

*Full Paper*

## **Acetanilide Modified Carbon Paste Electrode for the Electrochemical Detection of Dopamine: A Cyclic Voltammetric Study**

**Sarojini Sharath Shankar, Bahaddurghatta E. Kumara Swamy\*, Kurangalara R. Mahanthesha, Tammanekar V. Sathisha and Chandrashekar C. Vishwanath**

*Department of PG Studies and Research in Industrial Chemistry, Kuvempu University, Shankaraghatta-577451, Shimoga, Karnataka, India*

\*Corresponding Author, Tel.:+91-8282-256228, Fax: +91-8282-256255

E-Mail: [kumaraswamy21@yahoo.com](mailto:kumaraswamy21@yahoo.com)

*Received: 29 September 2012 / Accepted: 3 February 2013 / Published online: 28 February 2013*

---

**Abstract-** The acetanilide modified carbon paste electrode (ANMCPE) was used for the voltammetric response of dopamine (DA) in an aqueous phosphate buffer solution (PBS). Modified carbon paste electrode was prepared by grinding the 5 mg of acetanilide (AN) with the mixture of graphite powder and silicon oil. Cyclic Voltammetric study improved the reversibility of the DA on the modified electrode. The effect of various experimental parameters such as acetanilide concentration, scan rate, and pH on the voltammetric response of DA was investigated. Under the chosen conditions, the differential pulse voltammetry peak current was found to be linear with DA concentration. The detection limit for modified electrode was found to be  $6 \times 10^{-7}$  M for DA determination.

**Key Words-** Electrocatalytic Oxidation, Acetanilide, Dopamine, Cyclic Voltammetry, Carbon Paste Electrode

---

### **1. INTRODUCTION**

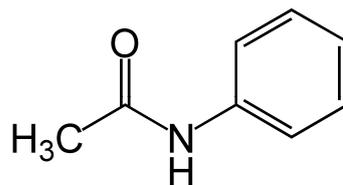
Carbon paste electrodes have been extensively employed in various electrochemical detection schemes due to their simple and fast preparation, facile surface renewing,

biocompatibility, non-toxic character, and relatively low-background characteristics [1-3]. Furthermore, carbon paste-based electrode material is extremely attractive for its subsequent bulk modification with different modifiers, e.g. electrocatalysts and/or enzymes by simply mixing them into the carbon paste matrix [4–9]. In addition to surface modification of carbon paste electrodes with thin metal films [10-11], (bio)recognition elements [12-14] and or protective membranes [15-16] is/are also widely applicable, although their bulk modification is more convenient and common. Mostly, carbon paste electrodes are used as conventional size electrodes in combination with different holders which facilitate their manipulation and renewing of the electrode surface.

Dopamine (DA) is a neurotransmitter occurring in wide variety of animals; including both vertebrates and invertebrates [17] is produced in several areas of the brain, including the substantia nigra and the ventral segmental area. DA is also a neurochrome released by the hypothalamus. Its main function as a hormone is to inhibit the release of prolactin from the anterior lobe of the pituitary. Dysfunction of the dopaminergic system in the central nervous system is related to neurological disorders such as schizophrenia and Parkinson's disease [18]. Therefore, real time monitoring of the DA level in real system shows an important issue in diagnosis of diseases. The fact that DA and other catecholamines are easily oxidizable compounds makes their detection possible by electrochemical methods based on anodic oxidation [19-23]. Determination of DA has been studied by different modified electrodes [24-33]. Venton et al. reported on the psychoanalytical electrochemistry of dopamine and behavior [34]. The modified electrodes were prepared by using different type of materials [35-39].

Acetanilide is an odorless, white flake solid or crystalline powder and it is used as an inhibitor of peroxides and stabilizer for cellulose ester varnishes. It is also used as a precursor in penicillin synthesis and other pharmaceuticals including painkillers and intermediates. It acts as an intermediate for the synthesis of rubber accelerators, dyes and dye intermediate and camphor (Scheme 1).

In continuation of our studies concerning the preparation of modified electrodes for the detection of DA [40-44], in the present work, we found that acetanilide modified carbon paste electrode (ANMCPE) possessing high stability and good electrocatalytic activity toward the electrocatalytic oxidation of DA. Cyclic voltammetry was used to characterize the electrochemical properties of the ANMCPE and to investigate its electrocatalytic effect on DA oxidation. Differential pulse voltammetry (DPV) was also used to evaluate the analytical performance of the modified electrode.



**Scheme 1.** Structure of acetanilide

## 2. EXPERIMENTAL PART

### 2.1. Reagents and Chemicals

Acetanilide, Dopamine hydrochloride, Potassium ferrocyanide, was obtained from Himedia chemical company. All chemicals were of analytical grade quality and were used without further purification. The water used was a double distilled. Dopamine stock solutions was prepared by adding dopamine to 0.1M perchloric acid and kept in darkness. In all the measurements, the supporting electrolyte used was 2 M phosphate buffer (pH 7).

### 2.2. Apparatus and Procedure

Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) were performed on Model EA-201 Electroanalyser (EA-201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire counter electrode and a potassium chloride (KCl) saturated calomel reference electrode (SCE).

### 2.3. Preparation of ANMCPE

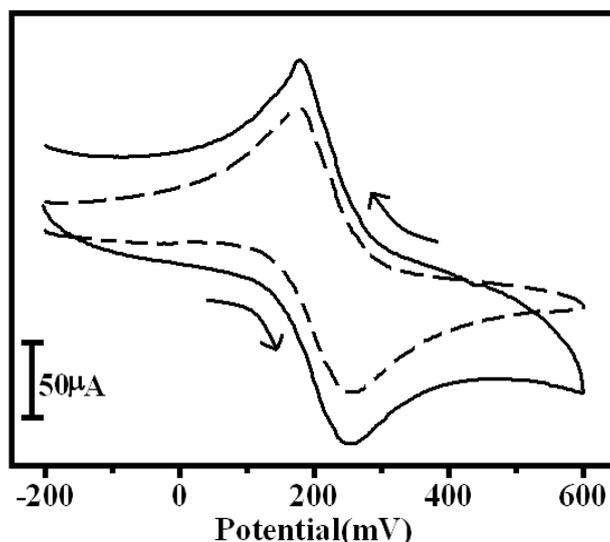
ANMCPE was prepared by thoroughly hand-mixing AN (5.0 mg), graphite powder (70%) and silicon oil (30%) in an agate mortar with a pestle for about 30 min to get homogenous ANMCPE. The modified carbon paste was packed into the hole of the electrode body and leveled off with a spatula and smoothed on a weighing paper. The BCPE was prepared without adding acetanilide. The pH was measured with a Digital pH meter MK IV model.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical response of $K_4Fe(CN)_6$ at ANMCPE

The electrochemical response of  $K_4Fe(CN)_6$  at ANMCPE was shown in Fig. 1 at a scan rate of  $50 \text{ mV s}^{-1}$ . At bare carbon paste electrode (BCPE) the voltammogram of  $K_4Fe(CN)_6$  showed electrochemical response (dashed line) with reversible behavior in 1 M KCl as supporting electrolyte. However, the voltammetric response was apparently improved at

ANMCPE (solid line) with well defined oxidation and reduction peaks due to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple were observed. At BCPE the anodic peak potential ( $E_{\text{pa}}$ ) was found to be 258 mV and cathodic peak potential ( $E_{\text{pc}}$ ) 176 mV (vs. SCE). The separation of redox potential peaks ( $\Delta E_{\text{p}}$ ) 82 mV. At ANMCPE, a pair of redox peak obtained with increase in both anodic cathodic peak current. The  $E_{\text{pa}}$  was found at 250 mV and  $E_{\text{pc}}$  at 181 mV. The separation of redox potential peaks  $\Delta E_{\text{p}}$  was found to be 69 mV.



**Fig. 1.** Cyclic Voltammograms of BCPE (dotted line) and ANMCPE (Solid line) in the presence of  $1 \times 10^{-3}$  M potassium ferrocyanide and 2 M potassium chloride solution, Scan rate  $50 \text{ mV s}^{-1}$

### 3.2. Effect of Acetanilide concentration

By increasing the quantity of acetanilide in the modification, the electrochemical cathodic ( $I_{\text{pc}}$ ) and anodic peak current ( $I_{\text{pa}}$ ) goes on increasing at certain ratio. The effect of concentration of acetanilide ranging from 1 mg to 11 mg on the CVs of  $0.5 \times 10^{-4}$  M DA in 0.2 M phosphate buffer solution pH 7 was studied. The Fig. 2A shows the plot of anodic peak current verses acetanilide (mg). As the figure illustrates DA oxidation peak is enhanced up-to 5 mg of the modifier and then decreases when the amount of modifier is increased further. Therefore 5 mg is used for the preparation of MCPE.

### 3.3. Material characterization

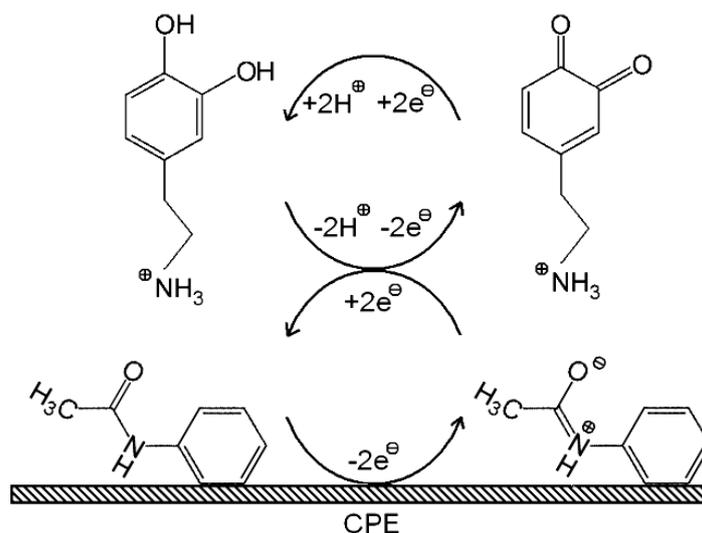
To characterize the surface morphology of the electrode scanning electron microscopic images were taken. The SEM image for BCPE and MCPE has shown in Fig. 2B and Fig. 2C and the surface morphology of BCPE and MCPE were entirely different form each other .The SEM image for BCPE shows only the mixture of graphite powder and silicon oil. But for the

acetanilide MCPE the microscopic image has shown the uniform distribution of acetanilide crystal with the mixture of graphite powder and silicon oil. From this observation it is clear that acetanilide crystals were distributed in the carbon paste electrode homogeneously.

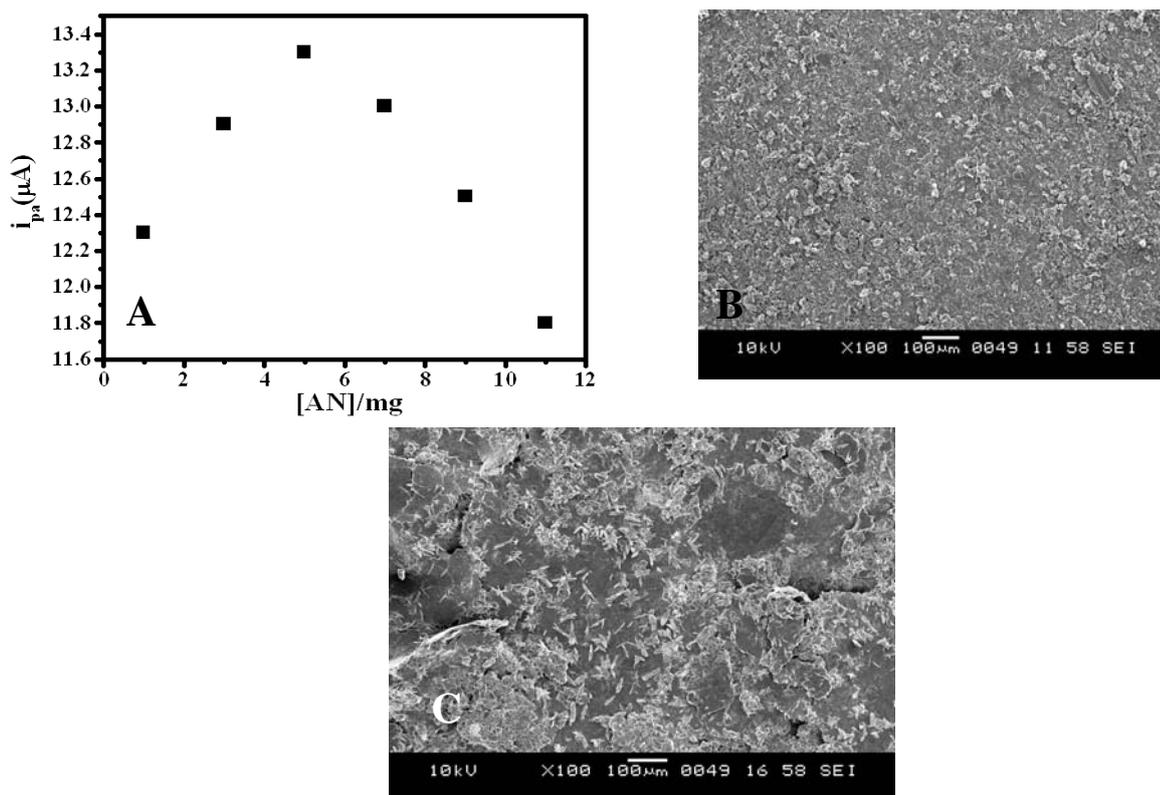
### 3.4. Electrocatalytic behaviour of dopamine on ANMCPE

The electrochemical response of  $0.5 \times 10^{-4}$  M DA at the BCPE and ANMCPE were shown in Fig. 3 with  $50 \text{ mV s}^{-1}$  scan rate owing to the complex properties and roughness of the electrode surface. The cyclic voltammogram of DA in the absence of acetanilide was low signal (dashed line), however the voltammetric response was improved in the presence of acetanilide, reflected by the enlargement of both anodic and cathodic peak currents (solid line).

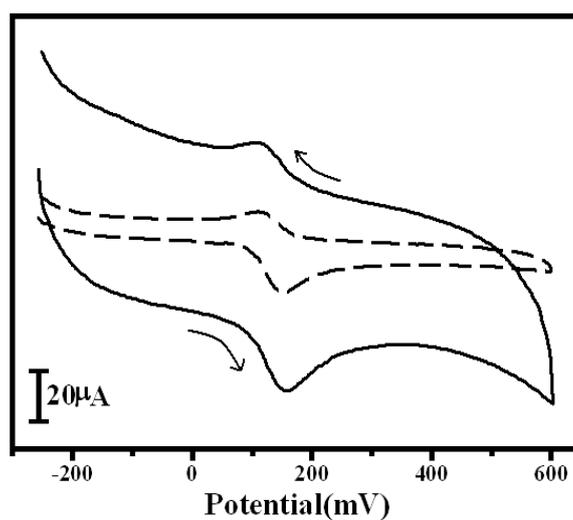
The probable mechanism for this enhancement current was given in scheme 2. During the scanning towards the positive direction the highly electronegative oxygen atom of keto group present in the acetanilide molecule could takes the electron towards itself and become more electron rich. This highly electronegative oxygen atom could exert strong electrostatic attraction with the cation present in the dopamine molecule and enhance the rate of electron transfer by converting dopamine to dopa ortho quinone, hence the acetanilide modified carbon paste electrode shows more current enhancement when compared to the bare carbon paste electrode. While in reverse scan both dopa ortho quinone, and anionic acetanilide get back their original position.



**Scheme 2.** Oxidation mechanism of dopamine at the surface of acetanilide modified carbon paste electrode



**Fig. 2.** A) Plot of current vs. concentration of acetanilide (from 1-11 mg) in  $0.5 \times 10^{-4}$  M DA and 2 M PBS 7, Scan rate  $50 \text{ mV s}^{-1}$ , B) Scanning electron microscopic image of bare carbon paste electrode, C) Scanning electron microscopic image of acetanilide modified carbon paste electrode



**Fig. 3.** Cyclic Voltammograms of  $0.5 \times 10^{-4}$  M DA at BCPE (dotted lines) and ANMCPE (solid line) at scan rate  $50 \text{ mV s}^{-1}$  in 0.2 M PBS (pH 7)

### 3.5. Scan rate effect

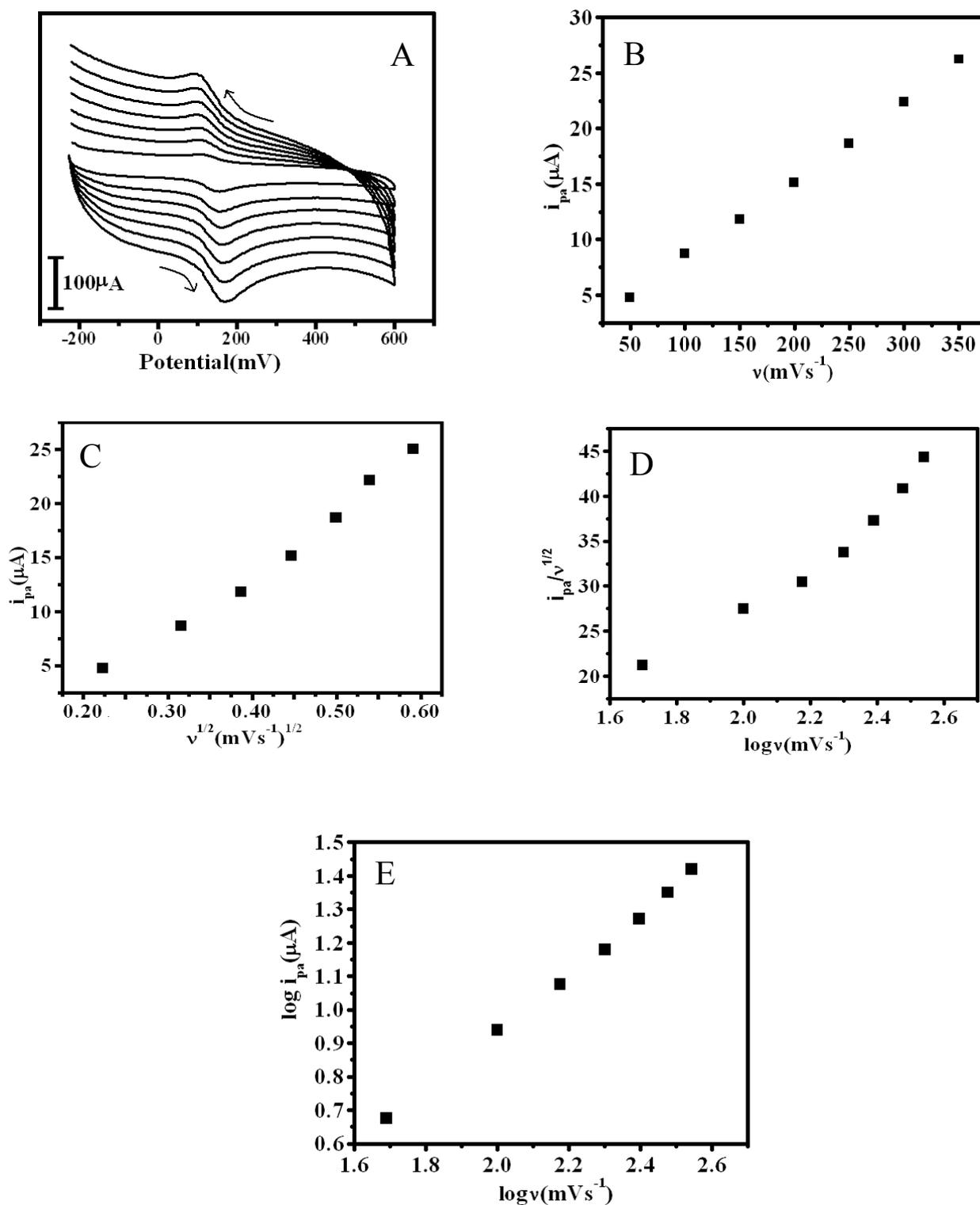
The effect of scan rate on the anodic peak current of DA was investigated experimentally. Fig. 4A. shows the CVs obtained from  $0.5 \times 10^{-4}$  M DA in 0.2 M PBS pH 7 at ANMCPE. While increasing the scan rate from 50 to 350  $\text{mV s}^{-1}$  both the anodic and cathodic peaks are increasing. The anodic peak current was proportional to the scan rate in the range from 50 to 350  $\text{mV s}^{-1}$  as shown in Fig. 4B. The linearity of the plot was good and the correlation coefficient was 0.99771. It was therefore assumed that the electrode reaction of DA at the ANMCPE was typical of an adsorption controlled process. Further the study shows that a good linear relationship was obtained between the anodic peak current and square root of scan rate (Fig. 4C) in the same range with correlation coefficient 0.99759 which indicates a diffusion controlled process occurring at the ANMCPE. The plot of  $i_p/v^{1/2}$  vs.  $\log v$  (Fig.4D) indicated an increase in the peak current with an increase in sweep rate and also the slope of  $\log i_{pa}$  vs.  $\log v$  (Fig. 4E) was 0.8608 which is larger than theoretical expected value 0.53 for purely diffusion controlled process [45] from all these results the anodic process is dominated by both adsorption and diffusion controlled for DA simultaneously.

### 3.6. Effect of concentration of dopamine at ANMCPE

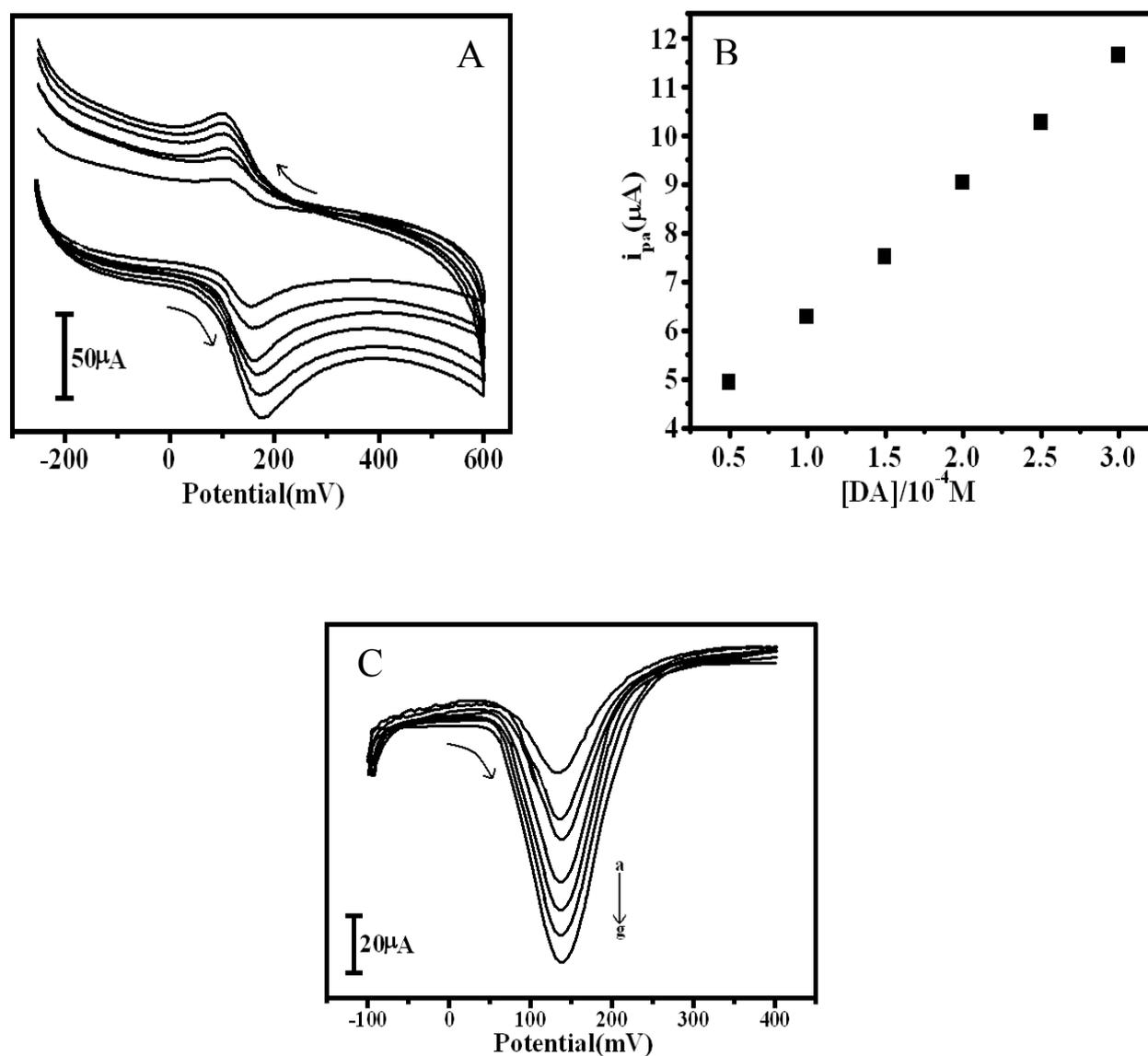
Response of various concentrations of DA at ANMCPE in the range of  $0.5 \times 10^{-4}$ - $3 \times 10^{-4}$  M was studied. From the Fig. 5A. Increasing the concentration of DA both the anodic and cathodic peak increases. The Fig. 5B shows graphical interdependence between concentration and the anodic oxidation current of DA at the ANMCPE. From the plot it is clear that there is a linear enhancement in anodic peak current with the DA concentration.

**Table 1.** Determination results of DA in injection (n=10)

Sample	Content ( $\text{mg mL}^{-1}$ )	Found ( $\text{mg mL}^{-1}$ )	Recovery (%)	RSD(%)(n=10)
1	10.0	9.9	99	2.3
2	10.0	10.2	102	1.8
3	10.0	10.1	101	1.9
4	10.0	9.9	99	2.5
5	10.0	9.8	98	2.8



**Fig. 4.** A) Cyclic Voltammograms for the effect of variation of scan rate of dopamine from 50–350  $\text{mV s}^{-1}$  in 0.2 M PBS (pH 7), B) Plot of current vs. scan rate, C) Plot of current vs. square root of scan rate, D) Plot of  $i_p/v^{1/2}$  vs.  $\log v$ , E) Variation of the logarithm of peak current with the logarithm of the



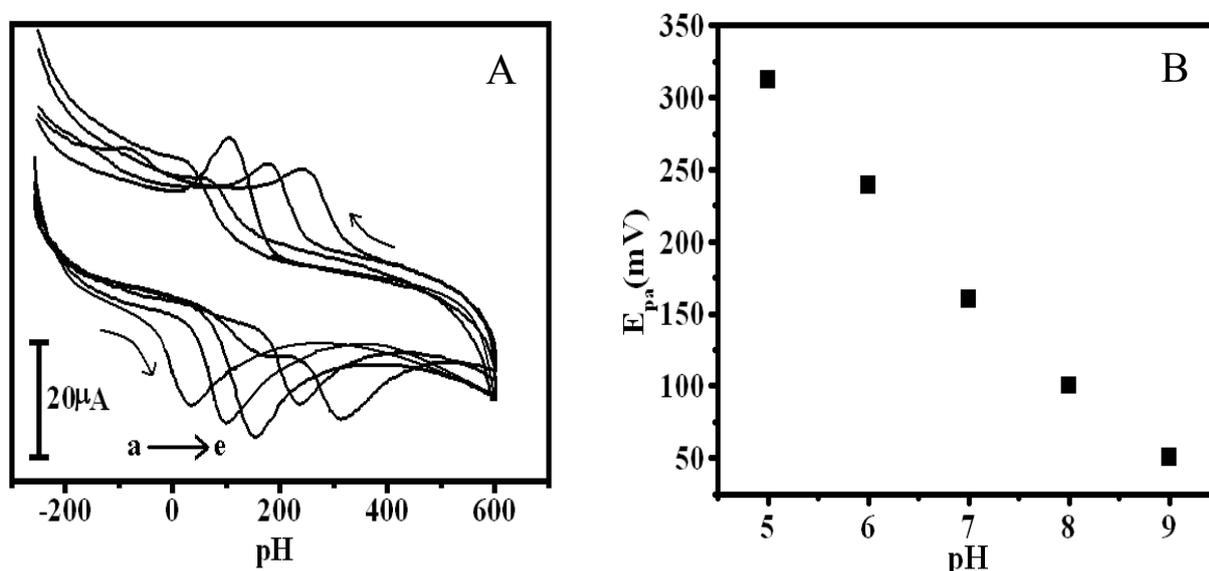
**Fig. 5.** **A)** Cyclic Voltammograms obtained for different concentration of DA ( $0.5 \times 10^{-4}$  to  $4 \times 10^{-4}$  M.) in 0.2 M phosphate buffer solution at pH 7 scan rate  $50 \text{ mV s}^{-1}$ , **B)** The plots of the anodic peak as a function of DA concentration, **C)** Differential pulse voltammograms of ANMCPE in 0.2 M PBS (pH 7) containing different concentrations of DA (a-g):  $0.5 \times 10^{-4}$ ,  $1 \times 10^{-4}$ ,  $1.5 \times 10^{-4}$ ,  $2 \times 10^{-4}$ ,  $2.5 \times 10^{-4}$ ,  $3 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$  M

Fig. 5C shows the differential pulse voltammograms (DPVs) obtained for the oxidation of different concentrations of DA at the ANMCPE. Since DPV has a much higher current sensitivity and better resolution than cyclic voltammetry, it was used to estimate the lower limit of detection of DA. In addition, the charging current contribution to the background current, which is a limiting factor in the analytical determination, is negligible in DPV mode. The DA concentration was varied from  $0.5 \times 10^{-4}$  to  $4 \times 10^{-4}$  M. The anodic peak current of DA

was increased with respect to the concentration of DA without shifting the peak potential and the detection limit was found to be  $6 \times 10^{-7}$  M. From the analysis the ANMCPE is stable and does not undergo surface fouling during the voltammetric measurements. This result also demonstrates the fact that the results obtained at the ANMCPE are reproducible.

### 3.7. Effect of pH

To optimize the electrochemical response of modified carbon paste electrode for the oxidation and reduction of DA, the effect of pH on the electrode response was studied. The effect of solution pH over the range 5 to 9 was investigated. Fig. 6A shows the cyclic voltammogram of  $0.5 \times 10^{-4}$  M DA at different pH. As shown in the figure a well distinguishable voltammogram was obtained at pH 7 PBS. The results indicate that at pH 7 the oxidation and reduction of DA was better as compared to other pH. Therefore physiological pH was chosen as the experimental pH value in the electrochemical detection of DA. The influence of pH on the anodic peak potential of DA was also investigated (Fig. 6B) in the pH range from 5 to 9, the anodic peak potential decreases with increase of pH which indicates that uptake of electrons is accompanied by equal number of protons. Since DA involves a two electrons change process the number of electrons and protons will be equal to two.



**Fig. 6.** A) Cyclic Voltammograms for the effect of variation of pH of PBS in  $0.5 \times 10^{-4}$  DA at scan rate  $50 \text{ mV s}^{-1}$  (a-e): 5, 6, 7, 8 and 9, B) Plot of anodic peak potential vs. pH

### 3.8. Sample analysis

The modified electrode was also used to analyze the DA in injection samples. The injection samples were used after suitable dilution. The results are shown in Table 1. The

results were satisfactory and the ANMCPE could be efficiently used for the determination of DA in injection.

#### 4. CONCLUSIONS

Acetanilide modified carbon paste electrode has been fabricated. SEM has been used to characterize the surface morphology of the working electrode. This study has indicated that the chemically modified acetanilide carbon paste electrode acts as a good sensor, exhibited strong promoting effect and stability towards the electrochemical oxidation of dopamine at pH 7 in phosphate buffer solution. The electrochemical behavior of the modified electrode is strongly dependent on solution pH. Electrochemical process was found to be both adsorption and diffusion controlled. The low cost and easy of preparation; the acetanilide modified carbon paste electrode seems to be great utility for further sensor development. The proposed method has been applied for detecting DA in real sample with satisfactory results.

#### REFERENCES

- [1] K. Kalcher, J.-M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, and Z. Yang, *Electroanal.* 7 (1995) 5 .
- [2] H. Samo, and B. Ogorevc, *Talanta* 74 (2007) 405.
- [3] K. Vytras, I. Svancara, and R. Metelka, *J. serb. Chem. Soc.* 74. (2009) 1021 .
- [4] S. B. Hocevar, I. Svancara, K. Vytras, and B. Ogorevc, *Electrochim. Acta* 51 (2005) 706 .
- [5] G. L. Luque, M. C. Rodriguez, and G. A. Rivas, *Talanta* 66 (2005) 467.
- [6] P. Kotzian, P. Brazdilov, K. Kalcher, K. Handlir, and K. Vytras, *Sens. Actuator B*, 124 (2007) 297.
- [7] J. Wang, L. Chen, S. B. Hocevar, and B. Ogorevc, *Analyst* 125 (2000) 1431.
- [8] B. Rezaei, S. Meghdadi, and M. Rezazadeh, *J. Anal Chem.* 64 (2009) 513.
- [9] G. U. Flechsig, M. Kienbaum, and P. Grundler, *Electrochem. Commun.* 7 (2005) 1091.
- [10] K. Schachl, H. Alemu, K. Kalcher, J. Jezkova, I. Svancara, and K. Vytras, *Analyst* 122 (1997) 985.
- [11] B. S. Sherigara. Y. Shivaraj, R. J. Mascarenhas, and A. K. Satpati, *Electro. Chim. Acta* 52 (2007) 3137.
- [12] E. V. Ivanova, V. S. Sergeeva, J. Oni, C. Kurzawa, A. D. Ryabov, and W. Schuhmann, *Bioelectrochem.* 60 (2003) 65.
- [13] C. Nistor, J. Emneus, L. Gorton, and A. Ciucu, *Anal. Chim. Acta* 387 (1999) 309.
- [14] X. Yang, F. Wang. And S. Hua, *Colloid. Surface. B* 52 (2006) 8.
- [15] J. Zheng, and X. Zhou, *Bioelectrochem.* 70 (2007) 408.

- [16] S. Alpat, S. K. Alpat, and A. Telefoncu, *Anal. Bioanal. Chem.* 383 (2005) 695.
- [17] R. M. Wightman, C. Amatorh, R. C. Engstrom, P. D. Hale, E. W. Kristensen, W. G. Kubr, and L. J. May, *Neurosci.* 25 (1988) 513.
- [18] G. Z. Hu, D. P. Zhang, W. L. Wu, and Z. S. Yang, *Colloid. Surface. B* 62 (2008) 199.
- [19] A. Ciszewski, and G. Milczarek, *Anal. Chem.* 71(1999) 1055.
- [20] L. Yavich, and J. Tiihonen, *J. Neurosci. Meth.* 104 (2000) 55.
- [21] H. Zhao, Y. Zhang, and Z. Yuan, *Anal. Chim. Acta* 441 (2001) 117.
- [22] E. Shams, A. Babaei, A. R. Taheri, and M. Kooshki, *Bioelectrochem.* 75 (2009) 83 .
- [23] M. Chen, and H. Li, *Electroanal.* 10 (1998) 477.
- [24] L. Zhang, and Y. G. Sun, *Anal. Sci.* 17(2001) 939.
- [25] X. Cao, L. Luo, Y. Ding , X. Zou, and R. Bian, *Sens. Actuators B* 129 (2008) 941.
- [26] Z. Nasri, and E. Shams, *Electrochim. Acta* 54 (2009) 7416.
- [27] X. L. Wen, Y. H. Jia, and Z. L. Liu, *Talanta* 50 (1999) 1027.
- [28] L. Zhang, and X. Jiang, *J. Electroanal. Chem.* 583 (2005) 292.
- [29] S. Alwarappan, K. S. A. Butcher, and D. K. Y. Wong, *Sens. Actuators B* 128 (2007) 299.
- [30] R. E. Sabzi, S. Zare, K. Farhadi, and G. Tabrizivanda, *J. Chin. Chem. Soc.*52 (2005) 1079.
- [31] W. Sun, M. Yang, and K. Jiao, *Anal. Bioanal. Chem.* 389 (2007) 1283.
- [32] M. Ates, K. Yilmaz, A. Shahryari, S. Omanovic, and A. S. Sarac, *Sens. J.* 8 (2008) 1628 .
- [33] S. L. Suely, Castro, R. J. Mortimer, M. F. de Oliveira, and N. R. Stradiotto, *Electrode. Sensors* 8 (2008) 1950.
- [34] B. Jill Venton and R. Mark Wightman, *Anal. Chem.* 75 (2003) 414 A.
- [35] Y. Chen, L. R. Guo, W. Chen, X. J. Yang, B. Jin, L. M. Zheng, and X. H. Xia, *Bioelectrochem.* 75 (2009) 26 .
- [36] Y. Wang, and Z. Z. Chen, *Colloid. Surface. B* 74 (2009) 322.
- [37] P. Wang, Y. Li, X. Huang, and L. Wang, *Talanta* 73 (2007) 431.
- [38] S. Lupua, C. Leteb, M. Marin, N. Totir, and P. C. Balaurec, *Electrochim. Acta* 54 (2009) 1932.
- [39] H. R. Zare, N. Nasirizadeh, and M. M. Ardakani, *J. Electroanal. Chem.* 577 (2005) 25.
- [40] S. S. Shankar, B. E. K. Swamy, U. Chandra, J. G.Manjunatha, and B. S. Sherigara, *Int. J. Electrochem. Sci.* 4 (2009) 592.
- [41] U. Chandra, B. E. K. Swamy, O. Gilbert, M. Pandurangachar, and B. S. Sherigara, *Int. J. Electrochem. Sci.* 4 (2009) 1479.
- [42] O. Gilbert, B. E. K. Swamy, U. Chandra, and B. S. Sherigara, *J. Electroanal Chem.* 636 (2009) 80.

- [43] E. Niranjana, B. E. Kumara Swamy, R. Raghavendra Naik, B. S. Sherigara, and H. Jayadevappa, *J. Electroanal. Chem.* 631 (2009)1.
- [44] O. Gilbert, U. Chandra, B. E. Kumeara Swamy, M. Pandurangachar, C. Nagaraj, and B. S. Sherigara, *Int. J. Electrochem. Sci.* 3 (2008) 1186.
- [45] D. K. Gosser (Ed), *Cyclic Voltammetry*, VHC, New York (1994).