

Full Paper

Simultaneous Voltammetric Determination of Norepinephrine, Ascorbic Acid and Uric Acid by TTAB Modified Carbon Paste Electrode

S. Sharath Shankar, Bahaddurghatta E. Kumara Swamy *, Kurangalara R. Mahanthesha, Chandrashekar C. Vishwanatha and Mohan Kumar

Department of P.G. Studies and Research in Industrial Chemistry, Kuvempu University, JnanaSahyadri, Shankaraghatta-577 451, Karnataka, India

*Corresponding Author, Tel.: +918282256225; Fax: +918282256255

E-Mail: kumaraswamy21@yahoo.com

Received: 19 June 2013 / Accepted: 12 October 2013 / Published online: 31 October 2013

Abstract- A cationic surfactant tetradecyl trimethyl ammonium bromide modified carbon paste electrode (TTABMCPE) was fabricated and the electrochemical behavior of norepinephrine at the modified electrode was investigated by cyclic voltammetric and differential pulse voltammetric techniques. A well-defined oxidation peak was observed at 174 mV and the significant increase in peak current at modified carbon paste electrode compared to bare carbon paste electrode was obtained. The effect of scan rate on the oxidation of norepinephrine was examined and it was found that the anodic peak current was proportional to the concentration of norepinephrine in the range from 0.10 μM to 4 μM . Compared with other reported electrochemical method; this new sensing method has higher sensitivity, rapid response and extreme simplicity. TTABMCPE was used for the simultaneous determination of nor norepinephrine, ascorbic acid and uric acid. The analytical performance of this biosensor has been evaluated for the detection of norepinephrine in injection sample.

Keywords- Surfactant, Norepinephrine, Tetradecyl trimethyl ammonium bromide, Cyclic voltammetry, Differential pulse voltammetry

1. INTRODUCTION

Norepinephrine (NE) is one of the derivatives of catecholamines secreted in the adrenal medulla and plays important physiological roles in the central nervous system. The hormone norepinephrine is commonly used as the drug of choice as a vasoconstrictor, cardiac stimulator and bronchodilator. It exists in protonated form at physiological pH. It is synthesized in the body from L-tyrosine and secreted by the medulla of the adrenal gland along with epinephrine [1]. It affects muscle and tissue control, stimulates arteriole contraction, decreases peripheral circulation and activates lipolysis in adipose tissue [2]. It is also critical in mental disease, heart failure; DNA breaks in cardiac myoblast cells, and diabetes [3]. Recent reports have indicated that NE enhances adhesion of human immunodeficiency virus-1 (HIV-1)-infected leukocytes to cardiac microvascular endothelial cells and also accelerates HIV replication via protein kinase [4]. The level of NE is important for monitoring and diagnosing diseases [5,6]. Many diseases are related to changes of its concentration, and the determination of NE concentrations in biological systems provides important information on its physiological functions. NE is an electroactive species and can be detected with electrochemical oxidation at various modified electrodes [6-18]. NE determination can be interfered by the coexistence of ascorbic acid (AA) and uric acid (UA) with low NE level in biological samples. The separate detection of NE in the presence of AA and UA at bare electrode is difficult due to the overlaid oxidation peak potentials of these species. To overcome this problem, chemically modified electrodes have been utilized to determine NE in the presence of AA and UA for electrochemical oxidation of NE without their interference. The many chemically modified electrodes include carbon based electrodes [6-9], self-assembled monolayers gold electrodes [10], lead-ruthenium oxide electrodes [11], carbon nanotubes [12], and electropolymerized films [13-18] are used for the determination of norepinephrine. The separate detection of NE in the presence of AA and UA is difficult due to their overlaid oxidation peak potentials at the bare and even the modified electrodes. A noble modified electrode is required for selective NE determination in the mixture of catecholamines that have similar oxidation potentials.

Surface-active agents (surfactants) are widely used in recent researches field, particularly in electrochemical investigations. Due to the specific amphiphilic structure of surfactants, these molecules can be absorbed in the interfaces and surfaces. In general, adsorption begins well below the CMC of the surfactant. Adsorption of surfactants on electrodes and solubilization of electrochemically active compounds in micellar aggregates might significantly change the redox potential, charge transfer coefficients and diffusion coefficients of electrode processes [19,20]. So at low concentrations, surfactants molecules adsorbed on the electrode surface and make a layer of surfactant on electrode surface. Ionic surfactant adsorption on the electrode makes charged (cationic surfactant give it positive charged and anionic surfactants make negative charged on electrode surface). Charged

electrodes can affect the charge transferring rates in measurement cell and consequently affect the oxidation potential in electrochemical measurements. At high concentrations of surfactants, micelle has been formed. Micelles affect the charge transferring in opposite manner, due to this fact, electroactive agent distribute in micelle and bulk water phases. The surfactant-modified electrodes have been reported previously [21–25]. The present study is concerned with TTAB effect on electrode behavior and electro-oxidation of AA, NE and UA individually and simultaneously at TTABMCPE.

2. EXPERIMENTAL

2.1. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed in Model EA-201 Electroanalyser (EA-201, Chemilink System) potentiostat respectively. A conventional three-electrode cell assembly consisting of standard calomel electrode (SCE), reference electrode and Pt wire counter electrode were used for the electrochemical measurements. The working electrode was either an unmodified carbon paste electrode or TTABMCPE. All the potentials were reported versus the SCE. The bare carbon paste electrode (BCPE) was prepared by grinding 70% graphite powder (particle size 50 mm and density is 20 mg/100 ml) and 30% silicone oil in an agate mortar. The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper.

2.2. Materials

Norepinephrine, ascorbic acid and uric acid were obtained from Himedia chemicals and all other chemicals were of analytical grades. Freshly prepared NE, AA and UA solutions were used in all experiments. NE was dissolved in 0.1M perchloric acid and all other solutions were prepared with double distilled water. 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 were prepared in distilled water and mixed together for the pH 7.4 aqueous solution (PBS).

2.3. Preparation of TTABMCPE

The carbon paste was packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper. On to the carbon paste electrode surface 20 μL TTAB was immobilized by using a micro pipette for 15 minutes. After this, fabricated TTAB modified CPE was thoroughly rinsed with distilled water and was used for the determination of NE, AA and UA.

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic oxidation of NE at TTABCPE

Cyclic voltammogram of 1.0 μM NE at pH 7.4 PBS at a bare CPE and TTAB film modified CPE was recorded (Fig. 1). At BCPE (a) a pair of redox peak showed poor electrocatalytic activity with anodic peak potential of 182 mV and cathodic peak potential of 150 mV. Under the same condition TTABCPE (c) gave birth to significantly enhanced peak current and more reversible electron transfer process to NE with slight shift in redox peak potentials. A well-defined redox wave of NE was observed with anodic and cathodic peak potential at 174 mV and 126 mV respectively. Intensive increase in peak was also observed owing to the improvement in reversibility of electron transfer process and the larger real surface of TTAB film. The probable reason for this electrocatalytic activity is explained as following. When the solution pH was equal to 7.4, the $-\text{NH}_2$ group of NE molecules ($\text{pK}_a:8.7$) [28] could obtain a proton and form the positive ion of NE. This positively charged NE gets repelled by the positive layer formed on the modified electrode and promote the oxidation of NE (Scheme1). TTABMCPE was not given any peaks (b) in the absence of NE in PBS of pH 7.4. This suggests an efficient oxidation reaction toward NE at the TTABMCPE. The electrochemical oxidation mechanism of NE was given in the Scheme 2.

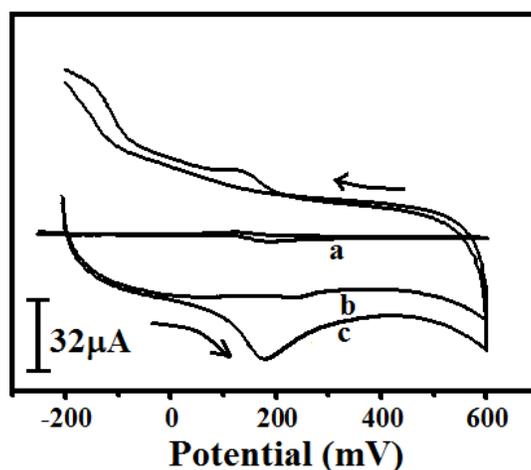


Fig. 1. CVs of 1.0 μM NE in 0.2 M PBS of pH 7.4 at BCPE (curve a) and at TABMCPE with (curve c) and without NE (curve b) at a scan rate of 50 mVs^{-1}

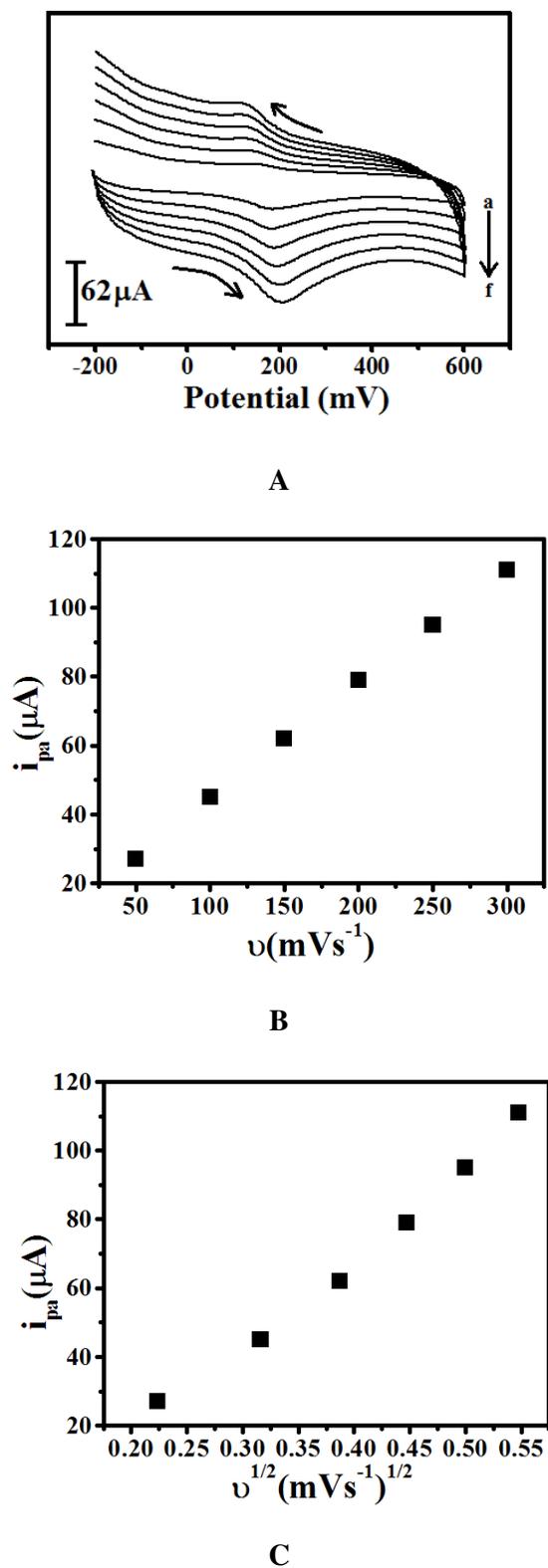


Fig. 2. (A) CVs of 1.0 μM NE at different scan rate at TTABMCPE in 0.2 M PBS at pH 7.4 (a) 50; (b) 100; (c) 150; (d) 200; (e) 250; (f) 300 mVs^{-1} ; (B) Graph of anodic peak current vs. scan rate (v); (C) Graph of anodic peak current vs. Square root of scan rate (v^2)

3.3. Effect of concentration of NE

The electrocatalytic oxidation of NE was carried out by varying its concentration at TTAB. Fig. 3A showed that, by increasing the concentration of NE, the electrochemical anodic and cathodic peak current goes on increasing with miniature shifting in redox peak potentials. The graph of anodic peak current vs. concentration of NE was plotted (Fig. 3B), the NE from 0.10 μM to 4.00 μM concentrations was proportional to electrochemical peak current with the linear regression equations as $i_{pa}(\mu\text{A})=0.00493+0.3735(C)_{NE} \mu\text{M/L}$. The correlation coefficient (r) was found to be 0.9993. The detection limit (LOD) and quantification limit (QL) was calculated by using the following formula [27,28] and it was found to be 0.016 μM and 0.054 μM . The comparison of this electrode with other reported modified electrode for the determination of NE was listed in Table 1.

$$\text{LOD} = 3S/M \quad (1)$$

$$\text{LOD} = 10S/M \quad (2)$$

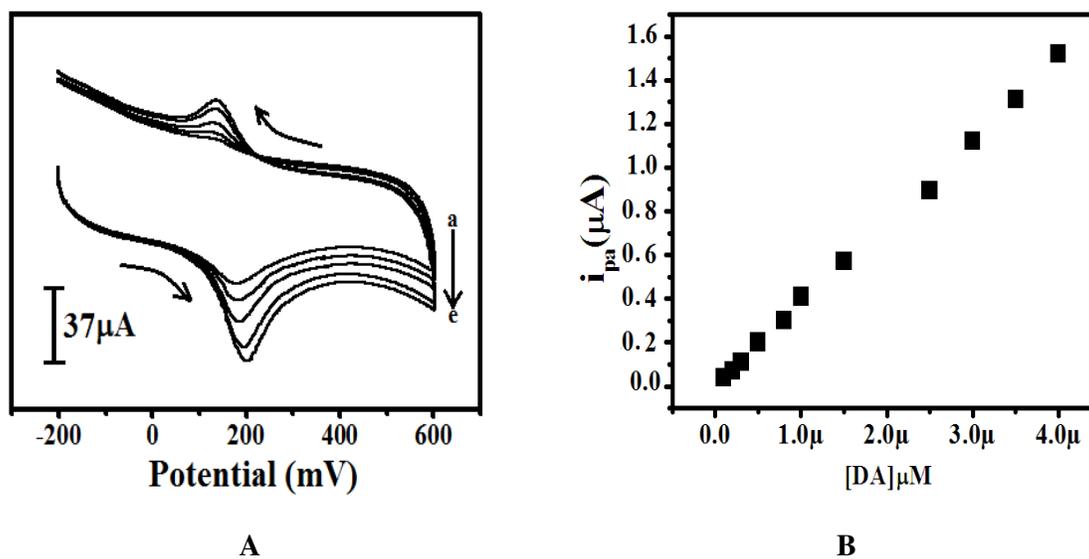


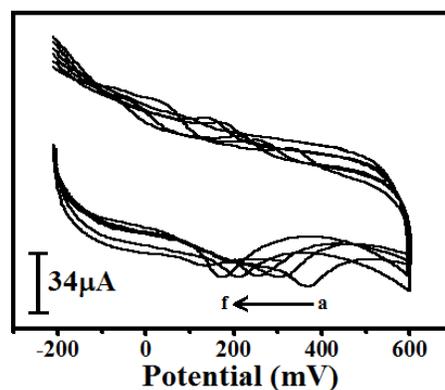
Fig. 3 (A) CVs of NE at different concentration (a–e; 1.0, 2.0, 3.0, 4.0 and 5.0 μM) on TTABMCPE in pH 7.4 PBS with scan rate 50 mVs^{-1} ; (B) Graph of i_{pa} versus concentration of NE (a–e; 1.0, 2.0, 3.0, 4.0 and 5.0 μM)

Table1. Comparison of TTABMCPE with other modified electrodes

Electrode	Detection limit	Linear range	Method	Reference
ME/Au SAMs	0.7 μM	2.0 μM to 100.0 μM	SWV	[38]
Ppy/b-CD-ME	0.8 μM	0. 4 μM to 4.0 μM	CV	[39]
FCDCNPE	0.022 μM	3.0 μM to 5000 μM	DPV	[40]
P(isotonic acid)GC	0.06 μM	0.4 μM to 100.0 μM	DPV	[41]
P(Cresolred)MGCE	0.2 μM	3.0 μM to 30.0 μM	DPV	[42]
(TLA/Au)	2.0 μM	40.0 μM to 2.0mM	CV	[43]
TTABMCPE	0.016 μM	0.1 to 40.0 μM	DPV	this work

3.4. Effect of solution pH in the electrocatalytic oxidation of

Cyclic voltammetry was applied to study the effect of pH on the electro-oxidation of NE at TTABMCPE. Fig. 4A shows the CV obtained for 1.0 μM NE at TTABMCPE in PBS at different values of pH. It can be clearly seen that the electrooxidation behavior of NE is dependent on the pH of the solution. The peak potential for oxidation of NE shifts to more positive potentials as the pH of the solution changes from neutral to acidic values. The relationship between the peak potential and pH has been investigated (Fig. 4B). The E_{pa} shifted negatively and were dependent linearly on pH with the slopes of 56 mV/pH, and a linear regression equation has been obtained ($E_{pa}=0.54871-0.06742\text{pH}$). The above result shows that the loss of electrons is accompanied by the loss of an equal number of protons. [29,30]. Effect of pH on the anodic peak currents was plotted (Fig. 4C). From the graph it is clear that the redox peak current was increased from 3.4 to 7.4 pH after that, the current was decreased for increase in pH. Hence PBS of 7.4 pH was chosen for further studies of NE.



A

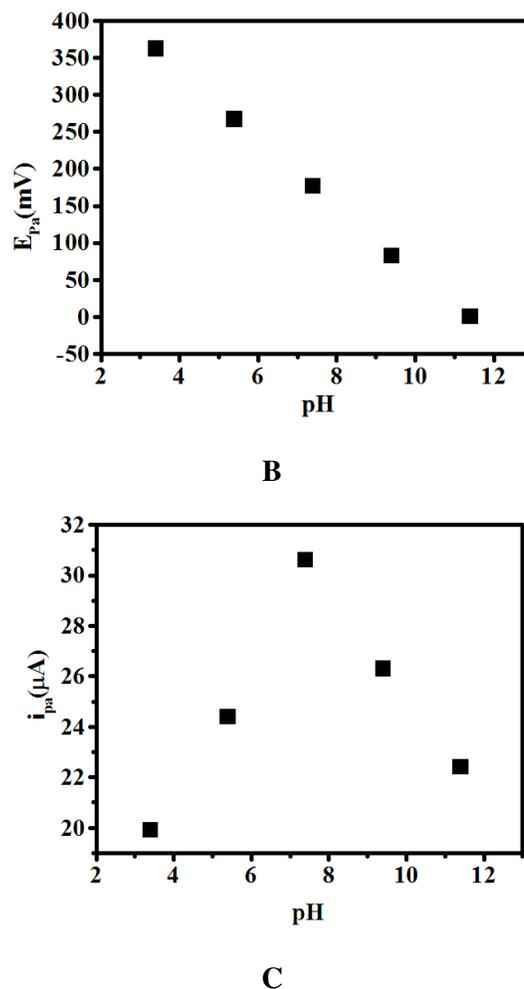


Fig. 4. (A) CVs obtained at the TTABMCPE in 0.2 M PBS in pH values, (a) 3.4 (b) 5.4 (c) 7.4 (d) 9.4, (e) 11.4, containing 0.1 mM NE at scan rate of 50 mVs^{-1} ; (B) Effect of 0.2 M PBS of different pH on anodic peak current with $1.0 \mu\text{M}$ NE at TTABMCPE; (C) Graph of 0.2 M PBS of different pH versus anodic peak potential with $1.0 \mu\text{M}$ NE at TTABMCPE

3.5. Electrochemical behavior of ascorbic acid

Fig. 5 shows cyclic voltammograms of 0.1 mM AA at the BCPE and TTABMCPE, in 0.2 M PBS (pH 7.4). At the BCPE the electrocatalytic oxidation was occurred at 201 mV . Compared with the unmodified carbon paste electrode, modified electrode exhibited high background current with the increase in the anodic peak current of AA. A well-defined oxidation peak current was appeared at -65.36 mV when potential initially swept from -200 to 600 mV and no peak was observed in the reversal scan, revealing that the electrode reaction of AA was a totally irreversible process. According to the accepted mechanism [31],

the oxidation reaction should be attributed to a two-electron oxidation of the hydroxyl group and the mechanism is shown in the Scheme 3.

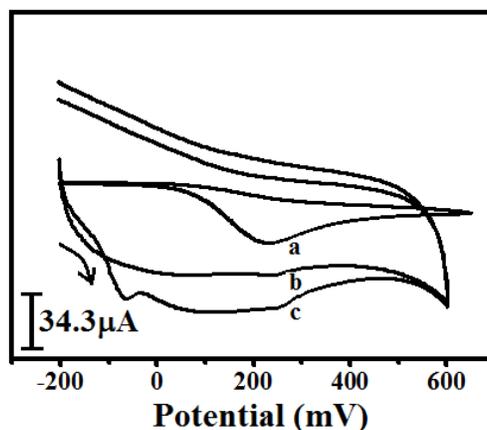
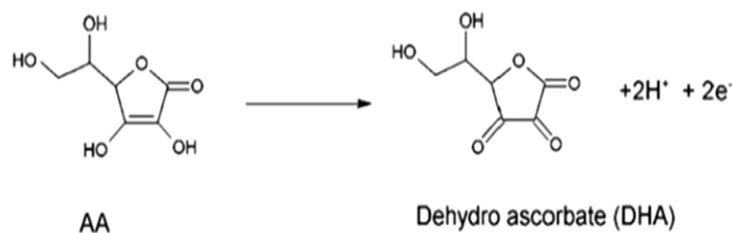


Fig. 5. CVs of 0.1 mM AA in 0.2 M PBS of pH 7.4 at BCPE (curve a) and at TTABMCPE with (curve c) and without AA (curve b) at a scan rate of 50 mVs⁻¹



Scheme 3. Mechanism of electrochemical oxidation AA

3.6. Effect of scan rate, solution pH and concentration of AA

The cyclic voltammogram recorded for 0.1 mM AA at different scan rate at TTABMCPE. The scan rate has a great influence on the peak current of AA on TTABMCPE. The voltammograms showed increased in current signals with increase in scan rate from 50 to 300 mVs⁻¹ (Fig. 6A). The graph of current i_{pa} vs. scan rate and square root of scan rate were straight line in the range from 50 to 300 mVs⁻¹ and the redox peak current is proportional to both the scan rate square root of scan rate with co-relation co-efficient 0.9983 and 0.9942 respectively. This indicates that electron transfer reaction is controlled by both adsorption and diffusion simultaneously.

Electrocatalytic oxidation of AA was carried out by varying concentration at TTABMCPE from 0.1 to 0.5 mM. By increasing the concentration of AA i_{pa} goes on

increasing with shifting E_{pa} towards positive potential. The graph of i_{pa} vs. concentration of AA reveals that the anodic peak current was linearly proportional to the concentration of AA.

The effects of pH on the oxidation peak current and oxidation potentials were investigated using cyclic voltammetry (Fig. 6B). The results showed that the slope of the peak potential for AA from pH 4.4 to 7.4. Is about 56 mV per pH, suggesting a $2e^-/2pH$ transfer process. Thus, the electrode reaction can be classified as an electrochemical reaction followed by a chemical reaction process, as reported previously [32–34]. Changes in anodic peak current with pH were also investigated. The peak current of AA in acidic solution was higher than that in basic solution and reached a maximum at about pH 7.4.

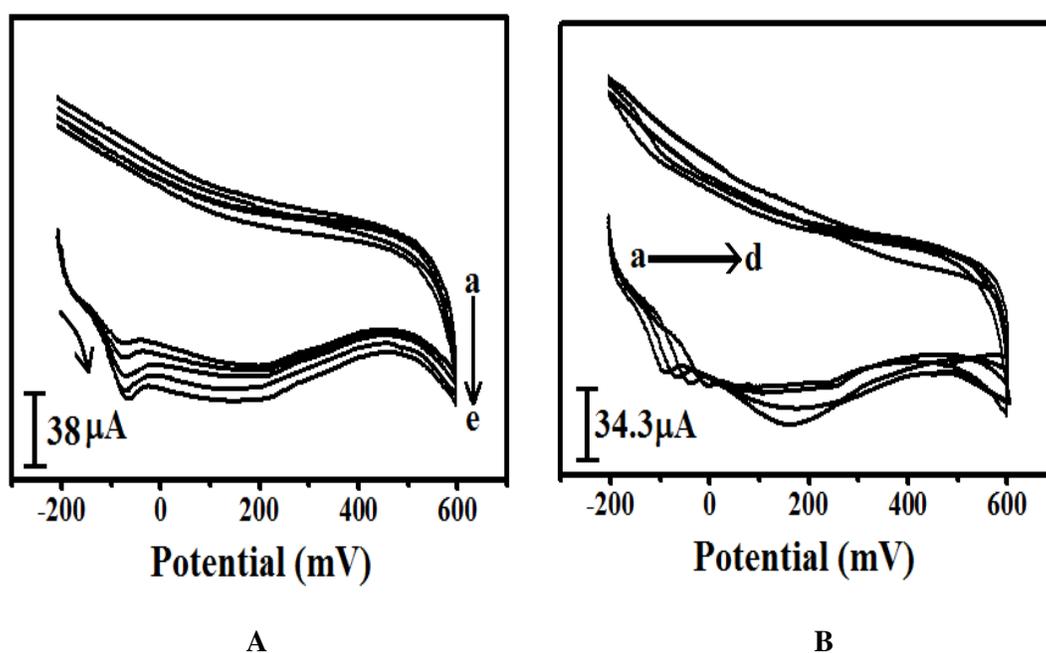


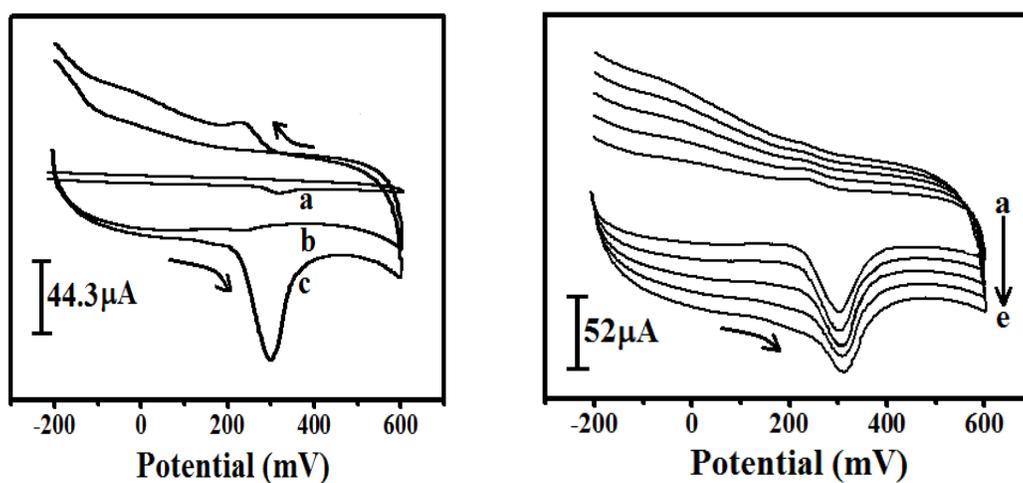
Fig. 6. (A) CVs of AA with different concentration at TTABMCPE in 0.2M PBS of pH 7.4 (a-e; 0.1, 0.2, 0.3, 0.4 and 0.5 mM); (B) CVs of 0.1 mM AA at TTABMCPE in 0.2 M PBS with different pH (a-d; 8.4, 7.4, 5.4, 4.4 pH)

3.7. Electrocatalytic oxidation of UA at TTABMCPE

Fig.7A reveals the oxidation of 10 μ M UA at BCPE and TTABMCPE in 0.2M PBS of pH 7.4 at sweep rate of 50 mVs^{-1} . From Fig. 7A it can be notice that the oxidation peak of UA (10 μ M) at BCPE was broad and poor in sensitivity (dashed line).The anodic potential was found around at 320 mV, suggesting a slow electron-transfer kinetic. However, a well-defined reversible redox pair with the oxidation peak at 300 mV and the reduction peak at 239 mV

($\Delta E_p=61$ mV) were obtained for UA at TTABMCPE (scan rate of 50 mVs $^{-1}$). A series of CVs were recorded at TTABMCPE by varying scan rate (Fig. 7B). The shape of CVs for UA at TTABMCPE may be scan rate-related. When the scan rate is lower than 20 mVs $^{-1}$, only anodic peak can be observed. However, when the scan rate increased, the cathodic peak appeared and increased readily. It seems that a relative higher scan rate can improve the electron-transfer reaction of UA oxidize at TTABMCPE. The graph of current (i_{pa}) vs. scan rate (v) was plotted. The graph obtained was good linearity between the scan rate and i_{pa} in the range from 50 to 300 mVs $^{-1}$, suggesting a adsorption-controlled mechanism. The enhanced peak currents with the negative shift of 300 mV in E_{pa} value strongly indicates the catalytic effect of TTABMCPE composite. These results reveal that the TTAB film improved electron transfer of UA and catalyzed its electro-redox on BCPE and the redox mechanism of UA [35] was shown in Scheme 4.

Cyclic voltammogram of UA in PBS with different pH values are shown in Fig. 7C. The peak potential of UA oxidation varied linearly with pH and shifted to more negative potentials with a slope of 54 mV per pH unit, respectively. These are very close to the theoretical value of 59 mV per pH unit for a two electron two-proton process. The peak currents of UA gradually increase with increasing pH, and reached maximal values at about pH 7.4. The electrocatalytic oxidation of UA was carried out by varying its concentration at TTABMCPE. Fig. 7D showed that, by increasing the concentration of UA, the electrochemical anodic and cathodic peak current goes on increasing with negligible shifting in redox peak potentials. The UA from 10 μ M to 20 μ M concentrations was proportional to electrochemical peak current with the correlation coefficient 0.9863 .



A

B

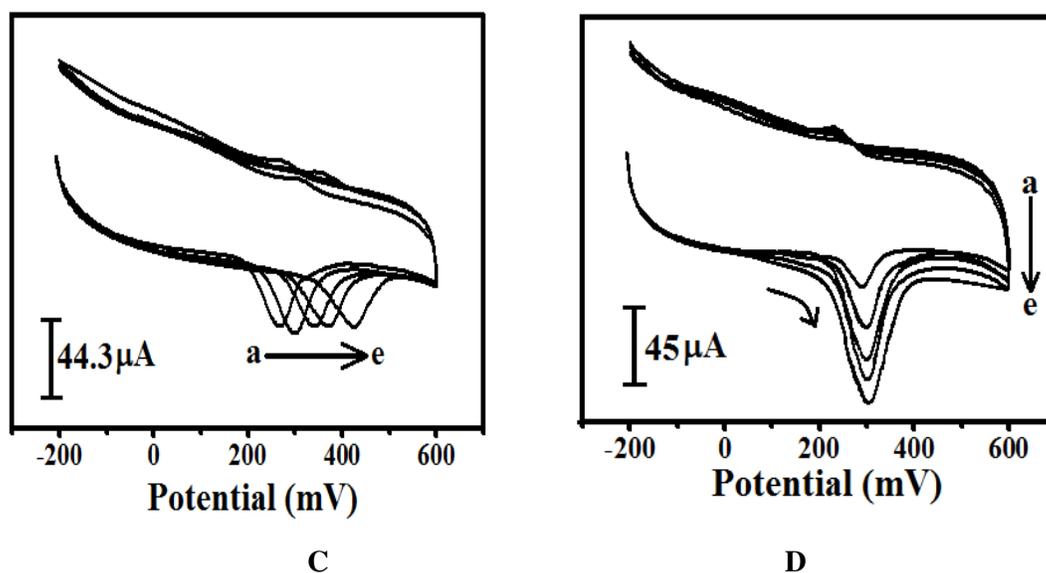
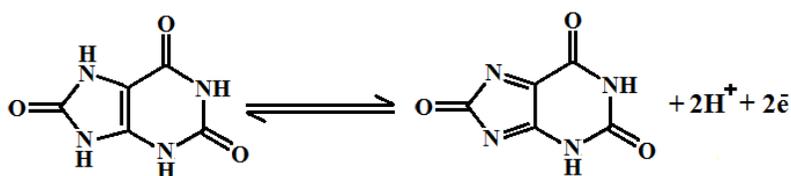


Fig. 7. (A) CVs of 10 μM UA in 0.2 M PBS of pH 7.4 at BCPE (dotted line) and at TTABMCPE with (solid line) and without UA (dashed line) at a scan rate of 50 mVs^{-1} ; (B) CVs of 10 μM UA on the TTABMCPE at different scan rates (a–e: 50, 100, 150, 200, 250 mVs^{-1}) in 0.2 M PBS of pH 7.4; (C) CVs of 10 μM UA in 0.2M PBS at TTABMCPE with different pH (a–e: 3.4,5.4,6.4,7.4,8.4) at a scan rate of 50 mVs^{-1} ; (D) CVs of UA at different concentration (a–e; 10,12,14,16,18 and 20 μM) on TTABMCPE in pH 7.4 PBS with scan rate 50 mVs^{-1}



Scheme 4. Electrochemical reduction mechanism of UA at TTABMCPE

3.8. Simultaneous determination of NE, AA and UA

In order to establish a sensitive and selective method for the quantification of NE, AA and UA, the TTABMCPE was used to simultaneously detect the mixtures of above three molecules. Fig. 8A presents the cyclic voltammograms in the potential range from -200 to 600 mV for the mixture of $1.0 \mu\text{M}$ NE, 0.1 mM AA and $10 \mu\text{M}$ UA at the TTABMCPE and BCPE in pH 7.4 PBS at scan rate of 50 mVs^{-1} . As can be seen, the CV of the ternary mixture

shows one broad and overlapped anodic peak at 185 mV at BCPE (a). So the peak potentials for NE, AA and UA are indistinguishable at a BCPE. Therefore, it is impossible to deduce any information from the broad and overlapped voltammetric peak. But when the TTABMCPE was used, the overlapped voltammetric peak is resolved into three well-defined CV peaks (c) at about -6.50, 199 and 326 mV, corresponding to the oxidation of AA, NE and UA, respectively. The separations of peaks were 205.5, 127 and 332.5 mV in CV between NE and AA, NE and UA and AA and UA, respectively, which were large enough to determine NE and UA simultaneously in the presence of high concentration of AA. TTABMCPE was not given any peaks in PBS of pH 7.4 (b).

This confirms the above results of simultaneous detection by using TTABMCPE. DPV technique can provide a better peak resolution and current sensitivity, which is very suitable for simultaneous determination of species in mixture. Fig. 8B shows the DPV curves in 1.0 μM NE, 0.1 mM AA and 10 μM UA mixture of solution at TTABMCPE. It can be seen from the figure, the modified electrodes gave three separated DPV peaks for these three species, at 16 mV, 148 mV and 309 mV respectively. From the above discussion it is clear that the TTABMCPE is suitable for the use of simultaneous determination.

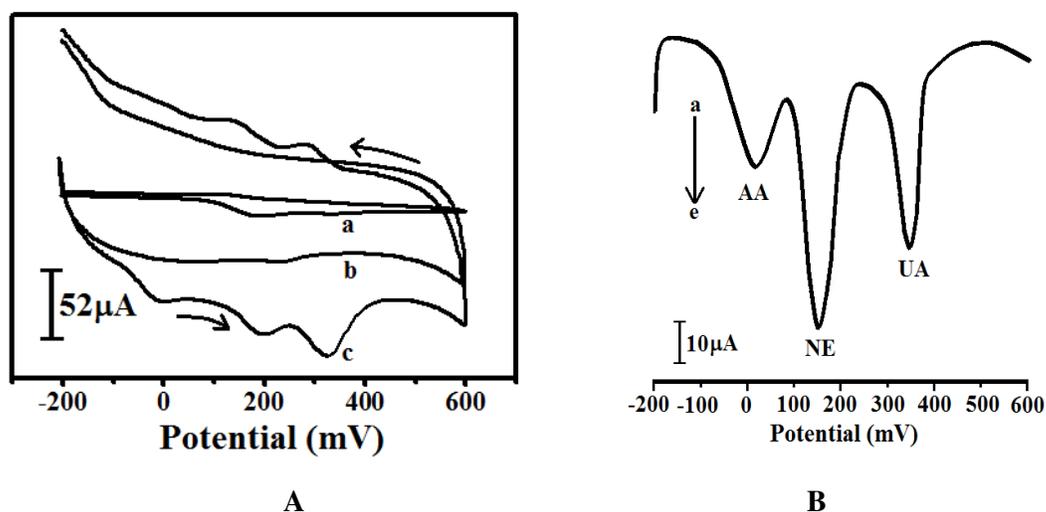
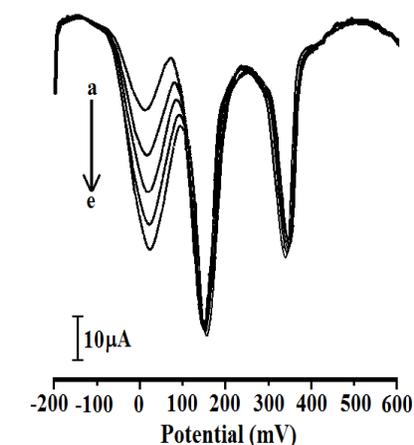


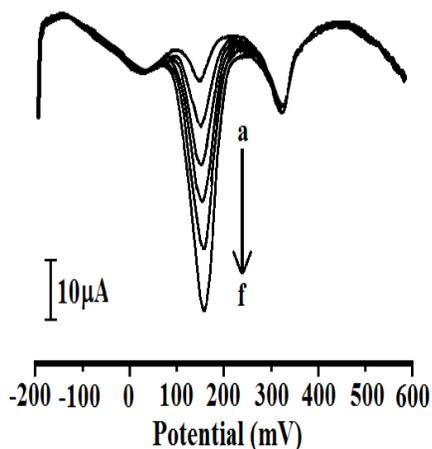
Fig. 8. (A) CVs at BCPE (curve a) and TTABMCPE (curve b and c) in 0.2M PBS of pH 7.4 (curve b) containing 1.0 μM NE, 0.1 mM AA and 10 μM UA (curve a and c) Scan rate: 50 mVs^{-1} ; (B) DPV for 1.0 μM NE, 0.1 mM AA and 10 μM UA at the TTABMCPE in PBS solution at pH 7.4, with a 20 mVs^{-1} scan rate

3.9. Interferences

Fig. 9A shows the DPVs obtained by increasing the concentrations of AA from 2 mM to 10mM in the presence of 1.0 μM NE and 10 μM UA. It could be seen that an increase in the peak current of AA was observed with the increasing AA concentration, and the voltammetric peak of NE and UA was almost unchanged during the oxidation of AA. Fig. 9B also shows that the various concentrations of NE (concentration range from 1.0 to 6.0 μM) in the presence of 2 m MAA and 10 μM UA exhibited excellent DPV responses, whereas the response to AA and UA remained almost constant. Fig. 9C shows DPV's of different concentration of UA (concentration varies from 10 to 20 μM) at in the presence of 10mM AA and 1.0 μM NE and there is no shifting and increase in the oxidation peak of AA and NE at the same time the oxidation peak current increased linearly. It could also be noted from these results that the responses to AA, NE and UA at the TTABMCPE were relatively independent.



A



B

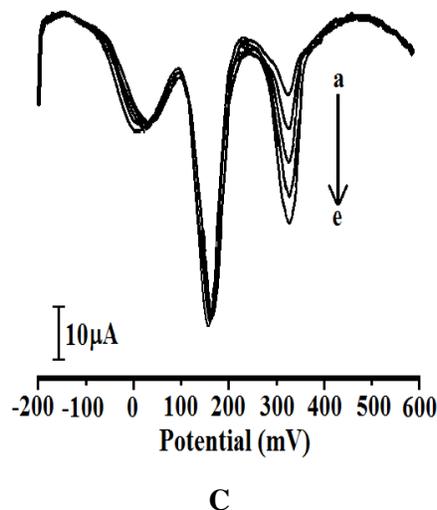


Fig. 9. (A) DPV of AA in the presence of 1.0 μM NE and 10 μM UA in 0.2M PBS (pH 7.4). AA concentrations (from a to e) [AA]: 2,4,6,8 and 10 mM; (B) DPV of NE in the presence of 2mM AA and 10 μM UA in 0.2M PBS (pH 7.4). NE concentrations (from a to e); [NE] 1.0, 2.0, 3.0, 4.0, and 5.0 μM ; (C) DPV of UA in the presence of 10 mM AA and 1.0 μM NE in 0.2M PBS (pH 7.4). UA concentrations from (a to e) [UA]: 10, 12, 14, 16, 18 and 20 μM

3.10. Stability and reproducibility of the modified electrode

The reproducibility of the proposed method for determining NE, AA and UA was tested in the PBS (pH.7.4) containing 0.1 μM NE, 10 mM AA and 10 μM UA by repetitive for 10 times. The results showed good reproducibility of the modified electrode with a relative standard deviation of 2.4%, 3.3% and 3.8% for NE, AA and UA respectively. After each determination the modified electrode was washed with PBS and scanned using cyclic voltammetry in the blank PBS until the redox response wave of NE disappeared at 50 mVs^{-1} in the potential range of -200 mV to 600 mV. After one week exposure of the modified electrode in air, it was found that the electrochemical activity of the TTABMCPE over the determination of NE, AA and UA remained almost same, which indicated the good reproducibility and stability of the modified electrode.

3.11. Analytical applications

The fabricated TTABMCPE was applied to the determination of noradrenaline bitartrate injection (Cipla 2 mg/ml). Using the proposed methods described above, the injection of noradrenaline bitartrate was analyzed by applying a calibration plot. In addition, a certain value of standard solution of NE was added into the corresponding injection for testing recovery and the results are shown in Table 2. It demonstrated a good performance of the

TTABMCPE with satisfactory reproducibility and the recoveries were acceptable, showing that the proposed methods could be efficiently used for the determination of NE in injection samples.

Table 2. Determination of noradrenaline in noradrenalin bitartrate injection sample

Sample	Added (μM)	Found (μM)	RSD (%)	Recovery (%)
1	5.00	4.92 \pm 0.84	2.01	98.4
2	5.00	5.13 \pm 0.06	1.77	102.6
3	5.00	4.87 \pm 0.54	2.18	97.4

4. CONCLUSION

This study has indicated that the TTABMCPE exhibits highly electrocatalytic activity to the oxidation of NE, UA and AA. The electrocatalytic oxidations of the NE, UA and AA at modified electrode were controlled by both adsorption and diffusion simultaneously. pH studies reveals that same number of protons and electrons involved in the catalytic oxidation of NE at TTABMCPE. In addition, it has been shown that this electrode has good stability, reproducibility, selectivity and sensitivity. Ascorbic acid, norepinephrine and uric acid coexisting in a homogeneous solution can be simultaneously determined at this modified electrode. The separations of peaks were large enough to determine NE and UA individually and simultaneously in the presence of high concentration of AA without any interference. The fabricated electrode used for the determination of norepinephrine in norepinephrine bitartrate injection with satisfactory results.

REFERENCES

- [1] S.Y.Ly, Y.H. Kim, I.K. Han, I.G.Moon, W.W. Jung, S.Y.Jung, H.J.Sin, T.K. Hong, and M.H. Kim, *J. Microchem.* 82 (2006) 113.
- [2] D. Voet, J.G. Voet., *Biochemistry*, 2nd ed.; Wiley: New York, (1995).
- [3] H. Yaghoubian, V. S. Nejad, and S.Roodsaz, *Int. J. Electrochem. Sci.* 5 (2010) 1411.
- [4] S. W. Cole, Y. D. Korin, J. L. Fahey, and J. A. Zack, *J. Immunol.* 161 (1998) 610.
- [5] R.M. Carney, K.E. Freedland, R.C. Veith, P.E. Cryer, J.A. Skala, T. Lynch, and A.S. Jaffe, *Biol. Psychiatry* 45 (1999) 458.
- [6] L. Lin, H. Yao, L. Huang, and X. Lin, *J. Anal. Chem.* 64 (2009) 189.
- [7] H. Yaghoubian, V. S. Nejad, and S. Roodsaz, *Int. J. Electrochem. Sci.* 5 (2010) 1411.

- [8] A.R. Taheri, A. Mohadesi, D. Afzali, H. K. Maleh, H.M. Moghaddam, H. Zamani, and Z. R. Zad, *Int. J. Electrochem. Sci.* 6 (2011) 171.
- [9] Y.Li,X.L.Wen, and Z.L.Liu, *Indian J. Chem.* 46 (2007) 962.
- [10] Q. Wang, and N. Li, *Talanta* 55 (2001) 1219.
- [11] J.M. Zen, A.S. Kumar, and J.C. Chen, *J. Electroanal.* 13 (2001) 457.
- [12] J. Wang, M. Li, Z. Shi, N. Li, and Z. Gu, *J. Electroanal.* 14 (2002) 225.
- [13] J. Du, G. Lv, C. Hu, and H. Wu, *Ann. Chim.* 97 (2007) 313.
- [14] S.M. Chen, and M.I. Liu, *J. Electroanal. Chem.* 579 (2005) 153.
- [15] H. Yao, Y. Sun, X. Lin, Y. Tang, and L. Huang, *Ann. Chim.* 97 (2007) 1217.
- [16] H. Jeong, H. Kim, and S. Jeon, *J. Microchem.* 78 (2004) 181.
- [17] A.L. Liu, S.B. Zhang, W. Chen, X.H. Lin, and X.H. Xia, *Biosens. Bioelectron.* 23 (2008) 1488.
- [18] H. Seol, H. Jeong, and S. Jeo, *J. Solid State Electrochem.* 13 (2009) 1881.
- [19] X.L. Wen, Y.H. Jia, and Z.L. Liu, *Talanta* 50 (1999) 1027.
- [20] R. Vittal, H. Gomathi, and K.J. Kim. *Adv. Colloid Interface Sci.* 119 (2006) 55.
- [21] L. Fernandez, C. Borrás, and H. Carrero, *Electrochim. Acta* 52 (2006) 872.
- [22] P. Manisankar, G. Selvanathan, and C. Vedhi, *Talanta* 68 (2006) 686.
- [23] R. Vittal, H. Gomathi, and K. J. Kim, *Adv. Coll. Interface Sci.* 119 (2006) 55.
- [24] L. Fernandez, and H. Carrero, *Electrochim. Acta* 50 (2005) 1233.
- [25] S. Yuan, W. Chen, and S. Hu, *Mater. Sci. Eng. C* 25 (2005) 479.
- [26] C. R. Ganellin, *J. Med. Chem.* 20 (1977) 579.
- [27] U. Chandra, B.E. K. Swamy, O. Gilbert, and B.S. Sherigara, *Electrochim. Acta* 55 (2010) 7166.
- [28] N. R. Hegde, B.E.K. Swamy, N. P. Shetti, and S. T. Nandibewoor, *J. Electroanal. Chem.* 635 (2009) 51.
- [29] S. Mahshid, C. Li, S.S. Mahshid, M. Askari, A. Dolati, L. Yang, S. Luo, and Q. Cai, *Analyst* 136 (2011) 2322.
- [30] H. Yao, Y. Sun, X. Lin, Y. Tang, and L. Huang, *Electrochim. Acta* 52 (2007) 6165.
- [31] S. Yilmaz, M. Sadikoglu, G. Saglikoglu, S. Yagmur, and G. Askin, *Int. J. Electrochem. Sci.* 3 (2008) 1534.
- [32] G.P.Jin, X.Q. Lin, and J. Gong, *J. Electroanal. Chem.* 569 (2004) 135.
- [33] L. Zhang, Y.G. Sun, and X.Q. Lin, *Analyst* 126(2001) 1760.
- [34] L. Zhang, and X.Q. Lin, *Analyst* 126 (2001) 367.
- [35] R.N. Goyal, M. S. Verma, and N. Kumar, *Bioelectroch. Bioenerg.* 43 (1997) 205.
- [36] X.H. Zhang, and S.F. Wang, *Sensors* 3 (2003) 61.
- [37] N. Izaoumen, D. Bouchta, H. Zejli, M.E. Kaoutit, and K. R. Temsamani, *Anal. Lett.* 38 (2005) 1869.
- [38] H. M. Moghaddam, and H. Beitollahi, *Int. J. Electrochem. Sci.* 6 (2011) 6503.

- [39] H.Zhao, Y. Zhang, and Z. Yuan, *Anal. Chim. Acta* 454 (2002) 75.
- [40] W.Chen, X. Lin, H. Luo, and L. Huang, *Electroanalysis* 17 (2005) 941.
- [41] Q. Wang, and N. Li, *Talanta* 55 (2001) 1219.