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Full Paper

Multi-walled Carbon Nanotube Modified Carbon Paste Electrode for the Voltammetric Determination of Folic Acid and Uric Acid

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Abstract- The multi-walled carbon nanotube modified carbon paste electrode (MWCNTMCPE) was used for the voltammetric investigation of folic acid (FA) and uric acid (UA) in physiological pH of 7.4. The scan rate and concentration study reveals that the electrode process was controlled by diffusion of the analytes. The sensitive separation for the binary mixture of FA and UA was observed by cyclic voltammetric and differential pulse voltammetric techniques. A simple modification procedure was reported for the determination of FA and UA.

Keywords- Folic acid, Uric acid, Multi-walled Carbon Nanotube, Voltammetry

1. INTRODUCTION

Carbon nanotubes (CNTs) are new kinds of porous nanostructure carbon materials, which are promising as immobilization substances because of their significant mechanical strength, excellent electrical conductivity, high surface area and good chemical stability [1,2]. Therefore, in recent years, CNTs can be used has an electrode materials in electrochemical devices because it shows increase the sensitivity for and promote electron transfer to

biomolecules. For example, a cyclic voltammograms for dopamine at a carbon nanotube paste electrode exhibited ideal, reversible behaviour. In addition to the enhanced electrochemical reactivity, CNT-modified electrodes have been shown to alleviate surface fouling effects by biomolecules such as NADH. These properties have led to the idea that CNT modified electrodes are excellent for use as biosensors for the detection of bioactive compounds [3-11].

Folic acid (FA) is a form of the water-soluble vitamin B9. Folic acid is a key factor in the making (synthesis) of nucleic acid which is one of a family of large molecules including DNA (deoxyribonucleic acid) and RNA (ribonucleic acid). Folic acid often regarded as a part of vitamin B complex, possesses the considerable biological importance for general human health, especially during periods of rapid cell division and growth [12,13]. It is an essential nutrient, plays a significant role in the synthesis of purines and pyrimidine's for DNA and in cell replication [14]. A lack of folic acid gives rise to gigantocytic anaemia, associated with leukopenia, devolution of mentality, psychosis etc. The determination of FA is often required in pharmaceutical, clinical and food samples. Methods used for it are generally spectrophotometry [15] and chromatography [16,17] and some electrochemical means are also reported for this vitamin[18-21].Folic acid, N-[p-{[(2-amino-4-hydroxy-6-pteridinyl) methyl] amino} benzoyl]-l-glutamic acid) also known as vitamin M folacin or folate (the anionic form). It is an important component of the haemapoietic system and is the co-enzyme that controls the generation of ferrohaeme. Vegemite or marmite also contains folate, with an average part (5 g) containing 100 μg. Folate is also synthesized in bacteria. FA is important for woman who planning for pregnancy. The Dietary Allowance (RDA) suggested for folate equivalents for pregnant woman is 600-800 μg and 400 μg for women who are not pregnant. Deficient in of FA gives rise to the gigantocytic anemia, associating with leucopoenia, devolation of mentality and psychosis etc.. There are many methods for the detection of FA, including high performance liquid chromatography (HPLC), spectrophotometer, calorimetry, flow injection, microbial method and electrochemical method. Among these methods electrochemical method is an important technique because of its convenience and low cost. Determination FA is often requisite in pharmaceutical, clinical and food samples.

Uric acid (2,6,8trihydroxypurine, UA), a major nitrogenous compound in urine, is a product of purine metabolism in human body and its higher levels lead to many clinical disorders [22]. High levels of UA in the blood (hyperuricemia or Lesch-Nyhan syndrome) are linked with the body disorders like gout, kidney, and cardiac problems. Many epidemiological studies have suggested that elevated serum UA is also a risk factor for cardiovascular disease [23-28]. In the present work different quantity of multi walled carbon nanotube is grinded with the carbon powder and silicon oil. The modified electrode is used to study the voltammetric response of folic acid and uric acid.

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen orthophosphate (NaH_2PO_4), silicone oil and multi walled carbon nanotube were purchased from Himedia chemicals. The folic acid, uric acid, graphite powder and NaOH procured from Merck chemicals. 25×10^{-4} M FA and 25×10^{-4} M UA were prepared in 0.1 M NaOH solution. Phosphate buffer solution (0.2 M) of pH 7.4 was used. All the stock solutions were prepared with double distilled water.

2.2. Apparatus

Cyclic voltammetry (CV) was performed in a model CHI-660c (CH Instrument-660 electrochemical workstation). All experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode, a platinum wire as counter electrode and saturated calomel as reference electrode.

2.3. Preparation of bare carbon paste electrode

The bare carbon paste electrode (BCPE) was prepared by hand mixing of graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and the electrical contact was provided by a copper wire connected to the paste in the end of the tube.

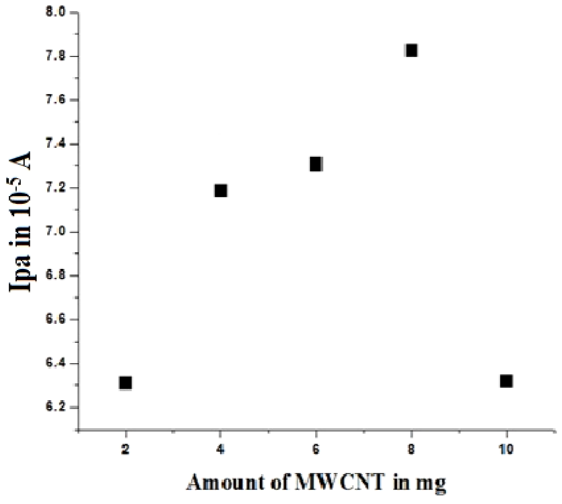


Fig. 1. Effect of quantity of MWCNT on anodic peak current oxidation of 0.2 mM FA in 0.2 M PBS of pH 7.4 with scan rate 100 mVs^{-1}

2.4. Preparation of multi-walled carbon nanotube modified CPE (MWCNTMCPE)

Multi-walled carbon nanotube modified carbon paste electrode (MWCNTMCPE) was prepared by adding different amount of multi-walled carbon nanotube to the graphite powder and silicon oil. By increasing the concentration of MWCNT in the carbon paste, the electrochemical redox peak current goes on increasing for the oxidation of 0.2 mM FA in 0.2 M PBS of pH 7.4. As the quantity of MWCNT increases from 2 mg to 8mg the current signal decreases with increasing quantity. The graph of peak current *vs*. concentration of MWCNT was plotted showed in Fig. 1. Maximum enhancement of current signal was observed for the 8 mg MWCNT. So, 8 mg MWCNT was used for the preparation of MWCNTMCPE.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of Folic acid at MWCNTMCPE

The electrochemical behaviors of FA at MWCNTMCPE have been investigated by cyclic voltammetric technique. Fig. 2 shows the cyclic voltammograms obtained at BCPE (dashed line) and MWCNTMCPE (solid line) for the oxidation of 0.2 mM Folic acid in 0.2 M PBS of pH 7.4 with the applied potential scan rate of 100 mVs^{-1}. At BCPE and MWCNT modified carbon paste electrode the oxidation peak occurs at 0.670 V. However, for the MWCNTMCPE the peak current of FA slightly increased when compared to BCPE. This indicates that the modified electrode acts as a good sensor and which improves the oxidation process of FA.

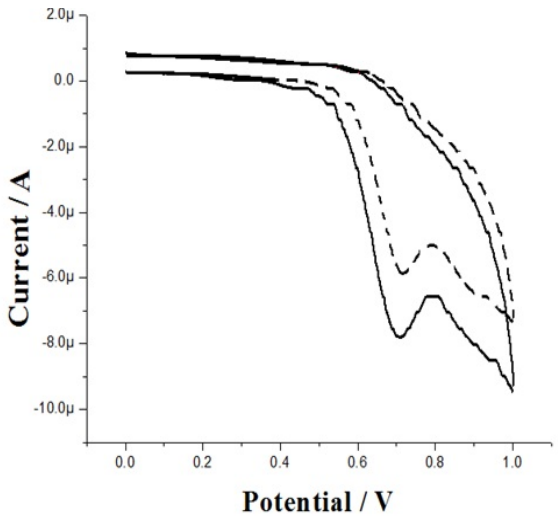
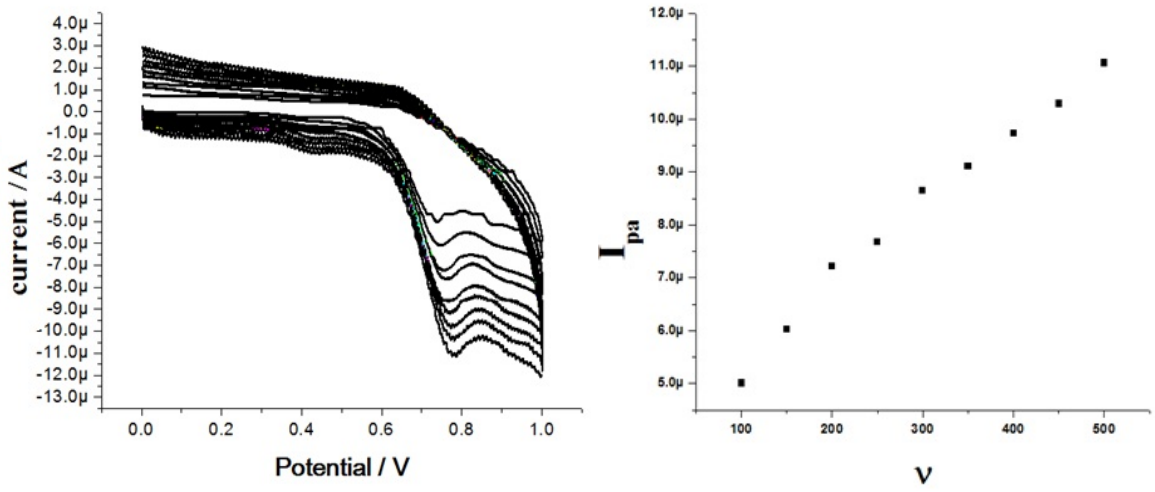


Fig. 2. Cyclic voltammograms of BCPE (dotted line) and MWCNTMCPE (Solid line) in the presence of 0.2 mM FA in 0.2 M PBS of pH 7.4 at the scan rate=100 mVs^{-1}

3.2. The effect of scan rate on MWCNTMCPE

According to Randles-Sevick's equation increase in the scan rate leads to increases in the peak current. Cyclic voltammogram for the oxidation of 2 mM FA in 0.2 M PBS of pH 7.4 at MWCNTMCPE was shown in Fig. 3a. The graph of anodic peak current (I_{pa}) versus scan rate (υ) was plotted and the graph obtained was nearly straight line as shown in Fig. 3b in the range from 100 to 500 mVs^{-1}. The anodic peak current was proportional to the scan rate (υ) with correlation coefficient 0.9923. This suggests the electrode transfer reaction is diffusion-controlled.



(a) **(b)**

Fig. 3. (a) Cyclic voltammograms with different scan rate in the presence of 2 mM folic acid and 0.2 M PBS of pH 7.4, scan rate 100 mVs^{-1}-500 mVs^{-1}; **(b)** Graph of anodic peak current versus scan rate of FA

3.3. Effect of Concentration

The anodic peak current was increased as the concentration of FA was increased. The CV curves were recorded for the oxidation of FA with varying concentration in the range 1×10^{-4} M to 4×10^{-4} M as shown in Fig. 4a. The plot of anodic peak current versus concentration of FA gives a linear relationship as shown in Fig. 4b.

3.4. Electrochemical behavior of Uric acid at MWCNT MCPE

The electrochemical behaviors of UA at MWCNTMCPE have been investigated by cyclic voltammetric technique. Fig. 5 shows the cyclic voltammograms of BCPE (dashed line) and MWCNTMCPE (solid line) electrodes in 0.2 mM UA in 0.2 M PBS of pH 7.4 as a

supporting electrolyte with the scan rate 100 mVs^{-1}. At BCPE and MWCNTMCPE the oxidation peak occurs at 0.310 V. In MWCNTMCPE the peak current of UA slightly increased when compared to BCPE.

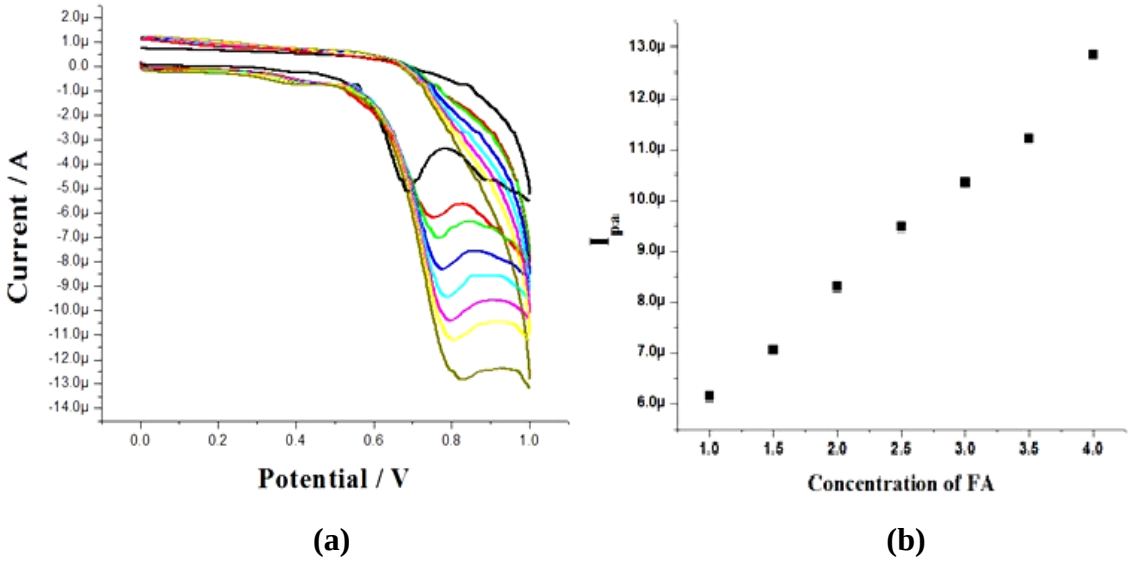


Fig. 4. (a) Cyclic voltammogram of variation of concentration of FA from 1×10^{-4} M to 4×10^{-4} M in presence of PBS of pH 7.4; (**b)** Effect of variation of concentration of FA versus anodic peak current

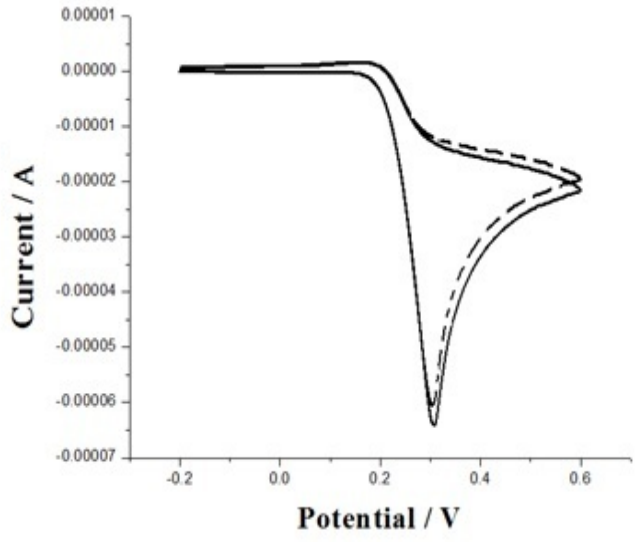


Fig. 5. Cyclic Voltammogram of BCPE (dotted line) and MWCNTMCPE (Solid line) in the presence of 0.2 mM UA and 0.2 M PBS, Scan rate=100 mVs^{-1}

3.5. The effect of scan rate MWCNT on MCPE

The CV curves were recorded for the oxidation of 2 mM UA in 0.2 M PBS of pH 7.4 at MWCNTMCPE. The result shows increase in the anodic peak current with increase in scan rate in the range 100 to 500 mVs^{-1} as shown in the Fig. 6a. The graph of I_{pa} versus υ was nearly a straight line as shown in Fig. 6b with correlation coefficient of 0.9894. This indicates the electrode transfer reaction was diffusion-controlled.

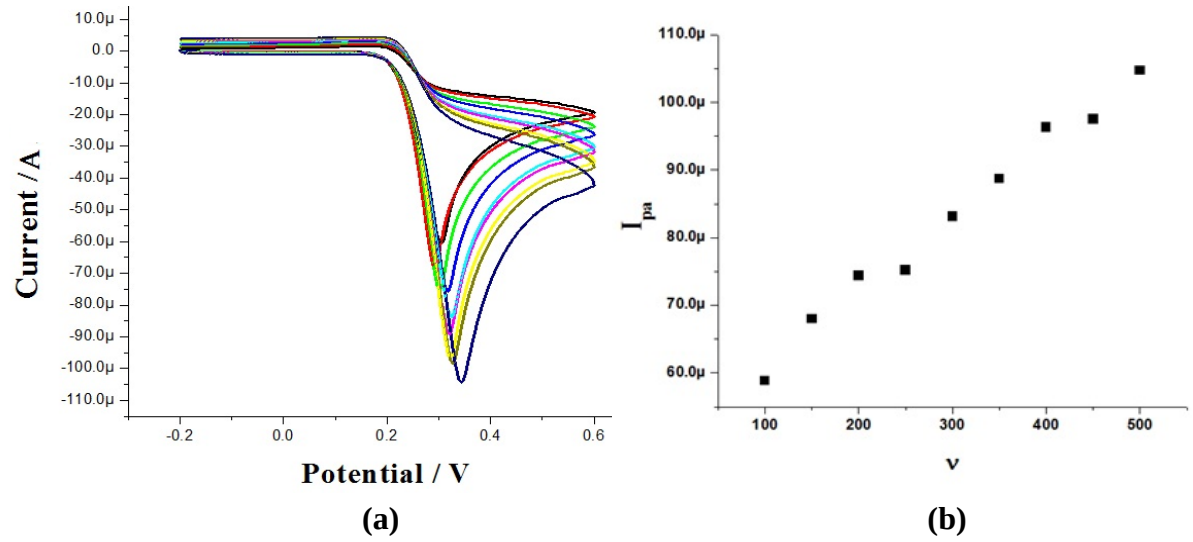


Fig. 6. (a) Effect of variation of scan rate on the anodic peak current of 2 mM UA in 0.2 M PBS of pH 7.4; **(b)** Graph of anodic peak current versus scan rate of UA

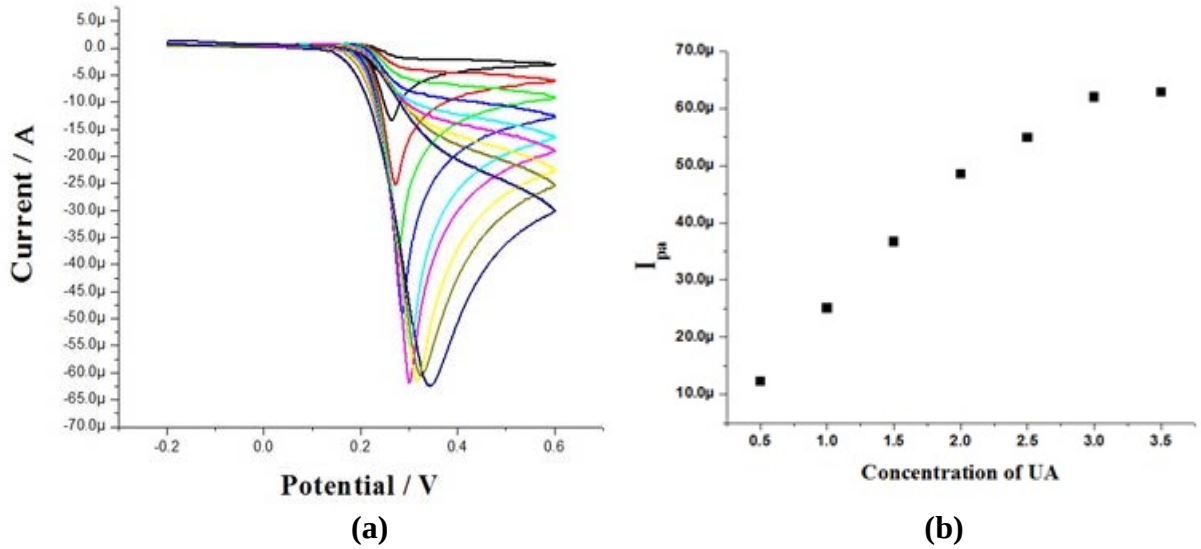


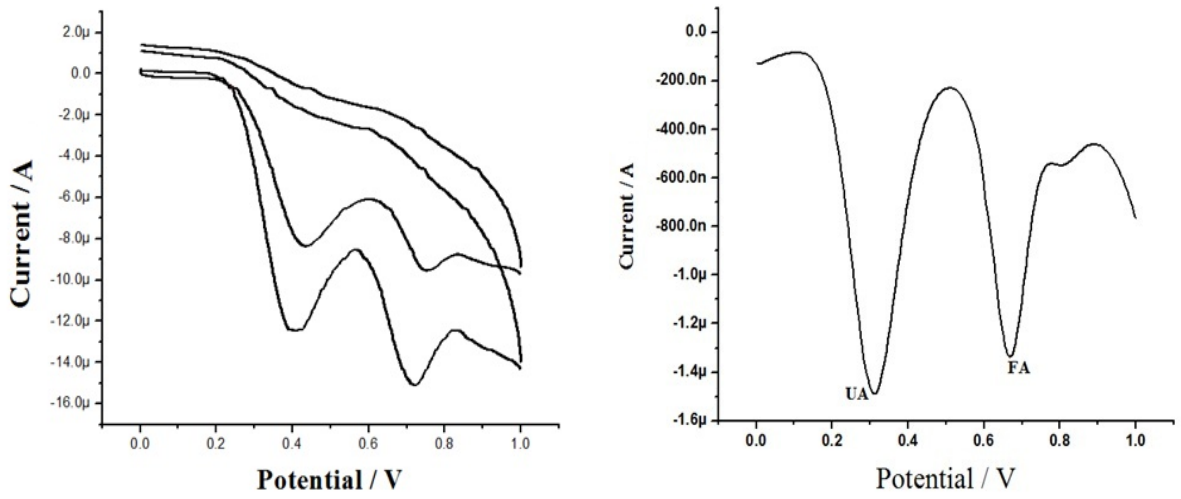
Fig. 7. (a) Cyclic voltammograms of variation of concentration of UA from 0.5×10^{-4} M to 4.5×10^{-4} M in 0.2 M PBS of pH 7.4; **(b)** Graph of anodic peak current versus concentration of UA

3.6. Effect of Concentration

The concentration of uric acid was increased from 0.5×10^{-4} M to 4.5×10^{-4} M as shown in Fig. 7a. The CV curve shows increase in the current response due to the increase in the concentration of UA. The graph of I_{pa} versus concentration of uric acid was plotted and it gives a linear relationship between I_{pa} in the range 0.5×10^{-4} M to 3.0×10^{-4} M as shown in Fig. 7b. The decrease in the sensitivity in second linear range was due to the kinetic limitation [29].

3.7. Simultaneous determination of FA and UA

The Fig. 8a shows the cyclic voltammetric response of 2 mM FA and 0.5 mM UA in 0.2 M PBS of pH 7.4 at BCPE (dotted line) and MWCNTMCPE (solid line). The modified electrode shows relatively good sensitivity as compared to the BCPE. The sensitive and simultaneous separation was observed at MWCNTMCPE. The differential pulse voltammetry (DPV) was used due to its high sensitivity and absence of background current. The Fig. 8b shows the DPV curve obtained for the mixture of 2 mM FA and 0.5 mM UA in 0.2 M PBS of pH 7.4. So, The MWCNTMCPE shows sensitive and simultaneous separation for the oxidation of FA and UA.



(a) **(b)**

Fig. 8. (a) Cyclic voltammogram of 2 mM FA and 0.5 mM UA at BCPE (dotted line) and MWCNTMCPE (solid line) in 0.2 M PBS of pH 7.4 at scan rate 50 mVs^{-1}; **(b)** Differential pulse voltammogram of 2 mM FA and 0.5 mM UA MWCNTMCPE in 0.2 M PBS of pH 7.4

4. CONCLUSION

The bare carbon paste was modified by grinding different quantities of multi walled carbon nanotube. The modified MWCNTMCPE was used for the sensitive determination of

FA and UA in physiological pH of 7.4 by CV and DPV techniques. The simultaneous study was conducted for the binary mixture of FA and UA, the sensitive separation was observed at the modified electrode by CV and DPV technique. The proposed method can be employed for the some other biological important molecules.

REFERENCE

[1] M. Zidan, W. T. Tan, Z. Zainal, A. H. Abdullah, and J. Kheng Goh, Int. J. Electrochem. Sci. 5 (2010) 501.
[2] A. R. Taheri, A. Mohadesi, D. Afzali, H. K. Maleh, H. M. Moghaddam, H. Zamani, and Z. Rezayatizad, Int. J. Electrochem. Sci. 6 (2011) 171.
[3] J. Wang, Electroanalysis 17 (2005) 2005.
[4] P. J. Britto, K. S. V. Santhanam, and P. M. Ajayan, Bioelectrochem. Bioenerg. 41 (1996) 121.
[5] M. Musameh, J. Wang, A. Merkoci, and Y. Lin, Electrochem. Commun. 4 (2002) 743.
[6] B. E. K. Swamy, and B. J. Venton, Analyst 132 (2007) 876.
[7] H. K. Maleh., F. T. Javazmi., A. A. Ensafi, R. Moradi, S. Mallakpour, and H. Beitollahi, Biosens. Bioelectron. 60 (2014) 1.
[8] H. K. Maleh, P. Biparva, and M. Hatami, Biosens. Bioelectron. 48 (2013) 270.
[9] M. E. lyasi, M. A. Khalilzadeh, and H. K. Maleh, Food Chem. 141 (2013) 4311.
[10] M. Najafi, M. A. Khalilzadeh., and H. K. Maleh, Food Chem. 158 (2014) 125.
[11] H. K. Maleh, F. T. Javazmi, N. Atar, M. L.Yola, V. K. Gupta, and A. A. Ensafi, Int. Eng. Chem. Res. 54 (2015) 3634.
[12] V. K. Gupta, R. Jain, S. Agarwal, R. Mishra, and A. Dwivedi, Anal. Biochem. 410 (2011) 266.
[13] N. Rastakhiz, H. Beitollahi, A. Kariminik, and F. Karimi, J. Mol. Liq. 172 (2012) 66.
[14] D. Manoj, D. R. Kumar, and J. Santhanalakshmi, Appl. Nanosci. 2 (2012) 223.
[15] G. R. Rao, G. Kanjilal, and K. R. Mohan, Analyst 103 (1978) 993.
[16] M. W. Dong, J. Lepore, and T. Tarumoto, J. Chromatogr. 442 (1988) 81.
[17] C. Paveenbampen, D. Lamontanaro, J. Moody, J. Zaremo, and C. J. Rehm, J. Pharm. Sci. 75 (1986) 1192.
[18] E. Jacobsen, and M. W. Bjornsen, Anal. Chim. Acta 96 (1978) 345.
[19] L. Rozanski, Analyst 103 (1978) 950.
[20] W. Szczepaniak, and M. Ren, Electroanalysis 6 (1994) 505.
[21] R. Ojani, J. B. Raoof, and S. Zamani, Electroanalysis 21 (2009) 2634.
[22] M. Syed. U. Ali, N. H. Alvi, Z. Ibupoto, O. Nur, M. Willander, and B. Danielsson, Sens. Actuator B 152 (2011) 241.
[23] J. C. Chen, H. H. Chung, C. T. Hsu, D. M. Tsai, A. S. Kumar, and J. M. Zen, Sens. Actuator B 110 (2005) 364.

[24] I. D. P. Wootton, and H. Freeman, Microanalysis in Medical Biochemistry (6th ed.), Churchill Livingstone, New York (1982).
[25] E. Liberopoulos, D. Christides and E. Moses, J. Hypertens. 20 (2002) 347.
[26] R. J. Johnson, D. K. Kang, D. Feig, S. Kivlighn, J. Kanellis, S. Watanabe, K. R. Tuttle, B. Rodriguez-Iturbe, J. Herrera- Acosta, and M. Mazzali, J. Hypertens. 41 (2003) 1183.
[27] M. Alderman, and K. J. V. Aiyer, Curr. Med. Res. Opin. 20 (2004) 369.
[28] P. S.Ganesh and B. E. K. Swamy, J. Electroanal. Chem. 752 (2015) 17.
[29] P. S. Ganesh, and B. E. K. Swamy, J. Anal. Bioanal. Tech. 6 (2015) 229

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