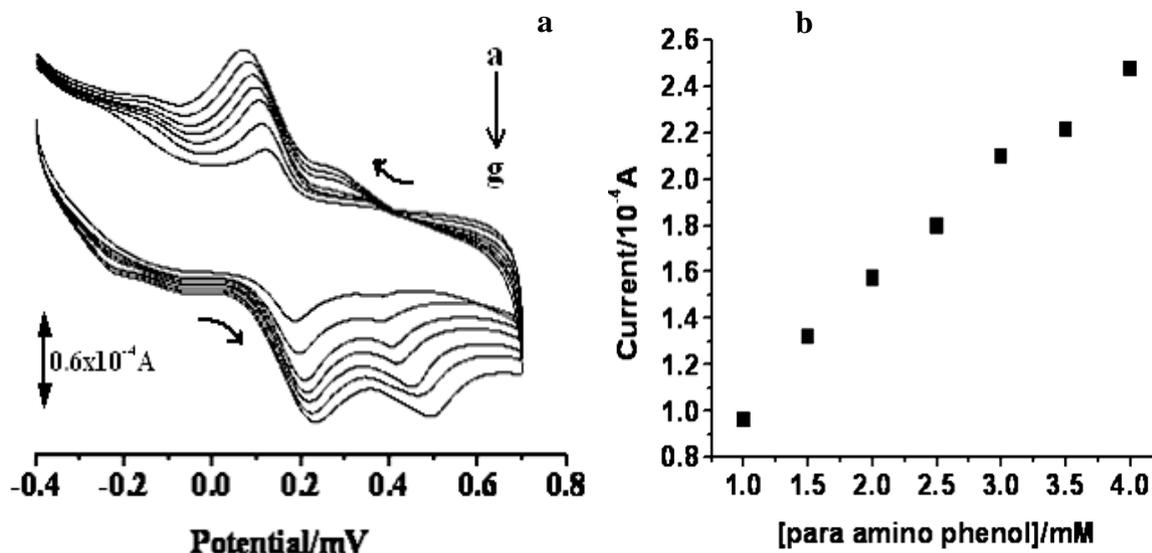


Fig. 3(a). Cyclic Voltammograms of different concentration of para amino phenol (a-g: 1 mM to 4 mM) at CTAB/CPE in 0.1 M PBS. Sweep rate – 100 mVs^{-1} (b). Plot of peak current vs. concentration of 4-aminophenol. Scan rate: 100 mV/s

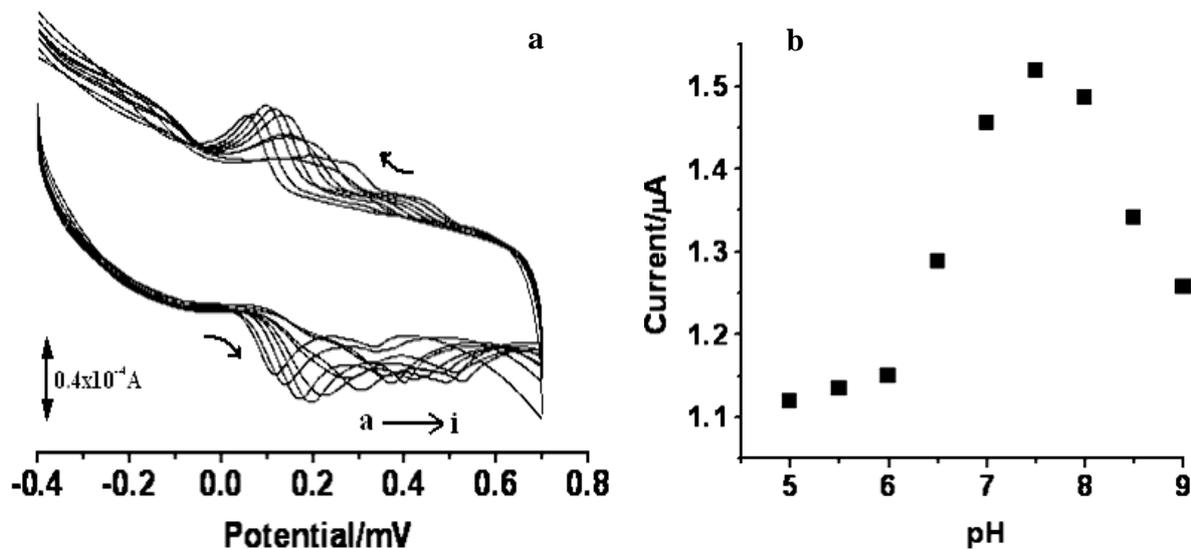


Fig. 4(a). Effect of pH on the oxidation of 4-aminophenol at the CTAB modified CPE (b). Plot of the relationship between solution pH and the oxidation peak current

3.5. Effect of Surfactant

Surfactants even in trace quantities can exert a strong effect on the electrode process. Adsorption of such substances at the electrode may inhibit the electrolytic process, bring about the irregularity in the voltammogram and cause shift in the wave to negative potential [26, 27]. The effect of surfactant concentration on 4-amino phenol oxidation/reduction peak currents are shown in Fig. 5(a) for immobilized form modified carbon paste electrode. The CTAB/CPE could increase the peak current due to the electrostatic interaction between the modifier and 4-aminophenol. 4-aminophenol has slight hydrophilic character which leads to the uniform distribution in the aqueous media. The peak current increases linearly with the increase in concentration of surfactant and optimised at 10 μL above which the voltammogram peak current could not be observed due to their high background current. The oxidation peak potential shift towards positive side and the reduction peak potentials tends to shift towards negative side. Hence the CTAB modified carbon paste electrode acts as good sensor for the determination of dopamine.

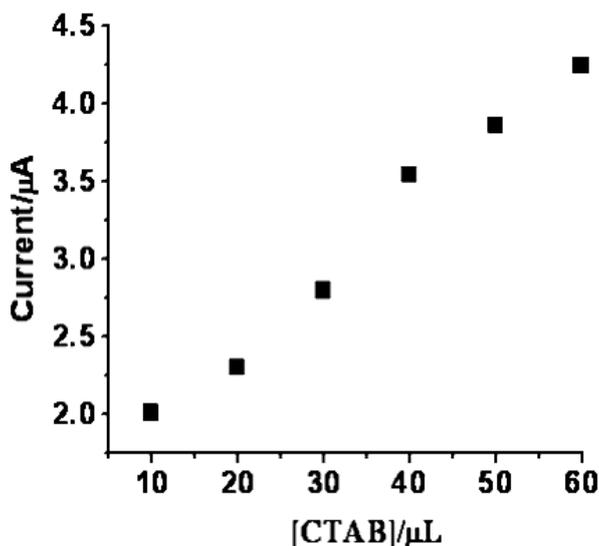


Fig. 5. Effect of different concentration of CTAB immobilised on the carbon paste electrode for cyclic voltammogram of 1 mM 4-aminophenol. Sweep rate- 100 mVs^{-1}

3.6. Stability and reproducibility of CTAB/CPE

Modified carbon paste electrode was switched into the sample was kept at room temperature and used the same without made it changes for the determination of 4-amino phenol. The current sensitivity of the modified electrode has been kept for one week is almost same as that of the freshly prepared modified electrode. Hence the relative stability of the CTAB/CPE is good and reproducibility upto 98%.

4. CONCLUSION

The modified electrode increased the amplitude of the current signal of 4-aminophenol when compared to non-coated carbon paste electrode and produced good response. A modified CTAB/CPE study revealed that 10 μ L CTAB in carbon paste electrode enhanced the electrocatalytic activity of 4-aminophenol. The effect of the CTAB surfactant showed the formation of monolayer on the bare carbon paste electrode which could have made the better sensor for the detection of 4-aminophenol and also exhibited the good reproducibility.

REFERENCES

- [1] J. B. Majeska, and H. E. Holden, *Environ. Mol. Mutagen.* 26 (1995) 163.
- [2] R. Yoshida, S. Oikawa, Y. Ogawa, Y. Miyakoshi, M. Ooida, K. Asanuma, and H. Shimizu, *Mutat. Res.* 415 (1998) 139.
- [3] C. Barbero, J. J. Silber, and L. Sereno, *J. Electroanal. Chem.* 291(1990) 81.
- [4] A. G. Brito-Madurro, L. F. Ferreira, S. N. Vieira, R. G. Ariza, L. R. Goulart-Filho, and J. M. Madurro, *J. Mater. Sci.* 42 (2007) 3238.
- [5] H. J. Salavagione, J. Arias-Pardilla, J. M. Perez, J. L. Vazquez, E. Morallon, M. C. Miras, and C. Barbero, *J. Electroanal. Chem.* 576 (2005) 139.
- [6] R. Andreozzi, M. S. L. Casale, R. Marotta, G. Pinto and A. Pollio, *Water. Res.* 34 (2000) 4419.
- [7] H. Yang, and A. J. Bard, *J. Electroanal. Chem.* 339 (1992) 423.
- [8] K. Yamada, K. Teshima, N. Kobayashi, and R. Hirohashi, *J. Electroanal. Chem.* 394 (1995) 71.
- [9] M. A. V. Garcia, P. T. Blanco, and A. Ivaska, *Electrochim. Acta* 43 (1998) 3533.
- [10] M. Gattrell, and D. W. Kirk, *J. Electrochem. Soc.* 139 (1992) 2736.
- [11] N. C. G. Tan, F. X. Prenafeta-Boldu, J. L. Opsteeg, G. Lettinga, and J. A. Field, *Appl. Microbiol. Biotechnol.* 51 (1999) 865.
- [12] S. Ahmed, M. A. Javed, S. Tanvir, and A. Hameed, *Biodegradation.* 12 (2001) 303.
- [13] A. Schenzle, H. Lenke, P. Fischer, P. A. Williams, and H. J. Knackmuss, *Appl. Environ. Microbiol.* 63 (1997) 1421.
- [14] J. S. Zhao, A. Singh, X. D. Huang, and O. P. Ward, *Appl. Environ. Microbiol.* 66 (2000) 2336.
- [15] W. Sun, K. Jiao, S. Zhang, C. Zhang, and Z. Zhang, *Anal. Chim. Acta* 434 (2001) 43.
- [16] J. Schwarz, W. Oelbner, H. Kaden, F. Schumer, and H. Hennig, *Electrochim. Acta* 48 (2003) 2479.
- [17] S. Ma, Y. Wu, and Z. Wang, *J. Electroanal. Chem.* 464 (1999) 176.
- [18] A. M. Heras, J. L. Avila, J. J. Ruiz, and F. García-Blanco, *Electrochim. Acta* 29 (1984) 541.

- [19] H. A. Menezes, and G. Maia, *J. Electroanal. Chem.* 586 (2006) 39.
- [20] S. Taj, M. F. Ahmed, and S. Sankarapapavinasam, *J. Electroanal. Chem.* 338 (1992) 347.
- [21] J. Shan, L. Han, F. Bai, and S. Cao, *Polym. Adv. Technol.* 14 (2003) 330.
- [22] L. F. Ferreira, J. F. C. Boodts, A. G. Brito-Madurro, and J. M. Madurro, *Polym. Int.* 57 (2008) 644.
- [23] B. N. Chandrasheka, B. E. K. Swamy, M. Pandurangachar, S. S. Shankar, O. Gilbert, J. G. Manjunatha, and B. S. Sherigara, *Int. J. Electrochem. Sci.* 5 (2010) 578.
- [24] B. E. Kumara Swamy, E. V. S. Subrahmanyam, B. S. Sherigara, and G. Venkateswaran, *Bulletin. Of. Electrochemistry* 16 (2000) 533.
- [25] J. Herovsky, and J. Rute, *Principles. Of. Polarography* (Academic Press, New York) (1965).
- [26] E. Niranjana, R. Ragavendra Naik, B. E. Kumara Swamy, B. S. Sherigara, and H. Jayadevappa, *Int. J. Electrochem. Sci.* 2 (2007) 923.